8.06: Quantum Physics III

Lecturer: Professor Max Metlitski

Notes by: Andrew Lin

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Recitations for this class are being taught by **Professor Iain Stewart**.

Introduction

Professor Metlitski works in the Condensed Matter Theory group, working on problems about quantum matter at low temperatures. So quantum physics will hopefully become "close to our heart" too!

The formal prerequisite for this class is a grade of C or higher in 8.05, but 8.06 is more challenging than 8.05, both conceptually and technically. Lots of stuff is packed into the class, so if we're unsure about our background, we should talk to the course staff.

Lectures, recitations, and office hours are all remote (and lectures will be recorded) – materials and problem sets will be on Canvas, and there is also a Piazza site linked to Canvas. We're encouraged to ask questions on Piazza (and to answer each others' questions as well).

Professor Barton Zwiebach's lecture notes are the main course reading for this class (soon to be a textbook). Chapter 1 is on Canvas, and for each week, the problem set will indicate what chapter to read. (The syllabus also contains a list of other good textbooks, but Professor Zwiebach's notes are the main source to consult. In particular, the level of this course is a bit higher than Griffiths.)

Grading will be **flexible** in that our grade will be maximized among the following windows: 8 problem sets (with 1 dropped) are worth between 25-40%, the term paper will be worth between 25-35%, and the final exam will be worth between 30-50%.

The **term paper** has historically been a fun part of the class – details about this are on Canvas in a separate document, which we should read carefully, but basically it can be about any topic in quantum physics that hasn't been covered in 8.04, 8.05, or 8.06. The main relevant deadlines are that a proposal is due on March 26 (which requires our topic, references, and a peer-editor in the class). After that, a first draft is due on April 21, and the final version is due on May 6. (Since this is a CI-M, we need a C or higher on the paper to pass the class.)

1 February 16, 2021

In 8.05, a lot of the formalism of quantum mechanics was developed, and now we're ready to apply this formalism to real problems and phenomena in quantum physics (the fine structure of hydrogen, decay of excited states, tunneling, motion of charged particles in a magnetic field, and so on). And these problems basically exemplify the early successes of quantum mechanics, so they're very important, and they illustrate a lot of physical concepts.

To approach these problems, we'll need some new tools, and these tools are often **certain approximations**. In almost any branch of physics, we'll see these tools being used, so it's good to get them into our toolbox!

We'll start with **time-independent perturbation theory**. In 8.05 (and also in 8.04), we saw certain physical systems, like the harmonic oscillator and the hydrogen atom, and we solved these systems exactly (finding the energies and eigenstates of the Hamiltonian). We cannot find the exact solutions to most problems in physics, but often we can use the exactly solvable systems as a starting point:

Example 1

A diatomic molecule consists of two atoms separated by some distance r, interacting via a potential $V(r)$ (with a minimum at some equilibrium distance $r = r_0$).

Any function near its minimum can be approximated by a parabola, so for oscillations close to the equilibrium separation, we can think of this system as (approximately) a simple harmonic oscillator. And at this zeroth order approximation, we do indeed know the energies and eigenstates. But then the **anharmonicities** turn on as we move away from equilibrium, and we're going to learn how to take these (small) deviations into account.

Example 2

A hydrogen atom sitting in vacuum can be exactly solved, but applying a small magnetic or electric field to the atom will shift the spectral lines (energy levels).

Again, these problems can be solved by starting with the exactly solvable system, and we need to adjust the Hamiltonian a little bit to get to our actual system.

With that, let's start with the formalism. We can write our Hamiltonian as

$$H = H^{(0)} + \delta H,$$

where $H^{(0)}$ is our exactly solvable system and δH is a small **perturbation**. (Note that $H^{(0)}$ and H are Hermitian because they are both Hamiltonians, so their difference δH must also be Hermitian.) We'll also assume here that all of these terms are **time-independent** (we'll study time-dependence later in the course).

Finding the energies and eigenstates of H is hard in general, but we will make an assumption that δH is small compared to $H^{(0)}$. It's not entirely clear what this means yet – they are operators, not numbers – but we'll develop some criteria for this over time. And this motivates the modified problem where we write

$$H(\lambda) = H^{(0)} + \lambda \cdot \delta H,$$

where λ is a dimensionless number in the range $[0, 1]$. In other words, we have a family of perturbations $H(\lambda)$, where $H(0) = H^{(0)}$ is our starting Hamiltonian, $H(1) = H^{(0)} + \delta H$ is the Hamiltonian that we want to study, and we can interpolate between the two. But this λ is also useful as an **expansion parameter**: even if δH is not that small, we can make λ small enough so that $\lambda \delta H$ is small. So expanding in λ (as a series) is basically like expanding in δH.

Before we do any calculations, we can try visualizing what might happen to our energies and eigenstates as λ goes from 0 to 1. At $\lambda = 0$, we know the energy spectrum exactly: for example, we might have a single (nondegenerate) ground state at some lowest energy, and then a two-fold degeneracy at the first excited state, followed by another nondegenerate state, and finally a three-fold degeneracy at the highest energy. If we "turn on" a finite λ, we can track what happens to these energies. They should **evolve continuously with** λ, so the ground state energy might wiggle a little bit in a continuous way (and so will the other nondegenerate state). But there are two states with the same energy at the first excited level, and those can either remain degenerate for all λ, or (more commonly) they will **split apart** at positive λ. (So understanding how this splitting takes place will be very important as we go on.) And this splitting of states can occur at different **orders** as well: perhaps in the three-fold degeneracy, two of the states evolve with the same "starting slope," but not the third. So these are just some potential illustrations of the evolution, and the point is that there are a lot of options.

We'll understand how to deal with nondegenerate states' energy evolution through **nondegenerate perturbation theory**, and we'll address the energy splitting through **degenerate perturbation theory** (which is a bit more subtle).

Remark 3. *In principle, for large enough λ or if δH is not small enough, the energies may cross. But we usually try to avoid these (for instance, by making λ small), and we'll discuss this point later on as well.*

Let's now begin to study nondegenerate perturbation theory. As before, we have a Hamiltonian $H^{(0)}$ with certain eigenstates $\left|k^{(0)}\right\rangle$ (**labeled** by an integer $k \geq 0$), such that

$$H^{(0)}\left|k^{(0)}\right\rangle = E_k^{(0)}\left|k^{(0)}\right\rangle$$

for corresponding energies $E_k^{(0)}$. We can choose these eigenstates to be orthonormal, so that

$$\left\langle k^{(0)} \middle| \ell^{(0)}\right\rangle = \delta_{k\ell},$$

and we'll order these states in nondecreasing energy, so that $E_0^{(0)} \leq E_1^{(0)} \leq E_2^{(0)} \leq \cdots$. (Equalities are possible because of degeneracies.) If we focus on a level that is initially nondegenerate, that means we're focusing on some level $|n_0\rangle$ so that $E_{n-1}^{(0)} < E_n^{(0)} < E_{n+1}^{(0)}$ (we now have strict inequalities), but no assumptions are being made on degeneracies **outside** of level $\left|n^{(0)}\right\rangle$.

So now we want to solve the eigenvalue problem with the full Hamiltonian

$$H(\lambda)\left|n\right\rangle_\lambda = E_n(\lambda)\left|n\right\rangle_\lambda.$$

We know that the answer reduces to the unperturbed energy and eigenstate at $\lambda = 0$, so $E_n(\lambda = 0) = E_n^{(0)}$, and $|n\rangle_{\lambda=0} = \left|n^{(0)}\right\rangle$. Our key assumption now is that the energy and state can **both be expanded in a power series** in λ, so that

$$E_n(\lambda) = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots,$$

and similarly

$$|n\rangle_\lambda = \left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \lambda^2\left|n^{(2)}\right\rangle + \cdots.$$

Here, the subscripts indicate the level, and the superscripts $(0), (1), \cdots$ indicate the order. (If we're unsure how to "expand" a vector like $|n\rangle_\lambda$, we can think about doing so component-by-component.) So our goal is to find these expansion coefficients $E_n^{(1)}, E_n^{(2)}, \cdots$ and $\left|n^{(1)}\right\rangle, \left|n^{(2)}\right\rangle, \cdots$ (and note that these coefficients are all λ-independent). In practice, then, we can compute the first few terms and truncate the power series expansion, and we hope (or check) that this is a good approximation.

Fact 4

We can always multiply the eigenstates by a constant, so we will not assume that $|n\rangle_\lambda$ is normalized here (and we can normalize them at the end if we want).

Our first step is to plug the ansatz for $|n\rangle_\lambda$ into our eigenvalue equation, which we first rearrange as

$$\left(H^{(0)} + \lambda\delta H - E_n(\lambda)\right)|n\rangle_\lambda = 0.$$

Plugging in our power series expansions, the term in parentheses becomes

$$(H^{(0)} - E_n^{(0)}) - \lambda \left(E_n^{(1)} - \delta H\right) - \lambda^2 E_n^{(2)} - \cdots - \lambda^k E_n^{(k)} - \cdots ,$$

where we've grouped terms by λ, and it's **acting on the state**

$$\left|n^{(0)}\right\rangle + \lambda \left|n^{(1)}\right\rangle + \lambda^2 \left|n^{(2)}\right\rangle + \cdots .$$

This looks pretty messy, but it isn't actually that bad – we solve this equation by separating things **order-by-order** in λ. (After all, we have an infinite polynomial in 0, so we're trying to make each term of that infinite polynomial 0.)

- The only way to get a λ^0 is to have no λ terms at all:

$$\boxed{\left(H^{(0)} - E_n^{(0)}\right)\left|n^{(0)}\right\rangle = 0}.$$

- We can get a first-order λ by taking one from the blue term or from the red term. This gives us (moving one of the terms to the other side)

$$\boxed{\left(H^{(0)} - E_n^{(0)}\right)\left|n^{(1)}\right\rangle = \left(E_n^{(1)} - \delta H\right)\left|n^{(0)}\right\rangle}.$$

- Similarly, there are three ways to get a second-order λ: $(0,2),(1,1),(2,0)$. We move the last two possibilities to the right side to get

$$\boxed{\left(H^{(0)} - E_n^{(0)}\right)\left|n^{(2)}\right\rangle = \left(E_n^{(1)} - \delta H\right)\left|n^{(1)}\right\rangle + E_n^{(2)}\left|n^{(0)}\right\rangle}.$$

- The pattern is now a bit more clear: if we want the kth order in λ, the equation looks like

$$\boxed{\left(H^{(0)} - E_n^{(0)}\right)\left|n^{(k)}\right\rangle = \left(E_n^{(1)} - \delta H\right)\left|n^{(k-1)}\right\rangle + E_n^{(2)}\left|n^{(k-2)}\right\rangle + \cdots + E_n^{(k)}\left|n^{(0)}\right\rangle}.$$

Studying the structure here, the zeroth order equation gives us nothing new – it's dealing with the unperturbed state and energy, so it's **automatically satisfied**. The first-order equation has two unknowns, $E_n^{(1)}$ and $\left|n^{(1)}\right\rangle$, which we can solve for. **Once we do that**, the only unknowns left in the second-order equation are $E_n^{(2)}$ and $\left|n^{(2)}\right\rangle$, and we can keep doing this process recursively (order-by-order in λ), so that we always have one unknown wavefunction and one unknown energy when solving each equation.

Proposition 5

We can choose our $\left|n^{(k)}\right\rangle$ vectors so that they are all orthogonal to $\left|n^{(0)}\right\rangle$.

Basically, we can always take the piece of the vector proportional to $\left|n^{(0)}\right\rangle$ and put it into $\left|n^{(0)}\right\rangle$ instead, and there are no normalization problems by our assumption. The argument is spelled out more carefully in Professor Zwiebach's notes, but for illustration, let's write it out for the λ^1 equation, which is (copying from above)

$$\left(H^{(0)} - E_n^{(0)}\right)\left|n^{(1)}\right\rangle = \left(E_n^{(1)} - \delta H\right)\left|n^{(0)}\right\rangle .$$

Suppose that $\left\langle n^{(0)} \middle| n^{(1)}\right\rangle$ is nonzero. Then we can find a new solution

$$\left|n^{(1)}\right\rangle' = \left|n^{(1)}\right\rangle + c\left|n^{(0)}\right\rangle ,$$

which is also a solution to the equation, and we pick c so that $\langle n^{(0)} | n^{(1)} \rangle' = 0$ (explicitly, we pick $c = -\langle n^{(0)} | n^{(1)} \rangle$). And this kind of process can be done for higher-order terms as well.

So now let's solve the λ^1 equation: both sides of the equation are vectors, and thus we can check equality by taking inner products with the orthonormal basis $|k^{(0)}\rangle$ (for all nonnegative integers k). First, let's act with $\langle n^{(0)}|$ on both sides, which gives us

$$\left\langle n^{(0)} \middle| H^{(0)} - E_n^{(0)} \middle| n^{(1)} \right\rangle = \left\langle n^{(0)} \middle| E_n^{(1)} - \delta H \middle| n^{(0)} \right\rangle,$$

which is an equality of numbers. But notice that the left-hand side is zero here, because

$$(H^{(0)} - E_n^{(0)}) \left| n^{(0)} \right\rangle = 0,$$

and then we can take the adjoint of both sides, noting that our operators are Hermitian, to get that

$$\left\langle n^{(0)} \right| (H^{(0)} - E_n^{(0)}) = 0.$$

So looking at the right-hand side, we have

$$0 = \left\langle n^{(0)} \middle| E_n^{(1)} - \delta H \middle| n^{(0)} \right\rangle = E_n^{(1)} \left\langle n^{(0)} \middle| n^{(0)} \right\rangle - \left\langle n^{(0)} \middle| \delta H \middle| n^{(0)} \right\rangle,$$

which means that (because $|n^{(0)}\rangle$ is taken to be normalized)

$$E_n^{(1)} = \left\langle n^{(0)} \middle| \delta H \middle| n^{(0)} \right\rangle.$$

In other words, we've found the energy correction (without needing to find the state correction)! And now let's generalize this to the kth order equation, which (again copying from above) is

$$\left(H^{(0)} - E_n^{(0)}\right) \left| n^{(k)} \right\rangle = \left(E_n^{(1)} - \delta H\right) \left| n^{(k-1)} \right\rangle + E_n^{(2)} \left| n^{(k-2)} \right\rangle + \cdots + E_n^{(k)} \left| n^{(0)} \right\rangle.$$

If we act with the bra $\langle n^{(0)}|$ again, the left-hand side is again zero, and orthogonality means that **everything except the first and last term on the right-hand side become zero**! So we're left with

$$0 = \left\langle n^{(0)} \middle| E_n^{(1)} - \delta H \middle| n^{(k-1)} \right\rangle + E_n^{(k)}$$

whenever $k > 1$, and we can even take out the $E_n^{(1)}$ term in the first term because of orthogonality again. So that leaves us with our final result:

Proposition 6

The higher-order corrections to the energy are given by

$$E_n^{(k)} = \left\langle n^{(0)} \middle| \delta H \middle| n^{(k-1)} \right\rangle.$$

Notice that this requires us to have the $(k-1)$th-order state correction to find the kth-order energy correction. So we'll start next lecture by understanding how to find the eigenstate correction $|n^{(1)}\rangle$!

Remark 7. *Analyticity in our Hamiltonians is okay to assume when we have finite-dimensional Hilbert spaces, but if we have infinite-dimensional Hilbert spaces, it depends on how our operators act – the resulting power series may not converge. Such* **asymptotic series** *can still be useful, though – we just need to sum the right number of terms and make sure we don't add up too many of them! But we won't worry too much about that in this course.*

2 February 17, 2021 (Recitation)

Professor Stewart's been at MIT for 17 years and is currently the director of the Center for Theoretical Physics, working on nuclear and particle physics (particularly quantum field theory).

Fact 8

Everyone in the class introduced themselves (name, location/time zone, year, what we did over IAP, and what we like doing outside of physics).

Some recitation materials have been posted on Canvas, so we can always scroll back to see what we talked about recently (as long as we refresh our browser). We can also use gather.town as a proximity video chat app: we can talk to just the people who are near us, see a shared whiteboard, and generally have the room serve as a "virtual classroom." So the idea is to work on our problem sets in here as a replacement to the physics common room, and it'll also be the space for office hours.

Fact 9

The office hours for this class are tentatively Tuesday 5-6 (Cagin), Wednesday 1-2 (Professor Stewart), Thursday 11-12 (Professor Metlitski), and Friday 2-3 (Cagin).

The point of recitations is not to teach much new formalism – instead, we'll review some concepts or do practice problems each time. But if we like or don't like something in particular, we should let Professor Stewart know.

We're doing perturbation theory right now, so we'll start by emphasizing the importance of perturbation theory ideas in physics. Basically any problem that we solve requires us to make some approximation (the system is nonrelativistic, or there are a certain discrete set of states we're considering). In 8.05, we often include these as part of the problem statement, but in 8.06 we'll be a bit more careful about what approximations we're making and what we can neglect.

Our first step is time-independent perturbation theory, and in lecture we started by only considering nondegenerate states (meaning that the energy levels are different). To review, we wrote our Hamiltonian as

$$H = H^{(0)} + \lambda \delta H,$$

and our goal is to solve the H eigenvalue problem $H|n\rangle = E_n|n\rangle$ given the answer to the $H^{(0)}$ eigenvalue problem $H^{(0)}\left|n^{(0)}\right\rangle = E_n^{(0)}\left|n^{(0)}\right\rangle$. The idea is to use the λ as a parameter to expand in a power series: we write the perturbed energies and eigenstates as

$$|n\rangle = \left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \lambda^2\left|n^{(2)}\right\rangle + \cdots,$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots.$$

(Some textbooks may use slightly different conventions about λ, so we should be aware of that.) A derivation done from lecture, assuming that $\left|n^{(k)}\right\rangle$ (for positive k) are all orthogonal to $\left|n^{(0)}\right\rangle$, led us to the result

$$E_n^{(1)} = \left\langle n^{(0)}\middle|\delta H\middle|n^{(0)}\right\rangle$$

as well as the more general answer

$$E_n^{(k)} = \left\langle n^{(0)}\middle|\delta H\middle|n^{(k-1)}\right\rangle.$$

So once we figure out how to find $\left|n^{(k)}\right\rangle$ (next lecture), we'll be able to find the coefficients of our power series. (The first answer will turn out to be $\left|n^{(1)}\right\rangle = -\sum_{k\neq n} \frac{\left|k^{(0)}\right\rangle\left\langle k^{(0)}\middle|\delta H\middle|n^{(0)}\right\rangle}{E_k^{(0)}-E_n^{(0)}}$, but we won't use that anywhere today.)

One of our questions to ask is "why can we do this expansion" in a specific problem, and in particular, what kinds of things can happen if the expansion is not okay.

Example 10

If something non-physical is being predicted (like an un-normalizable state, or a probability that's less than 0 or more than 1), then either we did an incorrect calculation or perturbation theory doesn't apply.

Example 11

There's also certain effects that are missed by perturbation theory – for example, if we approximate a double-hump potential by a quadratic function, we ignore the possibility of tunneling outside the humps. So if we care about that kind of situation, perturbation theory might not be the right tool to use.

Example 12

If we find that $\lambda E_n^{(1)}$ is on the same order of magnitude as $E_n^{(0)}$, then our perturbation isn't a good approximation, either. Similarly (but perhaps less intuitively), if the gap between the energy levels $E_{n+1}^{(0)} - E_n^{(0)}$ is on the same order as our perturbation $\lambda E_n^{(1)}$, then we might also run into problems.

To illustrate how some of these situations might come up, let's do a particular calculation:

Example 13

Consider two levels in a physical system, forming a two-state system. Let's try to analyze the question of "potential crossings" of energy levels more carefully.

The unperturbed Hamiltonian for this system is then

$$H^{(0)} = \begin{bmatrix} E_0^{(0)} & 0 \\ 0 & E_1^{(0)} \end{bmatrix}$$

(if the starting energy levels are $E_0^{(0)}$ and $E_1^{(0)}$). Suppose that our perturbation looks something like

$$\lambda\delta H = \lambda \begin{bmatrix} \omega_1 & \omega_0 \\ \omega_0 & -\omega_1 \end{bmatrix}:$$

let's try to understand how to solve this system exactly. The idea is that we'll **switch to Pauli matrices**: the diagonal terms of the perturbed Hamiltonian H are $E_0^{(0)} + \lambda\omega_1$ and $E_1^{(0)} - \lambda\omega_1$, and we want to write these as $\overline{E} - \Delta$ and $\overline{E} + \Delta$ (just by making a change of variables). Once we do that, the Hamiltonian can be written as

$$H = \begin{bmatrix} \overline{E} - \Delta & \lambda\omega_0 \\ \lambda\omega_0 & \overline{E} + \Delta \end{bmatrix}.$$

The exact eigenvalues here are

$$\lambda = \overline{E} \pm \sqrt{\Delta^2 + (\lambda\omega_0)^2},$$

and on problem 1 of our problem set, we'll see that we can get the first-order term here (after expanding the square root) using perturbation theory. But returning to the motivating question: Δ is the energy splitting, and $\lambda\omega_0$ is the scale of the perturbation, so this is an example where we need the energy difference to be much larger than the perturbation for the square-root expansion to be valid.

So looking at the form of the perturbed energies, we won't have any energy crossings unless the entire square root term is zero, meaning $\omega_0 = \Delta = 0$. And tuning two things to zero is very difficult, so we should not expect crossings in the generic case.

3 February 18, 2021

First, a quick review: last time, we started the study of non-degenerate perturbation theory, and the setup is that we have a perturbed Hamiltonian $H(\lambda) = H^{(0)} + \lambda\delta H$ (where the second term is small compared to the first). When trying to solve this $H(\lambda)\left|n\right\rangle_\lambda = E_n(\lambda)\left|n\right\rangle_\lambda$, we expanded a power series in terms of our parameter λ, and last time, we found the expressions for the energy coefficients $E_n^{(1)}, E_n^{(2)}, \cdots$ by plugging our ansatz back into the Schrodinger equation and collected **order-by-order terms**, which we could solve recursively. The first result we found was that

$$E_n^{(1)} = \left\langle n^{(0)}\middle|\delta H\middle|n^{(0)}\right\rangle,$$

and we arrived at this by basically "looking at the $\left|n^{(0)}\right\rangle$-components" by putting a $\left\langle n^{(0)}\right|$ on both sides of the order-by-order vector equations. So if we instead try looking at components along $\left\langle k^{(0)}\right|$, we find that

$$\left\langle k^{(0)}\middle|H^{(0)} - E_n^{(0)}\middle|n^{(1)}\right\rangle = \left\langle k^{(0)}\middle|E_n^{(1)} - \delta H\middle|n^{(0)}\right\rangle.$$

On the left-hand side, if we have the operator act on the bra instead of the ket, we get the expression $(E_k^{(0)} - E_n^{(0)})\left\langle k^{(0)}\middle|n^{(1)}\right\rangle$. Meanwhile, on the right-hand side, the term $\left\langle k^{(0)}\middle|E_n^{(1)}\middle|n^{(0)}\right\rangle$ is zero by orthogonality, so we end up with

$$(E_k^{(0)} - E_n^{(0)})\left\langle k^{(0)}\middle|n^{(1)}\right\rangle = -\left\langle k^{(0)}\middle|\delta H\middle|n^{(0)}\right\rangle \implies \left\langle k^{(0)}\middle|n^{(1)}\right\rangle = -\frac{\left\langle k^{(0)}\middle|\delta H\middle|n^{(0)}\right\rangle}{E_k^{(0)} - E_n^{(0)}},$$

and since the numerator is a matrix element, we'll introduce the notation

$$\delta H_{kn} = \left\langle k^{(0)}\middle|\delta H\middle|n^{(0)}\right\rangle,$$

and thus we have

$$\left\langle k^{(0)}\middle|n^{(1)}\right\rangle = -\frac{\delta H_{kn}}{E_k^{(0)} - E_n^{(0)}}.$$

This is actually enough to tell us the first-order correction $\left|n^{(1)}\right\rangle$: because our initial eigenstates form a complete orthonormal basis, we can write the resolution of the identity $1 = \sum_k \left|k^{(0)}\right\rangle\left\langle k^{(0)}\right|$

$$\left|n^{(1)}\right\rangle = \sum_k \left|k^{(0)}\right\rangle\left\langle k^{(0)}\middle|n^{(1)}\right\rangle.$$

When $k = n$, we have $\left\langle n^{(0)}\middle|n^{(1)}\right\rangle = 0$ by our "useful choice" from last lecture! So we can just restrict this sum to terms $k \neq n$, and thus we find that

$$\boxed{\left|n^{(1)}\right\rangle = -\sum_{k\neq n}\frac{\delta H_{kn}}{E_k^{(0)} - E_n^{(0)}}\left|k^{(0)}\right\rangle}.$$

Basically, if we want to calculate the first-order correction to the state $|n\rangle$, we get potential contributions from **all unperturbed states** $\left|k^{(0)}\right\rangle$.

Remark 14. *This is the first time we're encountering an energy difference in the denominator, but it'll come up much more in perturbation theory. And notice that this is the first time that we need the nondegeneracy (otherwise, it's possible that we'll have the denominator* $E_k^{(0)} - E_n^{(0)}$ *being zero!)*

Fact 15

For the purpose of this course, the perturbations aren't going to introduce new degrees of freedom, because $H^{(0)}$ and δH live in the same Hilbert space. So the resolution of the identity is indeed valid.

Last time, we also found the kth-order correction to the energy

$$E_n^{(\ell)} = \left\langle n^{(0)} \middle| \delta H \middle| n^{(\ell-1)} \right\rangle.$$

So if we plug in $\ell = 2$ and our expression above for $\left|n^{(1)}\right\rangle$, we find that

$$E_n^{(2)} = \left\langle n^{(0)} \middle| \delta H \middle| n^{(1)} \right\rangle = -\sum_{k \neq n} \frac{\delta H_{kn}}{E_k^{(0)} - E_n^{(0)}} \left\langle n^{(0)} \middle| \delta H \middle| k^{(0)} \right\rangle,$$

which further simplifies by our definition to

$$E_n^{(2)} = -\sum_{k \neq n} \frac{\delta H_{kn} \delta H_{nk}}{E_k^{(0)} - E_n^{(0)}}.$$

But because δH is a Hermitian operator, $\langle k^{(0)} | \delta H | n^{(0)} \rangle = \langle n^{(0)} | \delta H | k^{(0)} \rangle^*$, so $\delta H_{kn} = \delta H_{nk}^*$. Thus, we have our final answer

$$\boxed{E_n^{(2)} = -\sum_{k \neq n} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}}}.$$

For visualization, we can expand the numerator out explicitly as well:

$$E_n^{(2)} = -\sum_{k \neq n} \frac{\langle n^{(0)} | \delta H | k^{(0)} \rangle \langle k^{(0)} | \delta H | n^{(0)} \rangle}{E_k^{(0)} - E_n^{(0)}}.$$

So this numerator can be thought of as starting with our unperturbed state $\left|n^{(0)}\right\rangle$, transitioning to $\left|k^{(0)}\right\rangle$ (through the second term in the numerator), and the transitioning back to $\left|n^{(0)}\right\rangle$ (through the first term in the numerator), paying the energy difference in the denominator.

In summary, we've now calculated $|n\rangle_\lambda$ to first-order: we know that

$$\boxed{|n\rangle_\lambda = \left|n^{(0)}\right\rangle - \lambda \sum_{k \neq n} \frac{\delta H_{kn}}{E_k^{(0)} - E_n^{(0)}} \left|k^{(0)}\right\rangle + O(\lambda^2)},$$

and we've also calculated the energy $E_n(\lambda)$ to second order:

$$\boxed{E_n(\lambda) = E_n^{(0)} + \lambda \delta H_{nn} - \lambda^2 \sum_{k \neq n} \frac{\langle n^{(0)} | \delta H | k^{(0)} \rangle \langle k^{(0)} | \delta H | n^{(0)} \rangle}{E_k^{(0)} - E_n^{(0)}} + O(\lambda^3)}.$$

We can already say some things about our results now: for example, we can try taking $n = 0$.

Proposition 16

The first-order approximation to the ground state energy is always an overestimate (for any value of λ):

$$E_0^{(0)} + \lambda\delta H_{00} \ge E_0(\lambda).$$

Proof. We know that

$$E_0^{(0)} + \lambda\delta H_{00} = \left\langle 0^{(0)} \middle| H^{(0)} \middle| 0^{(0)} \right\rangle + \lambda \left\langle 0^{(0)} \middle| \delta H \middle| 0^{(0)} \right\rangle = \left\langle 0^{(0)} \middle| H^{(0)} + \lambda\delta H \middle| 0^{(0)} \right\rangle = \left\langle 0^{(0)} \middle| H(\lambda) \middle| 0^{(0)} \right\rangle,$$

and now the **variational principle** (with $\left|0^{(0)}\right\rangle$ as our test state) tells us that this must be at least the ground state energy of $H(\lambda)$, which is $E_0(\lambda)$ as desired. (And as a reminder, we prove the variational principle by expanding out the original ground state $\left|0^{(0)}\right\rangle$ as a linear combination of the new eigenstates.) ☐

This is in fact **consistent** with the Taylor expansion above: notice that the second-order correction for the ground state $E_0^{(2)}$ is **always negative**, because the numerators (squared norm) and denominators (differences to the ground state energy) are always positive, and there is a $-\lambda^2$ in front. But it's more powerful because we don't need to assume that we have small λ!

And now motivated by that discussion of positivity, if we turn our attention to arbitrary n, we have

$$E_n^{(2)} = -\sum_{k \ne n} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} = -\sum_{k>n} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} + \sum_{k<n} \frac{|\delta H_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}$$

(we've adjusted a few signs in the second term). So energy levels above n contribute a negative second-order correction, pushing it down, while energy levels below n contribute a positive second-order correction, pushing it up. So the levels kind of repel each other, and this principle of **level repulsion** will come up some more in the rest of this course!

So now that we've figured out the correct expressions, we'll turn to discussing the **validity** of this approach: when is it okay to write everything out as a power series? Basically, what does it mean for the operator $\lambda\delta H$ to be small, and how small does it need to be?

We'll do a simple case with a 2-dimensional Hamiltonian to study this:

Example 17

Suppose we have the 2×2 matrix Hamiltonian

$$H(\lambda) = H^{(0)} + \lambda\delta H = \begin{bmatrix} E_1^{(0)} & 0 \\ 0 & E_2^{(0)} \end{bmatrix} + \lambda \begin{bmatrix} 0 & V \\ V^* & 0 \end{bmatrix} = \begin{bmatrix} E_1^{(0)} & \lambda V \\ \lambda V^* & E_2^{(0)} \end{bmatrix}.$$

This is a problem which is simple enough that we can get the exact eigenstates and energies, and we can then compare the answer to perturbation theory. The exact solution comes from diagonalizing the matrix: we have

$$E_\pm(\lambda) = \frac{E_1^{(0)} + E_2^{(0)}}{2} \pm \frac{E_1^{(0)} - E_2^{(0)}}{2} \sqrt{1 + \frac{\lambda^2 |V|^2}{\left(\frac{E_1^{(0)} - E_2^{(0)}}{2}\right)^2}}.$$

We'll write this expression as

$$E_\pm(\lambda) = \frac{E_1^{(0)} + E_2^{(0)}}{2} \pm \frac{E_1^{(0)} - E_2^{(0)}}{2} f(z),$$

where $z = \frac{\lambda|V|}{(E_1^{(0)} - E_2^{(0)})/2}$ and $f(z) = \sqrt{1+z^2}$. But the perturbative solution is basically a Taylor series expansion of this exact answer around $z = 0$, meaning the Taylor series expansion is the expansion of $f(z)$:

$$\sqrt{1+z^2} = 1 + \frac{z^2}{2} - \frac{z^4}{8} + \frac{z^6}{16} - \frac{5z^8}{128} + O(z^{10});$$

we can ask what the radius of convergence is for this series. This function is analytic around $z = 0$, but there are branch cuts at $z = \pm i$ (distance 1 away from 0), so complex analysis tells us that this will converge for $|z| < 1$, meaning that we require

$$\lambda |V| < \frac{E_1^{(0)} - E_2^{(0)}}{2}.$$

Fact 18

Generically, we're saying that **all of the off-diagonal matrix elements of the perturbation** δH (in the original eigenstate basis) **must be much smaller than the energy differences** for our perturbation to be valid, and this ends up being a general criterion.

Going back to the more general results we've obtained, recall that the first-order correction to the state gives us coefficients of $\frac{\lambda \delta H_{kn}}{E_k^{(0)} - E_n^{(0)}}$ – here, the numerator is the matrix element of the perturbation, and indeed we're asking for that to be much smaller than the denominator. But the diagonal entries are much more benign – if our δH were fully diagonal, then we would actually preserve our eigenstates, and there wouldn't be as many issues.

And now we're ready to apply this formalism to an important example:

Example 19 (1D anharmonic oscillator)

Let $H^{(0)} = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$ be the Hamiltonian of the simple harmonic oscillator (in which the frequency of oscillations is classically independent of the amplitude, meaning that the energy levels are equally spaced in the quantum treatment). We add a small **anharmonicity** proportional to x^4, which will make the frequency depend a bit on the amplitude (classical) and make the energy levels not exactly equal (quantum). Specifically, let

$$\lambda \delta H = \lambda \hbar \omega \left(\frac{x}{d} \right)^4,$$

where $d = \sqrt{\frac{\hbar}{m\omega}}$ is the length scale (dictating the width of the Gaussian for the original ground state).

Our full Hamiltonian is then

$$H(\lambda) = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 + \lambda \hbar \omega \left(\frac{x}{d} \right)^4,$$

and we want to do perturbation theory on it. A good strategy here is to use raising and lowering operators:

$$\frac{x}{d} = \frac{1}{\sqrt{2}} (a + a^\dagger),$$

so we can rewrite

$$\delta H = \frac{1}{4} \hbar \omega (a + a^\dagger)^4.$$

We'll start with the first-order energy correction to the ground state:

$$E_0^{(1)} = \left\langle 0^{(0)} \middle| \delta H \middle| 0^{(0)} \right\rangle = \frac{1}{4} \hbar \omega \left\langle 0^{(0)} \middle| (a + a^\dagger)^4 \middle| 0^{(0)} \right\rangle.$$

Using the algebra of a and $a^\dagger$, we find that this energy coefficient is $\frac{3}{4} \hbar \omega$, meaning that we estimate

$$E_0(\lambda) = \frac{1}{2} \hbar \omega + \lambda \frac{3}{4} \hbar \omega + O(\lambda^2).$$

We can then calculate the second-order energy correction as well, meaning that we want

$$E_0^{(2)} = -\sum_{k\neq 0} \frac{|\delta H_{k0}|^2}{E_k^{(0)} - E_0^{(0)}}.$$

We know all of the unperturbed energy levels $E_k^{(0)} = \left(k + \frac{1}{2}\right)\hbar\omega$, and also

$$\delta H_{k0} = \frac{1}{4}\hbar\omega \left\langle k^{(0)} \middle| (a+a^\dagger)^4 \middle| 0^{(0)} \right\rangle.$$

In principle, these kinds of problems can be hard, but in this case only finitely many terms can contribute to the final energy coefficient, because we can only raise 0 at most four times! And the states that we can get out of $x^4 |0\rangle$ must all be even wavefunctions, because x^4 and $|0\rangle$ are both even. So that means that the only states that contribute at all are $k = 0, 2, 4$. Indeed, we find that

$$(a+a^\dagger)^4 |0\rangle = 2\sqrt{6}\,|4\rangle + 6\sqrt{2}\,|2\rangle + 3\,|0\rangle,$$

so

$$\delta H_{40} = \frac{\hbar\omega}{4} 2\sqrt{6} = \frac{\hbar\omega}{2}\sqrt{6}, \quad \delta H_{20} = \frac{\hbar\omega}{4} 6\sqrt{2} = \frac{\hbar\omega}{2} 3\sqrt{2}.$$

(Remember that the second-order correction only sums over $k \neq 0$.) And now plugging these expressions in,

$$E_0^{(2)} = -\frac{|\delta H_{20}|^2}{E_2^{(0)} - E_0^{(0)}} - \frac{|\delta H_{40}|^2}{E_4^{(0)} - E_0^{(0)}} = -\frac{(\hbar\omega)^2 \cdot \left(\frac{3\sqrt{2}}{2}\right)^2}{2\hbar\omega} - -\frac{(\hbar\omega)^2 \cdot \left(\frac{\sqrt{6}}{2}\right)^2}{4\hbar\omega} = -\frac{21}{8}\hbar\omega.$$

And our answer now is

$$E_0^{(2)} = \frac{1}{2}\hbar\omega\left(1 + \frac{3}{2}\lambda - \frac{21}{4}\lambda^2 + O(\lambda^3)\right).$$

People have in fact calculated this series to high order: the next terms are $\frac{333}{8}\lambda^3$ and $-\frac{30855}{64}\lambda^4$. And we can tell that the coefficients here are actually growing, but in fact we find that the radius of convergence is 0. So this is our first example of an **asymptotic series** – the way we use these is that for λ small, the first few terms will still look like we have convergence, so we just cut off the series at some point (and there are also techniques for resumming this series).

The reason this method breaks is that $E_0(\lambda)$ **isn't actually analytic** near $\lambda = 0$, but that doesn't necessarily mean it has to be large (for example, consider $e^{-1/\lambda}$ near $\lambda > 0$, which is not analytic but goes to 0 very quickly). And we could have guessed from the start that we wouldn't have had an analytic function, because the potential would have been unbounded from below if λ were any negative real number, meaning the ground state energy wouldn't be well-defined at all! Many other physical examples also lead to these kinds of asymptotic series, and we should keep an eye out for this in the future.

4 February 22, 2021 (Recitation)

(We'll usually start recitation with questions and clarifications about the problem set, but I won't write those questions and answers down here.)

This problem we'll do today is similar to the ones that we'll encounter on our homework:

Problem 20

Suppose we have two square wells (where one is a perturbation of the other). Specifically, let the starting Hamiltonian be $H^{(0)} = \frac{p^2}{2m} + V_{\infty\text{-well}}$, where $V_{\infty\text{-well}}$ is the potential which is 0 for $x \in [0, L]$, and consider the perturbation

$$\lambda \delta H = \lambda \begin{cases} -V_0 & 0 < x < L/2 \\ 0 & \text{otherwise.} \end{cases}$$

We know the solution for the (unperturbed) infinite square well already: since the wavefunctions must vanish outside of the range $[0, L]$, the normalized eigenfunctions take the form

$$\psi_n^{(0)} = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

for $n \ge 1$, with energies $E_n^{(0)} = \frac{n^2\pi^2\hbar^2}{2mL^2}$. And the perturbation changes our square well so that the height from 0 to $L/2$ is different from the height from $L/2$ to L: we want to know what this perturbation does to our energy eigenfunctions.

Our goal (in breakout rooms) is to find $E_n^{(1)}$ and $\psi_1^{(1)}$ (the perturbation to the ground state).

Solution. Recall that the formulas for the coefficients are

$$E_n^{(1)} = \left\langle n^{(0)} \middle| \delta H \middle| n^{(0)} \right\rangle, \quad \left| n^{(1)} \right\rangle = \psi_n^{(1)} = \sum_{k \ne n} \psi_k^{(0)} \frac{\delta H_{kn}}{E_k^{(0)} - E_n^{(0)}}$$

(these are the same formulas as from lecture, but we're using notation like $\psi_n^{(1)}$ instead of $\left|n^{(1)}\right\rangle$). Because we don't have a matrix representation of δH, the easiest way to calculate the matrix elements is to integrate directly:

$$\left\langle n^{(0)} \middle| \delta H \middle| n^{(0)} \right\rangle = -V_0 \int_0^{L/2} \left| \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \right|^2 dx = -\frac{V_0}{2}.$$

(We can compute this using symmetry arguments, or we can use the power reducing formula $\cos 2x = 1 - 2\sin^2 x$.) In other words, all of the energies E_n decrease by the same amount $\frac{\lambda V_0}{2}$, which is exactly half of the well decrease. (This makes sense, because particles spend half the time in the left side and half the time in the right side, no matter which eigenstate they're in, since the squared (unperturbed) wavefunctions are all symmetric about $\frac{L}{2}$).

Next, to find the perturbation to the ground state, we need to calculate the values of

$$\delta H_{k1} = \left\langle k^{(0)} \middle| \delta H \middle| 1^{(0)} \right\rangle = -V_0 \int_0^{L/2} \frac{2}{L} \sin\left(\frac{k\pi x}{L}\right) \sin\left(\frac{\pi x}{L}\right) dx.$$

Doing some manipulations gives us the answer for any $k \ge 2$,

$$= -V_0 \frac{2k}{\pi(1-k^2)} \cos\frac{k\pi}{2},$$

and this is nonzero only when k is even (in which case our answer is $(-1)^{k/2}$). The idea here is basically that the even wavefunctions are antisymmetric around $\frac{L}{2}$, but the odd wavefunctions are symmetric around $\frac{L}{2}$. So the overlap from 0 to $\frac{L}{2}$ will be the same as the overlap from $\frac{L}{2}$ to L for odd k, but the total overlap is 0 (because our starting eigenfunctions are orthogonal)! Therefore δH_{k1} is zero for odd k.

So returning to the expression,

$$\psi_1^{(1)}(x) = -\sum_{k \ne 1} \psi_k^{(0)}(x) \frac{\delta H_{k1}}{E_k^{(0)} - E_1^{(0)}},$$

we can now plug in δH_{k1} and $E_k^{(0)}$ to get our answer: since $E_k^{(0)} - E_1^{(0)} = (k^2-1)\frac{\pi^2\hbar^2}{2mL^2}$, we have

$$\psi_1^{(1)}(x) = -\sum_{k \text{ even}} \psi_k^{(0)}(x)\left(-\frac{2kV_0}{\pi(1-k^2)}(-1)^{k/2}\right)\frac{2mL^2}{\pi^2\hbar^2(k^2-1)},$$

and we could simplify this a bit more but won't get too much insight out of it. $\square$

We'll pose another question as well, related to the harmonic oscillator, just to remind us of some relevant formulas for the problem set (even though we don't have time to solve it yet):

Problem 21

Consider the harmonic oscillator $H^{(0)} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2$ for a charged particle, placed in an electric field in the x-direction, so that our perturbation is

$$\lambda\delta H = -\lambda qEx.$$

This is a linear perturbation (we talked about the cubic and quartic perturbation in other parts of the course). We'll think about the same quantities $E_n^{(1)}$ and $\left|n^{(1)}\right\rangle$ next time, but the useful harmonic oscillator facts to remember are the following:

- We can write $\hat{x}$ in terms of the raising and lowering operators

$$\hat{x} = \frac{d}{\sqrt{2}}(a + a^\dagger), \quad \hat{p} = \frac{i\hbar}{\sqrt{2}d}(a^\dagger - a),$$

  where $d^2 = \frac{\hbar}{m\omega}$ and we can check our work using that $[a, a^\dagger] = 1$.
- We can rewrite the Hamiltonian as $H^{(0)} = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right)$, so that

$$H^{(0)}\left|n^{(0)}\right\rangle = \left(n + \frac{1}{2}\right)\hbar\omega\left|n^{(0)}\right\rangle.$$

- The action of the raising and lowering operators on the energy eigenstates is

$$a^\dagger\left|k^{(0)}\right\rangle = \sqrt{k+1}\left|(k+1)^{(0)}\right\rangle, \quad a\left|k^{(0)}\right\rangle = \sqrt{k}\left|(k-1)^{(0)}\right\rangle.$$

5 February 23, 2021

Last time, we were discussing the ideas of time-independent perturbation theory by considering Hamiltonians of the form $H(\lambda) = H^{(0)} + \lambda\delta H$. We've been talking about energies that are non-degenerate so far in the first two lectures, and we solve the problems by assuming we can do power series expansions in λ.

Today, we'll discuss **degenerate perturbation theory**: we already know that we'll have some more trouble because the energy differences $E_k^{(0)} - E_n^{(0)}$ in the denominators can now be 0. So before we get into the formalism, we'll do a quick example:

Example 22

Consider a Hilbert space spanned by two states, and take the Hamiltonian to be the 2×2 matrix given by

$$H = H^{(0)} + \lambda\delta H = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \lambda\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = \begin{bmatrix} 1 & \lambda \\ \lambda & 1 \end{bmatrix}.$$

The unperturbed Hamiltonian $H^{(0)}$ has two energy levels, and they're both degenerate: we have $E_1^{(0)} = E_2^{(0)} = 1$ with eigenvectors $\begin{bmatrix} 1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \end{bmatrix}$.

Now let's forget everything we said about non-degenerate perturbation theory not working, and let's blindly apply the formulas and see what we get. Then the energy corrections to first-order, according to non-degenerate perturbation theory, are

$$E_1(\lambda) = E_1^{(0)} + \lambda \delta H_{11} = 1 + \lambda \cdot 0 = 1,$$

$$E_2(\lambda) = E_2^{(0)} + \lambda \delta H_{22} = 1 + \lambda \cdot 0 = 1.$$

So it looks like the energies don't change to first order, but this is **not actually true**: in such a system we can solve directly for the eigenvalues and eigenvectors for $\begin{bmatrix} 1 & \lambda \\ \lambda & 1 \end{bmatrix}$: they are $\frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}$ with eigenvalue $1 + \lambda$ and $\frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}$ with eigenvalue $1 - \lambda$ (because the matrix is $1 + \lambda \sigma_x$). So the eigenvalues do split at first order, and something is wrong with our non-degenerate treatment.

Also, the unperturbed eigenvectors that we wrote for $H^{(0)}$ above are in a completely different direction from the perturbed eigenvectors for $H(\lambda)$ that we directly calculated. So if we're not careful, it looks like the eigenvectors "jump" once λ becomes positive (even though all of the energy levels and eigenvectors are supposed to be continuous). But what's really happening here is that when we chose $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$ and $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$ above, that was only one potential choice for our eigenvectors – **any linear combination** of those two is also an eigenstate because we have a common eigenvalue! But for any positive λ, because our two energy levels split and become nondegenerate, we can't allow for an arbitrary combination anymore. So **determining what the split state reduces to at infinitesimal** λ is a key step in degenerate perturbation theory.

So now we're ready to dive into the formalism: we're starting with a set of energy levels that are N-fold degenerate at some energy $E_n^{(0)}$. In other words, this means we'll have energy levels that look like

$$E_0^{(0)} \le E_1^{(0)} \le \cdots < E_n^{(0)} = E_{n+1}^{(0)} = \cdots = E_{n+N-1}^{(0)} < E_{n+N}^{(0)} \le \cdots .$$

Also, we'll use an orthonormal basis $\left|n^{(0)}, 1\right\rangle, \left|n^{(0)}, 2\right\rangle, \cdots, \left|n^{(0)}, N\right\rangle$ for our states at this energy level $E_n^{(0)}$, so that

$$H^{(0)} \left|n^{(0)}, k\right\rangle = E_n^{(0)} \left|n^{(0)}, k\right\rangle, \quad \left\langle n^{(0)}, k \middle| n^{(0)}, \ell\right\rangle = \delta_{k\ell}.$$

These N states span the **degenerate subspace**

$$V_N = \text{span}\left\{\left|n^{(0)}, 1\right\rangle, \cdots, \left|n^{(0)}, N\right\rangle\right\},$$

so that any linear combination of these N states is also an energy eigenstate with the same energy $E_n^{(0)}$. And the rest of the energy eigenstates span the rest of the Hilbert space $\mathcal{H}$, in that

$$\mathcal{H} = V_N \oplus V_\perp$$

for the orthogonal complement $V_\perp$ spanned by all other energies:

$$V_\perp = \text{span}\left\{\left|p^{(0)}\right\rangle : p \ne n\right\}.$$

We should notice that we're using a different labeling for states in the degenerate subspace and otherwise: only one label p for everything outside our degenerate subspace. And for all such states $\left|p^{(0)}\right\rangle$, $E_p^{(0)}$ is always different from $E_n^{(0)}$, so $\left\langle p^{(0)} \middle| n^{(0)}, k\right\rangle = 0$. And we'll also additionally assume that we have orthonormality of those states, meaning that $\left\langle p^{(}0) \middle| q^{(0)} \right\rangle = \delta_{pq}$.

So now we can turn on the perturbation λ: we want to understand how the states evolve, and usually they will split into N states of different energies, which we'll label as $|\psi_{I=1}\rangle, |\psi_{I=2}\rangle, \cdots, |\psi_{i=N}\rangle$. These eigenstates must satisfy

$$H(\lambda)\,|\psi_I\rangle_\lambda = E_I(\lambda)\,|\psi_I\rangle_\lambda\,,$$

and our goal is to find $E_I(\lambda)$ and $|\psi_I\rangle_\lambda$ – we'll do this again by trying to find a power series expansion for the state and the energy

$$|\psi_I\rangle_\lambda = \left|\psi_I^{(0)}\right\rangle + \lambda\left|\psi_I^{(1)}\right\rangle + \lambda^2\left|\psi_I^{(2)}\right\rangle + \cdots\,,$$
$$E_I(\lambda) = E_n^{(0)} + \lambda E_{n,I}^{(1)} + \lambda^2 E_{n,I}^{(2)} + \cdots\,.$$

As $\lambda \to 0^+$, we can indeed check that the energies approach the perturbed $E_n^{(0)}$, but the states will approach $\left|\psi_I^{(0)}\right\rangle$. We know that $\left|\psi_I^{(0)}\right\rangle$ must be some **very particular** eigenstates of the unperturbed Hamiltonians, and we don't quite know what they are yet: we just know that

$$\left|\psi_I^{(0)}\right\rangle = \sum_{k=1}^{N}\left|n^{(0)}, k\right\rangle a_{Ik}$$

for complex coefficients a_{Ik}, because each of those eigenstates lives in the span of our original $\left|n^{(0)}, k\right\rangle$s. So we need to find the a_{Ik}s to find the $\left|\psi_I^{(0)}\right\rangle$s, which we'll call the **good states**. We know that for any positive λ, if the energies split, the good states must form an orthonormal basis. So we have $\left\langle \psi_I^{(0)} \middle| \psi_J^{(0)} \right\rangle = \delta_{IJ}$.

So now we're ready to do a similar strategy as in the non-degenerate case: plug our solutions into the eigenvalue equations, and expand them order-by-order. We'll then find that at zeroth order, we have

$$(H^{(0)} - E_n^{(0)})\left|\psi_I^{(0)}\right\rangle = 0,$$

at first order λ^1,

$$(H^{(0)} - E_n^{(0)})\left|\psi_I^{(1)}\right\rangle = (E_{n,I}^{(1)} - \delta H)\left|\psi_I^{(0)}\right\rangle,$$

and at second order λ^2,

$$(H^{(0)} - E_n^{(0)})\left|\psi_I^{(2)}\right\rangle = (E_{n,I}^{(1)} - \delta H)\left|\psi_I^{(1)})\right\rangle + E_{n,I}^{(2)}\left|\psi_I^{(0)}\right\rangle.$$

These are the same as before, just with some extra subscripts, but let's see what they mean this time. Again, the $\lambda = 0$ equation doesn't tell us anything new – we already knew that $\psi_I^{(0)}$ is in the degenerate subspace. So we turn to the next equation, and the first thing we need to do is to determine these good states $\left|\psi_I^{(0)}\right\rangle$ (**compare this to the non-degenerate case**, where we already knew the zeroth order state because there was no ambiguity). So we'll determine $\left|\psi_I^{(0}\right\rangle$ by hitting the λ^1 equation with $\left\langle n^{(0)}, \ell\right|$ for arbitrary $\ell \in 1, 2, \cdots, N$:

$$\left\langle n^{(0)}, \ell \middle| H^{(0)} - E_n^{(0)} \middle| \psi_I^{(1)} \right\rangle = \left\langle n^{(0)}, \ell \middle| E_{n,I}^{(1)} - \delta H \middle| \psi_I^{(0)} \right\rangle.$$

Just like before, applying $H^{(0)} - E_n^{(0)}$ to the bra on the left-hand side gives us 0, and then rearranging gives us

$$\left\langle n^{(0)}, \ell \middle| \delta H \middle| \psi_I^{(0)} \right\rangle = E_{n,I}^{(1)}\left\langle n^{(0)}, \ell \middle| \psi_I^{(0)} \right\rangle.$$

But we parameterized our $\psi_I^{(0)}$ as the linear combination $\sum_{k=1}^{N}\left|n^{(0)}, k\right\rangle a_{Ik}$, so plugging that in gives us

$$\sum_{k=1}^{N}\left\langle n^{(0)}, \ell \middle| \delta H \middle| n^{(0)}, k \right\rangle a_{Ik} = E_{n,I}^{(1)}\sum_{k=1}^{N}\left\langle n^{(0)}, \ell \middle| n^{(0)}, k \right\rangle a_{Ik}.$$

But our $\left|n^{(0)}, k\right\rangle$s are assumed to be orthonormal, so the right-hand side collapses to only have the term where $k = \ell$:

$$\sum_{k=1}^{N} \left\langle n^{(0)}, \ell \middle| \delta H \middle| n^{(0)}, k \right\rangle a_{Ik} = E_{n,I}^{(1)} a_{I\ell}.$$

We'll now make this more transparent by rewriting the matrix elements

$$[\delta H]_{\ell k} = \left\langle n^{(0)}, \ell \middle| \delta H \middle| n^{(0)}, k \right\rangle :$$

here, k, ℓ run over the states in the degenerate subspace that we **already** know, and then δH can be thought of as an $N \times N$ matrix whose entries are exactly those elements above. (Basically, we're just looking at δH projected to V_N.) And this re-interpretation as a matrix means that

$$\sum_{k=1}^{N} [\delta H]_{\ell k} a_{Ik} = E_{n,I}^{(1)} a_{I\ell}.$$

Here, I is just some fixed index, so a_I can be thought of as an N-component **column vector** $a_I = \begin{bmatrix} a_{I1} \\ a_{I2} \\ \vdots \\ a_{IN} \end{bmatrix}$, and the left-hand side can then be thought of as a matrix multiplication

$$([\delta H] \cdot a_I)_\ell = E_{n,I}^{(1)} (a_I)_\ell \implies \boxed{[\delta H] a_I = E_{n,I}^{(1)} a_I}.$$

So the coefficients of a_I must be the eigenvalues of the $N \times N$ matrix δH, and thus the first-order corrections are just the eigenvalues of that matrix! And those N different resulting eigenstates will be the N good states $\left|\psi_I^{(0)}\right\rangle$.

Fact 23

If the eigenvalues of $[\delta H]$ are indeed distinct, meaning that $E_{n,I}^{(0)} \neq E_{n,J}^{(0)}$ for all $I \neq J$, then we say that **the degeneracy is lifted at** $O(\lambda)$ (the energy levels "leave" $\lambda = 0$ with different slopes). We hope for this situation, because then the a_I eigenvectors are unambiguous and thus we've found the "good states" already. But it's possible that some of the eigenvalues of $[\delta H]$ are the same, and thus some energy levels don't split off until second order (or not at all).

Often this is because there is hidden symmetry in the problem, but regardless, we don't actually know all of the good states in this case just from this calculation (because $E_{n,I}^{(1)} = E_{n,J}^{(1)}$ implies that any linear combination of a_I and a_J will be an eigenvector). So we'd then need to look at higher-order λ, and we might do an example of this later on.

Fact 24

What we've basically done above is diagonalize $[\delta H]$ using the good basis, meaning that $\left\langle \psi_J^{(0)} \middle| \delta H \middle| \psi_I^{(0)} \right\rangle = E_{n,I}^{(1)} \delta_{IJ}$.

To see that, note that

$$\left\langle \psi_J^{(0)} \middle| \delta H \middle| \psi_I^{(0)} \right\rangle = \sum_{k=1}^{N} \sum_{\ell=1}^{N} a_{J\ell}^{*} \left\langle n^{(0)}, \ell \middle| \delta H \middle| n^{(0)}, k \right\rangle a_{Ik} = a_J^{\dagger} [\delta H] a_I,$$

where we've turned the double sum into a matrix multiplication, and this simplifies to

$$= E_{n,I}^{(1)} a_J^\dagger a_I = E_{n,I}^{(1)} \delta_{IJ}$$

(by choosing our a_Is orthonormal). In general, δH and H will not commute, so we can't actually simultaneously diagonalize the two operators. But the point is that $[\delta H]$ is only a block of the full matrix δH: if we use the good basis for V_N, the block of the full δH corresponding to V_N will be diagonal, but that doesn't mean that the good states are actually eigenstate of the full δH: they're **only eigenstates of δH restricted to the V_N subspace!** After all, the components of the matrix δH might have some contributions between V_N and $V_\perp$: a resolution of the identity gives

$$\delta H \left|\psi_I^{(0)}\right\rangle = \left(\sum_J \left|\psi_J^{(0)}\right\rangle \left\langle \psi_J^{(0)}\right| + \sum_{p \neq n} \left|p^{(0))}\right\rangle \left\langle p^{(0)}\right| \right) \delta H \left|\psi_I^{(0)}\right\rangle,$$

and evaluating this gives us

$$= \sum_J \left|\psi_J^{(0)}\right\rangle \left\langle \psi_J^{(0)}\middle|\delta H\middle|\psi_I^{(0)}\right\rangle + \sum_{p\neq n} \left|p^{(0)}\right\rangle \left\langle p^{(0)}\middle|\delta H\middle|\psi_I^{(0)}\right\rangle = E_{n,I}^{(1)} \left|\psi_I^{(0)}\right\rangle + \sum_{p\neq n} \left|p^{(0)}\right\rangle \left\langle p^{(0)}\middle|\delta H\middle|\psi_I^{(0)}\right\rangle.$$

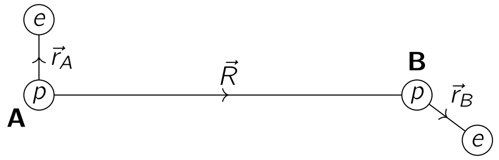
In other words, the first term behaves as we want it to, but the second term makes $\left|\psi_I^{(0)}\right\rangle$ not an actual eigenstate.

Finally, we'll elaborate on this point next time, but solving $[\delta H] \cdot a_I = E_{n,I}^{(1)} a_I$ can be difficult if we have a large degenerate subspace. So we'll examine how to use symmetry to simplify some work and get the eigenvectors without having to do very much!

6 February 24, 2021 (Recitation)

(As usual, problem set discussion is omitted.)

Today, instead of looking more at the harmonic oscillator, we'll discuss the **Van der Waals** force, which is a way of thinking about how two neutral hydrogen atoms interact with each other (at a higher order than the ordinary Coulomb force). The idea is that we have two atoms **A** and **B** which classically look like the diagram below:



We'll let the horizontal axis be the $\hat{z}$-direction, and we want to look at the limit when $R = |\vec{R}| \gg |\vec{r}_A|, |\vec{r}_B|$ (where $\vec{r}_A$ and $\vec{r}_B$ have typical length approximately equal to the Bohr radius a_0). To do perturbation theory, we're saying that our original Hamiltonian treats the two atoms as if they were completely separate:

$$H_0 = \left(\frac{\vec{p}_A^2}{2m} - \frac{e^2}{r_A}\right) + \left(\frac{\vec{p}_B^2}{2m} - \frac{e^2}{r_B}\right).$$

Since the Hamiltonian is a sum of two terms, the solutions for wavefunctions are just direct products $|n_A, \ell_A, m_A\rangle\, |n_B, \ell_B, m_B\rangle$ of the individual hydrogen atom wavefunctions, and the energies are similarly

$$E^0_{n_A n_B} = -\frac{e^2}{2a_0}\frac{1}{n_A^2} - \frac{e^2}{2a_0}\frac{1}{n_B^2}$$

(we're ignoring spin for the problem). So now if we want to do perturbation theory, we need to account for the six different pairwise electromagnetic interactions between the four charges. Two of them are already being considered, and the remaining terms are

$$\delta H = \frac{e^2}{R} + \frac{e^2}{|\vec{R} + \vec{r}_B - \vec{r}_A|} - \frac{e^2}{|\vec{R} + \vec{r}_B|} - \frac{e^2}{|\vec{R} - \vec{r}_A|}.$$

To use this to solve our problem, we're going to need to do some expansion of the distances (which gets a bit complicated), which results in the expression

$$\delta H = \frac{e^2}{R} + \frac{e^2}{\sqrt{(x_B - x_A)^2 + (y_B - y_A)^2 + (R + z_B - z_A)^2}} - \frac{e^2}{\sqrt{x_B^2 + y_B^2 + (R + z_B)^2}} - - \frac{e^2}{\sqrt{x_A^2 + y_A^2 + (R + z_A)^2}},$$

where we're letting the A proton be at $(0, 0, 0)$ and the B proton be at $(0, 0, R)$ (and then (x_A, y_A, z_A) and (x_B, y_B, z_B) are the coordinates of the two vectors $\vec{r}_A$ and $\vec{r}_B$. Then expansion of the square roots (in Taylor series) gets us the expression

$$\begin{aligned} &= \frac{e^2}{R} + \frac{e^2}{R}\left(1 - \frac{z_B - z_A}{R} + \frac{3}{2}\frac{(z_B - Z_A)^2}{R^2} - \frac{1}{2}\frac{(x_A - x_B)^2 + (y_A - y_B)^2 + (z_A - z_B)^2}{2R^2}\right) \\ &\quad - \frac{e^2}{R}\left(1 - \frac{z_B}{R} + \frac{3}{2}\frac{z_B^2}{R^2} - \frac{1}{2R^2}(x_B^2 + y_B^2 + z_B^2)\right) - \frac{e^2}{R}\left(1 + \frac{z_A}{R} + \frac{3}{2}\frac{z_A^2}{R^2} - \frac{1}{2R^2}(x_A^2 + y_A^2 + z_A^2)\right). \end{aligned}$$

The overall system is neutral, so there shouldn't be a long-range potential, and indeed we can see here that zeroth and first order terms in the x, y, z all cancel out. So if we expand out those second-order terms, we get a pretty simple expression for the perturbation:

$$\boxed{\delta H} = \frac{e^2}{R^3}(x_A x_B + y_A y_B - 2 z_A z_B) + O\left(\frac{1}{R^4}\right).$$

We can then rewrite this in the dot product form

$$= \boxed{\frac{e^2}{R^3}(\vec{r}_A \cdot \vec{r}_B - 3(\hat{z} \cdot \vec{r}_A)(\hat{z} \cdot \vec{r}_B))}.$$

We'll now treat $\vec{r}_A$ and $\vec{r}_B$ as quantum mechanical operators (they're decoupled from the point of view of $H^{(0)}$), and now we're getting close to the van der Waals force (it's really a dipole-dipole force, so we could have written this in terms of electric fields instead if we wanted). To do our perturbation theory, we'll think about the ground state: the first order shifts look like

$$\langle 100; 100 | \vec{r}_A \cdot \vec{r}_B | 100; 100 \rangle$$

(where the semicolon means we have a product state), and because the A and B parts are independent, this can be written as

$$\langle 100 | \vec{r}_A | 100 \rangle \cdot \langle 100 | \vec{r}_B | 100 \rangle .$$

Remark 25. *For more mathematical rigor (because $\vec{r}_A \cdot \vec{r}_B$ is a dot product and not separated on its own), we can first write this as the sum $\sum_i \langle 100; 100 | r_{iA} \cdot r_{iB} | 100; 100 \rangle$ and then separate as $\sum_i \langle 100 | r_{iA} | 100 \rangle \langle 100 | r_{iB} | 100 \rangle$, and then rewrite that as the dot product above.*

But remember that the ground state is spherically symmetric, so the expectation value of $\vec{r}_A$ or $\vec{r}_B$ is zero! (Alternatively, we can think about parity – the ground state is even, while the operator is odd.) And similarly, this type of argument makes the second term's matrix element also zero, and thus the entire first-order energy shift is zero.

So we have to go to second order, and we end up with

$$E_{11}^{(2)} = \sum_{N \text{ not ground}} \frac{|\langle N | \delta H | 100; 100 \rangle|^2}{E_{11}^{(0)} - E_N^{(0)}}$$

(where we've moved the negative sign into the denominator). Because the ground state is non-degenerate, we notice that $E_N^{(0)}$ will never be the same as $E_{11}^{(0)}$, so our denominators will always be nonzero. Unfortunately, calculating the matrix elements in the numerator is pretty hard, so we'll just say a few things about them. We'll get something similar to the $\langle 100|\vec{r}_A|100\rangle \cdot \langle 100|\vec{r}_B|100\rangle$ term from above, but with various excited states on the left instead of the ground states, and we need to excite both atoms to get something nonzero. Instead of calculating directly, we'll just estimate: since $-E_{22}^{(0)} \geq -E_N^{(0)}$ for all states N (this is the minimal amount of excitement that we can do on the atoms), we have $\frac{1}{E_{11}^{(0)}-E_N^{(0)}} \geq \frac{1}{E_{11}^{(0)}-E_{22}^{(0)}}$for all N, and thus we can estimate this expression above by removing the complicated weighting in the denominator:

$$E_{11}^{(2)} \geq \sum_{N \text{ not ground}} \frac{|\langle N|\delta H|100;100\rangle|^2}{E_{11}^{(0)} - E_{22}^{(0)}} = \frac{1}{E_{11}^{(0)} - E_{22}^{(0)}} \sum_N \langle 100;100|\delta H|N\rangle \langle N|\delta H|100;100\rangle .$$

And now because we have a sum over different eigenstates N, we can use **completeness**: adding back the cases that vanish, we get the operator $\sum_N |N\rangle\langle N| = 1$ appearing in our sum, and thus we're just left with

$$= \frac{1}{E_{11}^{(0)} - E_{22}^{(0)}} \left\langle 100;100\middle|(\delta H)^2\middle|100;100\right\rangle .$$

And now we can calculate this for real:

$$= \frac{1}{E_{11}^{(0)} - E_{22}^{(0)}} \frac{e^4}{R^6} \left\langle 100;100\middle|(x_A x_B + y_A y_B - 2z_A z_B)^2\middle|100;100\right\rangle ,$$

and now this is an overlap of hydrogen wavefunctions and we can do the integral explicitly. It turns out the answer we end up with (after substituting in all of the energies that we know) is

$$\boxed{E_{11}^{(2)} \geq} \frac{1}{-2\left(1-\frac{1}{4}\right)\left(\frac{e^2}{2a_0}\right)} \frac{e^4}{R^6} 6a_0^4 = \boxed{-\frac{8e^2 a_0^5}{R^6}}.$$

It turns out the exact answer (without the approximation) has a factor of -6.5 or so instead of -8, so we did a pretty good job. And the important thing is that we have a potential that goes as $\frac{1}{R^6}$ between the atoms, and that's exactly the **van der Waals potential** (that's why the force is proportional to $\frac{1}{R^7}$, where R is the distance between the two protons).

Remark 26. *Notice that even though our ground state is not degenerate, there are other (excited) states that are degenerate, so we proceeded without thinking about diagonalizing δH. But this is okay, because we get the same answer whether we use the diagonalized basis or the original one.*

For example, suppose that $|1\rangle, |2\rangle, |3\rangle$ in a system are degenerate at energy $E_1^{(0)}$, but $|0\rangle$ (the state we're trying to estimate) is not. Then our second-order energy correction looks like

$$-\frac{1}{E_1^{(0)} - E_0^{(0)}} \sum_{m=1,2,3} \left\langle 0^{(0)}\middle|\delta H\middle|m^{(0)}\right\rangle \left\langle m^{(0)}\middle|\delta H\middle|0^{(0)}\right\rangle + \sum_{m\geq 4} \cdots ,$$

and the key reason that the sum over $m = 1, 2, 3$ is okay (even if we don't use the "good states" mentioned in lecture) is that the change of basis which gets us to the good states $\left|m'^{(0)}\right\rangle$

$$\left|m^{(0)}\right\rangle = \sum_{m'} U_{mm'} \left|m'^{(0)}\right\rangle$$

has a unitary matrix U (meaning $U^\dagger U = I$), and under any such transformation we have (check this by plugging in our expression for $\left|m'^{(0)}\right\rangle$ from above)

$$\sum_m \left|m^{(0)}\right\rangle \left\langle m^{(0)}\right| = \sum_{m'} \left|m'^{(0)}\right\rangle \left\langle m'^{(0)}\right|.$$

So as long as the state that we're trying to estimate is non-degenerate, we don't need to worry about degenerate perturbation theory! But we'll get into the details of that in the future.

7 February 25, 2021

Professor Metlitski wants to make sure we all know about the **gather.town** space that was set up by Professor Stewart – it's a good place for us to work on problem sets and go to office hours, and the link is on Canvas.

Last time, we continued studying time-independent perturbation theory, starting to consider the case where we have energy degeneracies. In other words, we start with an energy level $E_n^{(0)}$ which is N-fold degenerate, and we study how it evolves as the perturbation is turned on. (Generically, the degeneracy will split into N different states.) These states $|\psi_I\rangle$ must satisfy the Schrodinger equation, and we looked for a power series expansion in λ for the perturbed states. And remember that the main difference is that **we don't know the zeroth-order states** or **good states** at the beginning: instead, we pick out those particular eigenvectors via

$$\left|\psi_I^{(0)}\right\rangle = \sum_{k=1}^{N} \left|n^{(0)}, k\right\rangle a_{Ik},$$

where the coefficients a_{Ik} are obtained from the eigenvector equation

$$[\delta H] a_I = E_{n,I}^{(1)} a_I,$$

where the matrix elements are basically the perturbation restricted to the degenerate subspace: $[\delta H]_{\ell k} = \left\langle n^{(0)}, \ell \middle| \delta H \middle| n^{(0)}, k \right\rangle$.

At the end of last lecture, we mentioned that diagonalizing this $[\delta H]$ matrix (which is smaller than the δH full matrix) can still be difficult, but we can simplify our lives using symmetry in the Hamiltonian. And that's what we'll be doing in today's lecture!

Proposition 27

Suppose there exists a Hermitian operator K such that $[H^{(0)}, K] = [\delta H, K] = 0$. (So K commutes with $H^{(0)} + \lambda \delta H$ for any λ.) Then we can choose eigenstates of $H^{(0)}$, specifically those in V_N, that are also simultaneously eigenstates of K. If $K\left|n^{(0)}, p\right\rangle = \mu_p \left|n^{(0)}, p\right\rangle$, then $[\delta H]_{pq} = 0$ unless $\mu_p = \mu_q$.

In other words, using a basis of states which are eigenstates of K will "split up" V_N into different spaces based on eigenvalue of K, meaning that $[\delta H]$ takes a "block diagonal form." And this can make fully diagonalizing $[\delta H]$ much easier, especially if all of the eigenvalues μ_p are different (in that case, $\left|n^{(0)}, p\right\rangle$ are actually already the good states we're looking for!).

Proof. Since $[\delta H, K] = 0$, we know that

$$0 = \left\langle n^{(0)}, p \middle| [\delta H, K \middle| n^{(0)}, q \right\rangle = \left\langle n^{(0)}, p \middle| \delta H K - K \delta H \middle| n^{(0)}, q \right\rangle.$$

But because our bra and ket here are eigenstates of K, acting with the Ks (to the right and left, respectively), we get

$$0 = \mu_q \left\langle n^{(0)}, p \middle| \delta H \middle| n^{(0)}, q \right\rangle - \mu_p \left\langle n^{(0)}, p \middle| \delta H \middle| n^{(0)}, q \right\rangle = (\mu_q - \mu_p) \left\langle n^{(0)}, p \middle| \delta H \middle| n^{(0)}, q \right\rangle,$$

so either $\mu_q = \mu_p$ or the matrix element $\langle n^{(0)}, p | \delta H | n^{(0)}, q \rangle$ vanishes, as desired. ☐

Fact 28

The matrix K often has to do with symmetry in the Hamiltonian: for example, $K = L_z$ works if we have rotational symmetry, and other common choices are $\vec{L}^2$ and p.

Example 29

Consider the case $N = 3$, where we have three degenerate energy eigenstates $|n^{(0)}, 1\rangle, |n^{(0)}, 2\rangle, |n^{(0)}, 3\rangle$ chosen to be eigenstates of K. Suppose that they have eigenvalues μ_1, μ_1, μ_2 with $\mu_1 \neq \mu_2$. Then δH in this basis will take matrix form $\begin{bmatrix} * & * & 0 \\ * & * & 0 \\ 0 & 0 & * \end{bmatrix}$ (with all $*$s arbitrary, except that the matrix is Hermitian), and in particular $|n^{(0)}, 3\rangle$ is one of our good states (because it is an eigenvalue). The other two good states are then some linear combination of $|n^{(0)}, 1\rangle$ and $|n^{(0)}, 2\rangle$.

It turns out we can work out the higher-energy terms as well, and we can read or work out the derivation on our own. But the results are as follows. First of all, our second-order energy correction is

$$E_{n,I}^{(2)} = -\sum_{p \neq n} \frac{\left| \left\langle p \middle| \delta H \middle| \psi_I^{(0)} \right\rangle \right|^2}{E_p^{(0)} - E_n^{(0)}}.$$

Notice that we need to take matrix elements with the good states $\left|\psi_I^{(0)}\right\rangle$, and the intermediate states p must lie **outside the degenerate subspace** (to avoid denominator being zero). And the corresponding first-order state correction has a small difference as well: because our Hilbert space is a direct sum $\mathcal{H} = V_N \oplus V_\perp$, we get contributions for each piece:

$$\left|\psi_I^{(1)}\right\rangle = \left|\psi_I^{(1)}\right\rangle\Big|_{V_\perp} + \left|\psi_I^{(1)}\right\rangle\Big|_{V_N}.$$

The first piece here is similar to the non-degenerate case, in that

$$\left|\psi_I^{(1)}\right\rangle\Big|_{V_\perp} = -\sum_{p \neq n} \frac{\left\langle p^{(0)} \middle| \delta H \middle| \psi_I^{(0)} \right\rangle}{E_p^{(0)} - E_n^{(0)}} \left| p^{(0)} \right\rangle$$

(remember again that we're using good states) is a linear combination of terms in $V_\perp$, so this part of the correction is in $V_\perp$. And the piece for V_N is rather different from what we're used to:

$$\left|\psi_I^{(1)}\right\rangle\Big|_{V_N} = \sum_{J \neq I} \frac{1}{E_{n,J}^{(1)} - E_{n,I}^{(1)}} \sum_{p \neq n} \frac{\left\langle \psi_J^{(0)} \middle| \delta H \middle| p^{(0)} \right\rangle \left\langle p^{(0)} \middle| \delta H \middle| \psi_I^{(0)} \right\rangle}{E_p^{(0)} - E_n^{(0)}}.$$

Notice that we're assuming in this formula that **all of the states in the degenerate subspace split at first order**, so that the energy corrections $E_{n,J}^{(1)}$ are all different. If the degeneracy is not fully lifted at $O(\lambda)$, we have to work harder, and remember that we don't even know all of the good states in that case! So we'll try to discuss that a little bit now.

For example, suppose that we have the diagonalized matrix

$$[\delta H] = \begin{bmatrix} E_1^{(1)} & 0 & 0 \\ 0 & E_1^{(1)} & 0 \\ 0 & 0 & E_2^{(1)} \end{bmatrix}.$$

This means that two of our states exit $\lambda = 1$ with the same "slope," and the last one exits with a different slope – more concretely, the energies are $E^{(0)} + \lambda E_1^{(1)}$ and $E^{(0)} + \lambda E_2^{(1)}$ to first order, and the good state corresponding to the latter energy is $\left|n^{(0)}, 3\right\rangle$ (but we don't know at order λ what the good states $\alpha\left|n^{(0)}, 1\right\rangle + \beta\left|n^{(0)}, 2\right\rangle$ are supposed to be). So then we have to use the second-order equation in λ, and here's the general strategy for that in the case when we have a **fully unlifted degeneracy at** $O(\lambda)$, meaning we have $[\delta H] = E_n^{(1)} \cdot I$ for the $N \times N$ identity matrix I: we construct a matrix $M^{(2)}$ such that $M^{(2)} a_I = E_{n,I}^{(2)} a_I$, where (instead of $[\delta H]$) we have the matrix

$$M_{\ell k}^{(2)} = -\sum_{p \neq n} \frac{\left\langle n^{(0)}, \ell\middle|\delta H\middle|p^{(0)}\right\rangle \left\langle p^{(0)}\middle|\delta H\middle|n^{(0)}, k\right\rangle}{E_p^{(0)} - E_n^{(0)}}.$$

This should look a lot like the second-order energy correction in the non-degenerate case, and in fact when the levels are non-degenerate this is exactly a 1×1 matrix whose entry is the energy correction! So everything we've discussed so far is consistent, and we can visualize this numerator in the same way that we described a few lectures ago: $M_{\ell k}^{(2)}$ describes all of the contributions from "jumping energy levels" from $\left|n^{(0)}, k\right\rangle$, then to $\left|p^{(0)}\right\rangle$, and then back to $\left|n^{(0)}, \ell\right\rangle$, over various energy states that aren't at the same level as $\left|n^{(0)}, k\right\rangle$ and $\left|n^{(0)}, \ell\right\rangle$.

So if we diagonalize $M^{(2)}$ and find its eigenvectors, we hope that the eigenvalues are all different (meaning that we finally know the eigenvectors a_I and thus we know the good states). But if some of them are still the same, we then go to third order, or fourth order, and so on.

Remark 30. *We'll apply this kind of formalism to two of the problems on next week's problem set, which is now posted.*

That's all we'll do for the formalism of time-independent perturbation theory; we'll now apply it to a classic problem, the **fine structure of the hydrogen atom**.

Example 31

The usual Hamiltonian for the hydrogen atom is

$$H^{(0)} = \frac{\vec{p}^2}{2m} - \frac{e^2}{r},$$

where we're using Gaussian units (so no ε_0s) and m is the reduced mass $\frac{m_e m_p}{m_e + m_p} \approx m_e$.

First, we'll do a bit of review: recall that the characteristic length of the hydrogen atom system is the **Bohr radius**

$$a_0 = \frac{\hbar^2}{me^2} \approx 0.53 \text{ angstroms}$$

(where an angstrom is 10^{-10} meters), with energies written in terms of a_0 as

$$E_n = -\frac{e^2}{2a_0}\frac{1}{n^2} = -\frac{\text{Ry}}{n^2}$$

for the Rydberg constant Ry ≈ 13.6 eV, where n is a positive integer known as the **principal quantum number**. It's also useful to write things in terms of the dimensionless constant

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137},$$

because we can then write

$$\frac{e^2}{a_0} = \frac{me^4}{\hbar^2} = \alpha^2 mc^2,$$

where mc^2 is the rest energy of the electron. This means that the typical energies of the hydrogen atom are smaller than the rest energy by a factor of $\alpha^2 \approx \frac{1}{19000}$.

We can also think about this system in terms of the typical momentum of the hydrogen atom: we know that the momentum will be on the scale of

$$p \sim \frac{\hbar}{a_0} = \frac{me^2}{\hbar} = \alpha mc$$

(because there's a position gradient in the momentum operator and a_0 is the length scale). So the typical velocity of the electron is αc (about 1 percent of the speed of light), which is basically nonrelativistic, though there will be small corrections due to relativity not included in $H^{(0)}$. And figuring out those energy corrections will be our goal later, but we'll ignore relativistic corrections for now.

Talking about the hydrogen atom spectrum in a bit more detail, recall that it is highly degenerate: for any fixed n, the energy $E_n = -\frac{e^2}{2a_0}\frac{1}{n^2}$ can have orbital angular momentum $\ell \in [0, 1, \cdots, n-1]$, and for any fixed ℓ, we can have azimuthal quantum number $m \in [-\ell, -\ell+1, \cdots, \ell]$. For any fixed n, we then have the angular momentum states $|\ell, m\rangle$ satisfying the eigenvalue relations

$$\vec{L}^2 |\ell, m\rangle = \hbar^2 \ell(\ell+1) |\ell, m\rangle, \quad L_z |\ell, m\rangle = \hbar m |\ell, m\rangle.$$

So for each principal quantum number n, we have a total degeneracy of

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

For example, for $n = 3$, we have one state in $\ell = 0$, three states in $\ell = 1$, and five states in $\ell = 2$, for a total of 9. We often return to $\ell = 0, 1, 2, 3$ states as being in the s, p, d, f states (this comes from the various orbitals in chemistry), and the wavefunctions for these various eigenstates are

$$\psi_{n,\ell,m}\vec{r} \sim \left(\frac{r}{a_0}\right)^{\ell} \cdot (\text{polynomial of degree } N \text{ in } \tfrac{r}{a_0}) e^{-r/na_0} Y_{\ell,m}(\theta, \phi),$$

where $Y_{\ell,m}$ is the angular momentum harmonic and $n = N + \ell + 1$. (In particular, the lowest energy state for each ℓ has $N = 0$, and N represents the **number of nodes** in the radial wavefunction.) The $\left(\frac{r}{a_0}\right)^{\ell}$ is particularly relevant because the wavefunctions for all $\ell > 0$ vanish at the origin. In particular, the simplest wavefunction is the ground state

$$\psi_{1,0,0} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}.$$

So returning to the degeneracy in energy, we should note that this is not a general property of central potentials $V(r)$: we know that states form angular momentum multiplets (over all values of m), but in general states of different values of ℓ do not need to have the same energy. What's happening is a four-dimensional symmetry, the conservation of the **Runge-Lenz vector**, and we'll see that relativistic corrections will make some of these degeneracies split!

We know that the electron also has a spin, so the full Hilbert space should be a tensor product $\mathcal{H} = V_{\text{orbitals}} \otimes \mathbb{C}^2$, with basis given by $\psi_{n,\ell,m}(\vec{r}) \otimes |\uparrow\rangle$ and $\psi_{n,\ell,m}(\vec{r}) \otimes |\downarrow\rangle$ (over various allowed values of n, ℓ, m), where $|\uparrow\rangle$ represents the $\left|\frac{1}{2}, \frac{1}{2}\right\rangle$ state and $|\downarrow\rangle$ represents the $\left|\frac{1}{2}, -\frac{1}{2}\right\rangle$ state.

The idea is that spin has been ignored so far, because $H^{(0)}$ doesn't do anything to the spin part of the tensor product space. So there's an additional two-fold degeneracy because of the spin, and thus we've now found that the nth energy level actually has a $2n^2$-fold degeneracy.

Remark 32. *In experiments, we often apply an electric field or magnetic field to our system and see how the spectral lines change, and we'll see throughout the next few weeks what the effects of those external fields are on the spectrum.*

Returning our discussion to the Hilbert space $\mathcal{H} = V_{\text{orbital}} \times \mathbb{C}^2$, we mentioned one choice of basis for this space above, which is the **uncoupled basis**. Basis vectors of this space are labeled as $|n, \ell, m_\ell, m_s\rangle$ (where the last number here is the S_z eigenvalue for the electron spin), and the idea is that the states here are all tensor products of the orbital and spin states. But as we start to study relativistic corrections, it makes sense to use a **coupled basis** instead, where we look at multiplets of the **total angular momentum** $\vec{J} = \vec{L} + \vec{S}$ from the combination of the orbital and spin angular momentum. Then we have eigenstates satisfying the familiar equations

$$\vec{J}^2 |j, m\rangle = \hbar^2 j(j+1) |j, m_j\rangle , \quad \vec{J}_z |j, m_j\rangle = \hbar m_j |j, m_j\rangle ,$$

where $m_j \in [-j, -j+1, \dots, j]$, and we have the angular momentum addition rules from 8.05: an angular momentum ℓ-multiplet tensored with a spin multiplet is a direct sum of various j-multiplets:

$$\ell \otimes \frac{1}{2} = \left(\ell + \frac{1}{2}\right) \oplus \left(\ell - \frac{1}{2}\right)$$

(except without the second term here when $\ell = 0$). So we construct our basis as follows: for any fixed n, ℓ, we have construct our coupled basis vectors

$$|n, \ell, j, m_j\rangle = \sum_{m_\ell, m_s} |n, \ell, m_\ell, m_s\rangle C^{j,\ell}_{m_\ell, m_s}$$

for the **Clebsch-Gordan coefficients** $C^{j,\ell}_{m_\ell, m_s}$. And our coupled basis vectors are all eigenstates of the operators $\vec{J}^2$, J_z, and also $\vec{L}^2$ and $H^{(0)}$ (because we formed these states out of states that have a definite ℓ quantum number and energy)! But these new basis vectors are combining different values of m_ℓ and m_s together, so they are **not** eigenstates of L_z or S_z.

This coupled basis is just another choice which turns out to be useful for the hydrogen atom when we take relativistic corrections into account, because L and S individually don't commute with the Hamiltonian – only the total angular momentum is conserved!

We'll use the notation nL_j for our various $|n, \ell, j\rangle$ states, where n and j are numbers and L is s, p, d, f (and so on).

Example 33

For $\ell = 1, n = 2$, we have six states in total: $3 \cdot 2$ in the uncoupled basis, and $2 + 4$ in the coupled basis, labeling the coupled multiplets as $2P_{3/2}$ and $2P_{1/2}$. For $\ell = 2, n = 3$, we have ten states in total: $5 \cdot 2 = 10$ in the uncoupled basis, and $4 + 6$ in the coupled basis, labeling the coupled multiplets as $3D_{3/2}$ and $3D_{5/2}$.

We'll bring in the relativistic corrections next time and bring in the perturbation theory!

8 March 1, 2021 (Recitation)

We'll cover some more degenerate time-independent perturbation theory today and then start moving towards the fine structure of hydrogen.

Fact 34

The hydrogen atom has both **bound** and **unbound** states – the latter are often called scattering states, and they are necessary for completeness. But we won't need that explicitly for the problem set.

Recall that we were studying the Van der Waals force as an example of perturbation theory last time: we studied the energy shift of the ground state (which had no degeneracy) to get the $\frac{1}{R^6}$ potential. And if we go back over the notes, we'll find that our calculation has some similarities to the problem set.

Example 35

Today, we'll continue studying the Van der Waals force by studying some degenerate states above the ground state.

Recall that we can characterize our two-atom system by looking at the states indexed by $(n_A, \ell_A, m_A), (n_B, \ell_B, n_B)$. The ground state of this system is $(1, 0, 0), (1, 0, 0)$, and now let's try to think about the first excited state. For the next lowest energy, we can either have $(2, \cdot, \cdot); (1, 0, 0)$ or $(1, 0, 0); (2, \cdot, \cdot)$, and ℓ can range from 0 to $2 - 1 = 1$ for the excited atom. Then m ranges from $-\ell$ to ℓ, so there are 3 states for $\ell = 1$ and 1 state for $\ell = 0$. This gives a total of $\boxed{2(3+1) = 8}$ total states at the first excited energy level:

$$|100; 200\rangle, |200; 100\rangle, |100; 21m\rangle, |21m; 100\rangle$$

where $m \in \{-1, 0, 1\}$. So we want to know how the Van der Waals interactions influence these states, and to do that, we need to do degenerate perturbation theory. The first thing we need to figure out is how to diagonalize the $[\delta H]$ matrix, and we do this by calculating the matrix elements

$$\langle n_A \ell_A m_a, n_B \ell_B m_B | \delta H | n'_A \ell'_A m'_A; n'_B \ell'_B m'_B \rangle.$$

This looks like we have to do a lot of different calculations, because there are 8 states we can put on the left and 8 states we can put on the right. So we'll start by thinking about where there are zeros in this matrix $[\delta H]$: remember that the δH has a $\vec{r}_A \cdot \vec{r}_B$ component, so when we evaluate we end up with something that looks more like

$$\langle n_A \ell_A m_A | \vec{r}_A | n'_A \ell'_A m'_A \rangle$$

(times the analogous expression for B). But the $\vec{r}_A$ term in the middle is odd, so the only way to make this expression nonzero is if one of the states is odd and the other is even. And it turns out that when ℓ is even, we get even polynomials in the wavefunction, and when ℓ is odd, we get odd polynomials. So that means we only get nonzero values if ℓ_A and ℓ'_A are of different parity – specifically, one of them must be 0 and the other must be 1 in this case. So if we want a nonzero overlap with $|100; 21m\rangle$, we need another state where we have $|?1?; ?0?\rangle$ for some numbers ?. And the only way this can happen is if we are computing the matrix overlap with $|21m'; 100\rangle$! So that simplifies our calculations significantly – in particular, $|100; 200\rangle$ and $|200; 100\rangle$ have zero overlap with any of the states, and we just need to compute

$$\langle 100; 21m | \delta H | 21m'; 100 \rangle$$

for various values of m, m'. And furthermore, the δH doesn't give a perturbation to the m quantum number, because (letting $L_{Az} + L_{Bz}$ be the total angular momentum in the z-direction)

$$[\delta H, L_{Az} + L_{Bz}] = 0,$$

because δH only has terms of the form $\vec{r}_A \cdot \vec{r}_B$ or $(\vec{r}_A \cdot \hat{z})(\vec{r}_B \cdot \hat{z})$, which are symmetric around rotations in the z-direction. And this tells us that the only way to get a nonzero matrix element is **if** $m = m'$! That's because we can compute the matrix elements of $0 = [\delta H, L_{Az} + L_{Bz}]$, which will turn out to be things like

$$0 = \langle 100; 21m | [\delta H, L_{Az} + L_{Bz}] | 21m'; 100 \rangle = (m - m') \langle 100; 21m | \delta H | 21m'; 100 \rangle.$$

This means we end up with three 2×2 matrix problems (for $m = -1, 0, 1$) instead of an 8×8 matrix, and that breaks the degeneracy for everything except the $|100; 200\rangle$ and $|200; 100\rangle$ states. So this method gives us **six of the eight good states**, but we need to go to higher-order to figure out the other two.

Let's focus on what we can compute, though: we get results like

$$\langle 100; 21m|\delta H|21m; 100\rangle = \frac{1}{R^3} k_m$$

for some numbers k_m, and that means each of the 2×2 matrices looks like $\begin{bmatrix} 0 & \Delta \\ \Delta & 0 \end{bmatrix}$ for some Δ. We therefore find that we have energies of $\boxed{\pm \frac{k_m}{R^3}}$ with the respective eigenstates

$$\boxed{\frac{1}{\sqrt{2}}(|100; 21m\rangle \pm |21m; 100\rangle)}.$$

So first-order perturbation theory has given us an interesting result: we have a $\frac{1}{R^3}$ potential for Van der Waals, which is stronger than in the ground state and can be both attractive and repulsive (depending on the superposition).

We'll now move onto another example:

Example 36

Suppose we have a spin-1 particle with original Hamiltonian $H^{(0)} = AS_z^2$ and perturbation $\lambda \delta H = \lambda(S_x^2 - S_y^2)$.

The thing for us to remember about spin operators here is that the raising and lowering operators are useful: working with the operators

$$S_\pm = S_x \pm iS_y$$

is good for calculations, because we know that angular momentum operators give us

$$J_\pm |j, m\rangle = \hbar\sqrt{j(j+1) - m(m \pm 1)}\, |j, m \pm 1\rangle\,,$$

and the $S_\pm$ operators serve that purpose here. In particular, we can rewrite S_x and S_y in terms of the raising and lowering operators to find that

$$\lambda \delta H = \lambda \left(\frac{S_+^2 + S_-^2}{2} \right).$$

Problem 37

Let's determine the first order energy corrections $E_n^{(1)}$ for this perturbed Hamiltonian.

We should first find the eigenstates of the original Hamiltonian $H^{(0)}$, which are $|1, 1\rangle$, $|1, 0\rangle$, and $|1, -1\rangle$ (the eigenstates of S_z and of S_z^2 are the same). Since the eigenvalues of S_z are $\hbar m$, the eigenvalues of $H^{(0)}$ will be $A(\hbar m)^2$ for $m = -1, 0, 1$ (meaning that $|1, 0\rangle$ has eigenvalue 0, and $|1, 1\rangle$ and $|1, -1\rangle$ both have eigenvalue $A\hbar^2$).

For the nondegenerate state, the energy correction is the matrix element

$$\langle 1, 0|\delta H|1, 0\rangle = A \left\langle 1, 0 \middle| \frac{S_+^2 - S_-^2}{2} \middle| 1, 0 \right\rangle.$$

This turns out to be $\boxed{E_{1,0}^{(1)} = 0}$ (because raising or lowering gives us no overlap). But it takes more work to compute the energy corrections for the degenerate states, and we need to compute the 2×2 matrix $[\delta H]$, which turns out to be $\begin{bmatrix} 0 & \hbar^2 \\ \hbar^2 & 0 \end{bmatrix}$. So that's the same structure as the problem above, and thus the good states are again the sum and difference of the original basis states: they are $\frac{|1,1\rangle \pm |1,-1\rangle}{\sqrt{2}}$ with eigenvalues $\boxed{E^{(1)} = \pm\lambda\hbar^2}$.

One thing we'll need in lecture tomorrow is the **addition of angular momentum**: for example, if we have an operator $\vec{J} = \vec{L} + \vec{S}$, and we have an $\ell = 2$ and $s = \frac{1}{2}$ system, we should be able to check that the allowed total states $|j, m\rangle$ must have either $j = \frac{3}{2}$ or $\frac{5}{2}$, and m can range from $-j$ to j (as usual). We usually write this as

$$2 \otimes \frac{1}{2} = \frac{3}{2} \oplus \frac{5}{2}.$$

Indeed, we can count how many states we have here: $5 \cdot 2 = 4 + 6 = 10$. We'll explore more about the Clebsch-Gordan coefficients and use them for the fine structure of hydrogen next time!

9 March 2, 2021

We started discussing the hydrogen atom last time, with the goal of understanding the fine structure. Recall that the unperturbed Hamiltonian $H^{(0)} = \frac{\vec{p}^2}{2m} - \frac{e^2}{r}$ has exact energy levels $E_n = -\frac{1}{2}\alpha^2 mc^2 \frac{1}{n^2}$ which are highly degenerate, and we can describe the degeneracy either in the **uncoupled basis** $|n, \ell, m_\ell, m_s\rangle$ (where ℓ is the orbital angular momentum quantum number, m_ℓ is the azimiuthal quantum number, and m_s is the azimuthal spin of the electron). With this, we calculated last time that there is a $(2n^2)$-fold degeneracy at each level n.

But the other basis we can use is to label using $|n, \ell, j, m_j\rangle$, where we use eigenstates of $\vec{J}^2$ and J_z (for the total angular momentum $\vec{J} = \vec{L} + \vec{S}$), where $j = \ell \pm \frac{1}{2}$ (from the rules for addition of angular momentum). We label our states in the coupled basis as nL_j (using **spectroscopic notation**), where n and j are the usual numbers and L is S, P, D, and so on (instead of $0, 1, 2, \cdots$).

Our goal now is get closer to the correct structure of the hydrogen by introducing relativistic corrections.

Proposition 38

Our Hamiltonian and Schrodinger equation are **not Lorentz invariant** – to see that, we can just look at the free-space version

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2\nabla^2}{2m}\psi,$$

in which time and space enter in different derivatives (not on the same footing).

So we're going to need a more general treatment, which comes from the **Dirac equation** (a relativistic upgrade of the Schrodinger equation). We won't discuss this equation much in lecture – we could use the full Dirac equation, but we only need it to give us **small corrections** to Schrodinger (because we know the electron is basically nonrelativistic). So our Hamiltonian will now look like

$$H = \left(\frac{\vec{p}^2}{2m} + V\right) - \frac{\vec{p}^4}{8m^3c^2} + \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{S}\cdot\vec{L} + \frac{\hbar^2}{8m^2c^2}\nabla^2 V.$$

The three terms added are known as δH_{rel}, $\delta H_{\text{S-O}}$ (spin-orbit), and δH_{D} (Darwin), and together these are known as the **fine structure perturbations**. We can first estimate their magnitude: recall that the zeroth order piece $H^{(0)}$ has typical energies proportional to $\alpha^2 mc^2$, so they're down by a factor of α^2 compared to the rest mass. It turns out that the other three terms here are on the order of $\alpha^4 mc^2$, so they're smaller by around a factor of $\alpha^2 \sim \frac{1}{19000}$. Let's check this now:

- We have $\delta H_{\text{rel}} \sim \frac{\vec{p}^4}{8m^3c^2} \sim \frac{(\alpha mc)^4}{m^3c^2} = \alpha^4 mc^2$.
- Plugging in the potential $V = -\frac{e^2}{r}$, we have $\delta H_{\text{S-O}} = \frac{1}{m^2c^2}\frac{e^2}{r^3}\vec{S} \cdot \vec{L} \sim \frac{1}{m^2c^2}\frac{e^2}{a_0^3}\hbar \cdot \hbar$. And now because $a_0 = \frac{\hbar^2}{me^2}$, plugging everything in gives us $\frac{1}{m^2c^2}\frac{e^8m^3}{h^6}h^2 \sim m\left(\frac{e^2}{\hbar c}\right)^4 c^2 = \alpha^4 mc^2$. (A similar calculation, plugging in the form of the potential V, shows the same thing for the Darwin term.)

So because we know that the corrections are indeed smaller than the unperturbed Hamiltonian, we can apply perturbation theory. Defining the fine structure perturbation

$$\delta H_{\text{fs}} = \delta H_{\text{rel}} + \delta H_{\text{S-O}} + \delta H_{\text{D}},$$

we can write $H = H^{(0)} + \delta H_{\text{fs}}$ and apply perturbation theory. Strictly speaking, we need to do degenerate perturbation theory, which involves forming a $2n^2$ by $2n^2$ matrix and diagonalizing the resulting $[\delta H]$ matrix. We'll do this term by term.

Example 39

First, let's look at the term $\delta H_{\text{rel}} = -\frac{(\vec{p}^2)^2}{8m^3c^2}$.

We can think of this as a relativistic correction to the energy of a relativistic particle $E_{\text{kin}} = \sqrt{p^2c^2 + m^2c^4} = mc^2\sqrt{1 + \frac{p^2}{m^2c^2}}$. And we're basically expanding the square root in a Taylor series as

$$= mc^2\left(1 + \frac{1}{2}\frac{p^2}{mc^2} - \frac{1}{8}\left(\frac{p^2}{m^2c^2}\right)^2 + \cdots\right).$$

The first term here is a rest energy (a constant, which doesn't really matter), and the second term is our familiar non-relativistic kinetic energy. So the next term after that is indeed the correction that we're making in δH_{rel} (and terms after that are of order α^6, so we won't take those into account).

To understand this term's effect on the spectrum, we need to compute matrix elements at energy level n which look like (in the **uncoupled basis**)

$$\langle n, \ell, m_\ell, m_s | \delta H_{\text{rel}} | n, \ell', m_\ell', m_s' \rangle .$$

But in fact, these elements all vanish whenever $\ell = \ell'$ or $m_\ell = m_\ell'$ or $m_s \neq m_s'$. In other words, **this matrix is already diagonalized in this uncoupled basis**, so we just need to compute the diagonal entries! And this happens because of the following fact from last lecture: if we have $[K, \delta H] = 0$ for some Hermitian operator K, and $K\left|n^{(0)}, q\right\rangle = \lambda_q \left|n^{(0)}, q\right\rangle$ for all q in the degenerate subspace, then $\left\langle n^{(0)}, q\middle|\delta H\middle|n^{(0)}, q'\right\rangle = 0$ unless $\lambda_q = \lambda_{q'}$. And we're applying the result here using the operators $K = \vec{L}^2, L_z$, and S_z – note that because $\vec{p}^2$ is rotationally invariant, it commutes with angular momentum $\vec{L}^2, L_z$, and therefore $\vec{p}^4$ will also commute with them. And furthermore, the δH_{rel} term doesn't act on spin at all, so it also commutes with S_z. (And because choosing K to be $\vec{L}^2, L_z, S_z$ give us eigenvalues of $\ell(\ell+1), m_\ell, m_s$, we can indeed only have equality if the quantum numbers line up.)

So now let's compute the energy shifts, which are given by the diagonal entries

$$E^{(1),\text{rel}}_{n,\ell,m_\ell,m_s} = \langle n, \ell, m_\ell, m_s | \delta H_{\text{rel}} | n, \ell, m_\ell, m_s \rangle .$$

Nothing happens to the spin, so this can be rewritten as

$$= -\frac{1}{8m^3c^2}\left\langle \psi_{n,\ell,m_\ell}\middle|(\vec{p}^2)^2\middle|\psi_{n,\ell,m_\ell}\right\rangle .$$

But now we can apply one copy of $\vec{p}^2$ onto the bra and one copy onto the ket, so this becomes

$$= -\frac{1}{8m^3c^2}\left\langle \vec{p}^2\psi_{n,\ell,m_\ell} \middle| \vec{p}^2\psi_{n,\ell,m_\ell}\right\rangle .$$

Furthermore, we know that ψ_{n,ℓ,m_ℓ} satisfy the unperturbed Schrodinger equation

$$\left(\frac{\vec{p}^2}{2m} + V\right)\psi_{n,\ell,m_\ell} = E_n^{(0)}\psi_{n,\ell,m_\ell},$$

so that

$$\vec{p}^2\psi_{n,\ell,m_\ell} = 2m(E_n^{(0)} - V)\psi_{n,\ell,m_\ell}.$$

So plugging this back in gives us

$$E^{(1),\text{rel}}_{n,\ell,m_\ell,m_s} = -\frac{(2m)^2}{8m^3c^2}\left\langle (E_n^{(0)} - V)\psi_{n,\ell,m_\ell} \middle| (E_n^{(0)} - V)\psi_{n,\ell,m_\ell}\right\rangle = -\frac{1}{2mc^2}\left\langle \psi_{n,\ell,m_\ell} \middle| (E_n^{(0)} - V)^2 \middle| \psi_{n,\ell,m_\ell}\right\rangle$$

(using that V is Hermitian). And now we expand the square out and plug in $V = -\frac{e^2}{r}$

$$= -\frac{1}{2mc^2}\left\langle \psi_{n,\ell,m_\ell} \middle| (E_n^{(0)})^2 - 2E_n^{(0)}\left(-\frac{e^2}{r}\right) + \frac{e^4}{r^2} \middle| \psi_{n,\ell,m_\ell}\right\rangle .$$

So all we need is the expectation value of $\frac{1}{r}$ and $\frac{1}{r^2}$ in our (unperturbed) hydrogen atom eigenstates, which is something we'll do on this week's problem set! It turns out that $\left\langle \frac{1}{r}\right\rangle = \frac{1}{n^2a_0}$, and $\left\langle \frac{1}{r^2}\right\rangle = \frac{1}{n^3(\ell+\frac{1}{2})a_0^2}$, so the final answer for the energy corrections due to δH_{rel} is

$$\boxed{E^{(1),\text{rel}}_{n,\ell,m_\ell,m_s} = -\frac{1}{8}\frac{\alpha^2mc^2}{n^4}\left(\frac{4n}{\ell+1/2} - 3\right)}.$$

Remark 40. *Notice that the shifts in energy are indeed of order α^4, as expected, and also notice that there is no m_s or m_ℓ dependence. The former is expected, and the latter is true because angular momentum commutes with δH_{rel}. So we haven't fully lifted the degeneracy yet.*

So the uncoupled basis looks like a good basis right now. Unfortunately, we have two more terms, and once we add those in, we'll find that the fine structure good basis is actually the **coupled basis**! So let's change bases and calculate

$$\left\langle n,\ell,j,m_j \middle| \delta H^{\text{rel}} \middle| n,\ell',j',m_j'\right\rangle .$$

Because the coupled states with some ℓ are a linear combination of uncoupled states with that same ℓ, these matrix elements will still be zero unless $\ell = \ell'$. Remembering that the energy corrections we found above depend on n,ℓ but not on m_ℓ, m_s, that tells us that **if we fix** n,ℓ, the resulting matrix of energy differences is

$$[\delta H^{\text{rel}}]_{m_\ell m_s, m_\ell' m_s'} = E^{(1),\text{rel}}_{n,\ell} I$$

for the identity matrix I of the right size. But the identity matrix is the same in any basis! So even in the coupled basis, for fixed n,ℓ,

$$[\delta H^{\text{rel}}]_{jm_j, j'm_j'} = E^{(1),\text{rel}}_{n,\ell} I,$$

and thus we arrive at

$$\left\langle n,\ell,j,m_j \middle| \delta H^{\text{rel}} \middle| n,\ell',j'm_j'\right\rangle = E^{(1),\text{rel}}_{n,\ell}\delta_{\ell\ell'}\delta_{jj'}\delta_{m_jm_j'}.$$

So both the coupled and uncoupled δH^{rel} are good states, and the point is really that this term isn't acting on spin at all.

Example 41

Next, we'll look at the Darwin term, which is $\delta H_{\text{D}} = \frac{\hbar^2}{8m^2c^2}\nabla^2 V$.

We know that $V = -\frac{e^2}{r}$, and when we take the Laplacian of $\frac{1}{r}$, we get a delta function $-4\pi\delta^3(\vec{r})$. So the Darwin term is actually proportional to the delta function:

$$\delta H_{\text{D}} = \frac{\pi}{2}\frac{e^2\hbar^2}{m^2c^2}\delta^3(\vec{r}).$$

But the delta function picks out the value of a wavefunction at the origin, so

$$\delta H_{\text{D}} \left|n, \ell, m_\ell, m_s\right\rangle = 0 \text{ if } \ell \neq 0$$

(the hydrogen wavefunctions vanish at the origin for states with nonzero ℓ). And the states with $\ell = 0$ are very simple – since $m_\ell = 0$, there's only a degeneracy from the spin term, and δH_{D} doesn't act on spin at all. So the matrix elements of our Darwin term are

$$\begin{aligned}\langle n, \ell, m_\ell, m_s|\delta H_{\text{D}}|n, \ell', m_\ell' m_s'\rangle &= \delta_{\ell,0}\delta_{\ell',0}\delta_{m_\ell,0}\delta_{m_\ell',0}\delta_{m_s,m_s'}\langle\psi_{n00}|\delta H_{\text{D}}|\psi_{n00}\rangle \\ &= \delta_{\ell,0}\delta_{\ell',0}\delta_{m_\ell,0}\delta_{m_\ell',0}\delta_{m_s,m_s'}\frac{\pi}{2}\frac{e^2\hbar^2}{m^2c^2}\int d^3r\psi^*_{n00}(\vec{r})\delta^3(\vec{r})\psi_{n00}(\vec{r}) \\ &= \delta_{\ell,0}\delta_{\ell',0}\delta_{m_\ell,0}\delta_{m_\ell',0}\delta_{m_s,m_s'}\frac{\pi}{2}\frac{e^2\hbar^2}{m^2c^2}|\psi_{n00}(0)|^2.\end{aligned}$$

It turns out that we have $|\psi_{n00}(0)|^2 = \frac{1}{\pi n^3 a_0^3}$ (we can check Griffiths to derive this), and thus the nonzero overlap is $\boxed{\alpha^4 mc^2\frac{1}{2n^3}}$. So putting this all together, the matrix elements for the Darwin term are diagonal in the uncoupled basis, and they vanish unless $\ell = m_\ell = 0$:

$$\boxed{E_n^{(1),\text{D}} = \alpha^4 mc^2\frac{1}{2n^3}}$$

(where this energy shift is only for two of the states). And we could have equivalently said this fact for the coupled basis, because $|\ell = 0, m_\ell = 0, m_s\rangle$ is the same as $\left|\ell = 0, j = \frac{1}{2}, m_j = m_s\right\rangle$ (since $0 \otimes \frac{1}{2}$ is just $\frac{1}{2}$).

Fact 42

The physical meaning of this term is that this electron (which is initially treated as a point particle) is "fattened" to a ball of radius $\frac{\hbar}{mc}$ (the relativistic Compton wavelength).

And this happens because the Dirac equation describes both the electron and the positron, but we get rid of the positron when we simplify to Schrodinger. (An electron, in the presence of $V(r)$, can "become a positron for a bit.") But we can read more about this in Professor Zwiebach's notes.

Example 43

Finally, we can study the spin-orbit coupling term $\delta H_{\text{S-O}} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{S}\cdot\vec{L}$

This is the only term which actually involves spin, and it is the reason why we use the coupled basis! This term also comes from the Dirac equation, but intuitively, we can imagine an electron with some velocity around a proton (which we lock at the origin). In the rest frame of the proton, the electron only sees an electric field, specified by

$q_e\vec{E} = -\vec{\nabla}V$, but in the rest frame of the electron, we see the proton moving, and thus there is also a magnetic field term, which we can figure out by doing a Lorentz transformation of the original electron field:

$$\vec{B}' = -\frac{1}{c}\vec{v} \times \vec{E} = -\frac{1}{c}\frac{\vec{p}_e}{m} \times \left(-\frac{\vec{\nabla}V}{q_e}\right) = -\frac{1}{c \cdot e}\frac{\vec{p}_e}{m} \times \left(\frac{\vec{r}}{r}V'(r)\right)$$

(using that $V(\vec{r}) = V(r)$ is a central potential, so that $\vec{\nabla}V = V'(r) \cdot \hat{r}$). But then $\vec{p} \times \vec{r} = -\vec{r} \times \vec{p}$, which gives us an angular momentum:

$$\vec{B}' = \frac{1}{mec}\frac{1}{r}V'(r) \cdot \vec{L}.$$

And because the electron is stationary in its rest frame, we can understand how a magnetic field couples to this stationary electron – it does so to the electron spin. But more generally, a magnetic field couples to the **magnetic dipole** to yield $H = -\vec{\mu} \cdot \vec{B}$, because we have (**classically**) magnetic moment from a loop of charge given by $\vec{\mu} = \frac{I}{c}\vec{a}$ (if $\vec{a}$ is a vector with magnitude equal to the area of the loop), and then if a charge q is going around a circle, it turns out that **magnetic moment is proportional to angular momentum**

$$\vec{\mu} = \frac{q}{2mc}\vec{L},$$

because the period of the motion is $T = \frac{2\pi R}{v}$, and then the current is $I = \frac{q}{T} = \frac{qv}{2\pi R}$, so

$$\mu = \frac{1}{c}\frac{qv}{2\pi R} \cdot \pi R^2 = \frac{qvR}{2c} = \frac{qL_z}{2mc}.$$

And even when the electron is not moving, it still has a magnetic moment from the spin, and we have

$$\vec{\mu}_e = g\frac{q}{2m_\ell c}\vec{S},$$

where g is a "fudge factor" which we know is 2.00231930436182(52) (to extreme precision), but we'll say it's 2 for our purposes. So putting it all together, we get

$$H = -\vec{\mu}_e \cdot \vec{B} = \frac{e}{m_\ell \cdot c}\vec{S} \cdot \vec{B},$$

and thus our spin-orbit coupling term is indeed

$$\delta H_{\text{S-O}} = \frac{1}{m^2c^2}\frac{1}{r}V'(r)\vec{L} \cdot \vec{S}.$$

So we're off by a factor of $\frac{1}{2}$ from the actual answer, and the actual source of the $\frac{1}{2}$ comes from the following error in our argument: we went to the electron's rest frame, but the electron's velocity is changing (because it's undergoing orbital motion). So we don't actually have an inertial frame (this is an effect known as **Thomas precession**), but the argument is close enough for us to get some intuition! Next time, we'll compute the effects of this term on the spectrum of hydrogen.

10 March 3, 2021 (Recitation)

We'll do a bit of review for the fine structure of hydrogen today, and we'll also explain why this method is relevant to other systems as well (in other words, is there any other example besides hydrogen where this kind of fine structure calculation is useful).

Recall that our Hamiltonian for the hydrogen atom is

$$H^{\text{Hydrogen}} = H^{\text{Bohr}} + H^{\text{Fine-structure}}$$

where our "unperturbed Hamiltonian" is $H^{\text{Bohr}} = \frac{\vec{p}^2}{2m} - \frac{e^2}{r}$ and there are three different terms in the fine-structure correction ($\vec{p}^4$, $\vec{L} \cdot \vec{S}$, and Darwin). It turns out that there are other corrections that we often make, which lead to interesting effects: for example, we have a **hyperfine structure** term H^{HFS}, which we discussed a little in 8.05, as well as terms from the **Stark effect** (giving us a $\vec{x} \cdot \vec{E}$) and **Zeeman effect** ($\vec{\mu} \cdot \vec{B}$).

There are always more corrections we can make, and they get more subtle – just for a sense of scale, the Bohr term has magnitude α^2, the fine-structure terms have magnitude α^4, the hyperfine structure term has magnitude $\alpha^4 \frac{m_e}{m_p}$, and the Stark and Zeeman effects depend on the magnitude of the external field. But then we have a Lamb shift term which is $\alpha^5 \ln \alpha$ at first order, and so on. Basically, there is a very rich structure of hydrogen, and a lot of it comes from relativistic and quantum relativistic corrections!

Example 44

Let's take a look at the hydrogen hyperfine structure, which involves a Hamiltonian which couples the electron and proton spin:

$$H_{\text{HFS}} = \frac{g_e g_p e^2}{4 m_e m_p c^2} \left[\frac{8\pi}{3} \vec{S}_e \cdot \vec{S}_p \, \delta^3(\vec{r}) + \frac{3(\vec{S}_p \cdot \hat{r})(\vec{S}_e \cdot \hat{r}) - \vec{S}_p \cdot \vec{S}_e}{r^3} \right]$$

(where g_e, g_p are the g-factors for the electron and proton). We'll only focus on the **first term** today.

In 8.05, we derived this by noting that the magnetic moment is proportional to the spin (for both the proton and electron). And we solved the problem by taking the two spin-1/2 particles (proton and electron) and going to a different basis with $\vec{S} = \vec{S}_e + \vec{S}_p$, and this is good because

$$\vec{S}_e \cdot \vec{S}_p = \frac{1}{2} \left(\vec{S}^2 - \vec{S}_e^2 - \vec{S}_p^2 \right)$$

is especially easy to deal with, since $\vec{S}_e^2$ and $\vec{S}_p^2$ both give us $\hbar^2 s_e(s_e + 1) = \frac{3}{4}\hbar^2$. So two of the terms here are proportional to the identity operator, and that means we'll write

$$\vec{S}_e \cdot \vec{S}_p = \frac{1}{2} \left[\vec{S}^2 - \frac{3}{2} \hbar^2 I \right].$$

We can then look at the combined spin states of the proton and electron: since $\frac{1}{2} \otimes \frac{1}{2} = 0 \oplus 1$, we have $s = 0$ or 1, and the eigenvalues of $\vec{S}^2$ are then either 0 or $2\hbar^2$. So what we did in 8.05 was to find the first-order correction

$$E^{(1)}_{\text{HFS}} = \langle n, \ell, m_\ell, s, m_s | H_{\text{HFS}} | n, \ell, m_\ell, s, m_s \rangle$$

(we should have (0) superscripts on both of the states above). We'll specialize to $\ell = 0$, and this energy correction then turns out to be

$$= \boxed{\frac{2\pi}{3} \frac{g_e g_p e^2}{m_e m_p c^2} |\psi_{n,\ell,m_\ell}(0)|^2 \cdot \begin{cases} -\frac{3}{4}\hbar^2 & s = 0 \\ \frac{1}{4}\hbar^2 & s = 1 \end{cases}}$$

(where the different cases comes from the total spin $\vec{S}$).

Now that we've reviewed this material from 8.05, let's consider a slightly different system:

Example 45

Suppose we replace the proton in the hydrogen atom with a **positron** e^+. (The positron and proton have the same spin.) Then the idea is that the positron and electron can form a bound state called **positronium**.

The equivalent Hamiltonian to the Bohr term for this system is

$$H^{(0)} = \frac{\vec{p}^2}{2m_R} - \frac{e^2}{r},$$

where m_R is the reduced mass of the system. This is basically just the electron mass in the hydrogen atom, but the mass of the electron and positron are the same, so the reduced mass here turns out to actually be $m_R = \frac{m_e}{2}$. But other than that, we have a very similar structure as hydrogen, so we can write down our energy levels (where $\alpha = \frac{e^2}{\hbar c}$)

$$E_n^{(0)} = -\frac{\alpha^2 c^2 m_R}{2n^2}.$$

So the first energy level is half of what it was before, and our Bohr radius $a_0 = \frac{\hbar^2}{m_R e^2}$ is twice as large as it was for the hydrogen atom.

But there are other things that are different about this system when we replace the proton with a positron: for example, the two particles might annihilate each other, which means that our bound state might not even form. This concept is beyond what we can calculate right now, but it turns out an electron and positron cannot annihilate to a single photon by three-momentum conservation (think about the center-of-mass frame where $\vec{p}_{e^+} + \vec{p}_{e^-} = 0$). So we need **at least two photons** – it turns out that the $s = 0$ state (para-positronium) decays to two photons, and the $s = 1$ state (ortho-positronium) decays to three.

Fact 46

It turns out having extra photons costs extra factors of α, so $e^+e^- \to \gamma\gamma$ (the $s = 0$ case) has a potential proportional to α^5, and $e^+e^- \to \gamma\gamma\gamma$ has an "effective potential" proportional to α^6.

So these are smaller than the $H^{(0)}$ energy levels, and actually even smaller than the hyperfine structure (which is actually the same size as fine structure because there's no $\frac{m_e}{m_p}$ term), so transitions are unlikely (the states stick around for a while) and positronium **does have a bound state** for some time. (We can think of what's going on here as having "imaginary potentials," which basically corresponds to a "loss of probability.")

Fact 47

The lifetime of the $e^+e^- \to \gamma\gamma$ decay is on the order of 10^{-10} seconds, and the lifetime of the $e^+e^- \to \gamma\gamma\gamma$ decay is on the order of 10^{-7} seconds. So these don't last very long, but they still exist for long enough to study.

So now if we return to the boxed formula for the hyperfine splitting above, the term $\frac{g_p}{m_p}$ must turn into $\frac{g_e^+}{m_e^+} = \frac{g_e}{m_e} = \frac{2}{m_e}$ (the positron and electron have many properties that are the same, including the g-factor and mass). And it turns out that $|\psi_{n,\ell=0}(0)|^2 = \frac{1}{a_0^3 \pi n^3} = \frac{1}{8}|\psi^{\text{Hydrogen}}(0)|^2$ (because our Bohr radius a_0 has changed by a factor of 2). So if we keep track of all of these different factors, we find that (again, we're **only doing the $\ell = 0$ case**)

$$H_{\text{HFS}} = \frac{8\pi e^2}{3m_e^2 c^2}\left[\delta^3 \vec{r}\, \frac{1}{2}\left(\vec{S}^2 - \frac{3}{2}\hbar^2 I\right) + \delta^3(\vec{r})\frac{3}{4}S^2\right]$$

where $\vec{S} = \vec{S}_{e^+} + \vec{S}_{e^-}$, but the calculation is the same as for hydrogen, and the $\delta^3(\vec{r})\frac{3}{4}S^2$ is a **new effect** (that has no analog in the hydrogen system). This new term comes from quantum mechanics allowing virtual photons (energy and momentum conservation can be violated for a very short amount of time), meaning that we get **quantum transitions** like $e^+e^- \to \gamma^* \to e^+e^-$. And the spin S^2 term comes from the spin of the photon being 1 (meaning that $s = 0$ gives 0 and $s = 1$ gives $2\hbar^2$). So our story is a little bit modified, and we'll end with the answer for the first-order energy correction:

$$\boxed{\langle n, \ell = 0, m = 0, s, m_s | H_{\text{HFS}} | n, \ell = 0, m = 0, s, m_s \rangle = \frac{8\pi e^2}{3m^2c^2} \left| |\psi_{e^+e^-}\rangle (0) \right|^2 \cdot \begin{cases} -\frac{3}{4}\hbar^2 & s = 0 \\ \hbar^2 & s = 1 \end{cases}}.$$

(The $\hbar^2$ comes from $\frac{1}{4}\hbar^2$ in hydrogen, plus the new $\frac{3}{4}\hbar^2$ effect in positronium.) So we've now seen the fine structure in another system besides hydrogen!

11 March 4, 2021

Last time, we started talking about the fine structure of hydrogen – the familiar Coulomb Hamiltonian is the leading-order approximation to the hydrogen Hamiltonian, but relativity and the Dirac equation give us fine structure corrections. We've identified three such terms (the $\vec{p}^4$ kinetic energy correction, the spin-orbit coupling, and the Darwin term), and we started using perturbation theory to figure out the energy shifts. We'll now finish this task for the spin-orbit coupling term and arrive at our final answer – the Hamiltonian we're now studying is

$$\delta H_{\text{S-O}} = \frac{e^2}{2m^2c^2} \frac{1}{r^3} \vec{S} \cdot \vec{L}.$$

Recall that in the coupled basis, the Darwin and the kinetic energy corrections are both diagonal, and it'll turn out that using this coupled basis helps with the spin-orbit coupling term. This is because we can write $\vec{S} \cdot \vec{L}$ in terms of squares of angular momentum operators, and $\vec{J} = \vec{L} + \vec{S}$ is convenient for this:

$$\vec{S} \cdot \vec{L} = \frac{1}{2}(\vec{J}^2 - \vec{S}^2 - \vec{L}^2).$$

To understand why the coupled basis is good for this Hamiltonian, we can make a few observations. Notice that the spin-orbit Hamiltonian $\delta H_{\text{S-O}}$ commutes with $\boxed{\vec{J}}$, the total angular momentum. We can check this as follows: first, we look at the angular momentum terms. We see that $\vec{J}^2$ commutes with $\vec{J}$ because it commutes with each component, $\vec{S}^2$ is just a constant $\frac{3}{4}\hbar^2$, and $\vec{J} = \vec{S} + \vec{L}$ commutes with $\vec{L}^2$ because $\vec{S}$ and $\vec{L}^2$ don't interact, and $\vec{L}$ and $\vec{L}^2$ commute. Additionally, the coefficients and $\frac{1}{r^3}$ in front also commute with spin because they are rotationally invariant. Similarly, we can check that $\delta H_{\text{S-O}}$ also commutes with $\boxed{\vec{J}^2}$ and $\boxed{\vec{L}^2}$ (because $\vec{L}$ commutes with $\vec{L}^2$, $\vec{S}$ and $\vec{L}^2$ don't interact, and so on).

Therefore, $|n, \ell, j, m_j\rangle$ must be a good basis for this Hamiltonian, because we can simultaneously diagonalize $\delta H_{\text{S-O}}$ with the various angular momentum operators. (In other words, $\left\langle n, \ell, j, m_j \middle| \delta H_{\text{S-O}} \middle| n, \ell', j', m_j' \right\rangle = 0$ unless $\ell = \ell'$, $j = j'$, and $m_j = m_j'$, because otherwise can apply $\delta H_{\text{S-O}}$ to either the bra or the ket and get different constants out as eigenvalues.) So we know that perturbation within this degenerate subspace is diagonal in our coupled basis, and we can read off the diagonal matrix elements to get the first-order energy corrections:

$$E^{(1),\text{S-O}}_{n,\ell,j,m_j} = \frac{e^2}{4m^2c^2} \left\langle n, \ell, j, m_j \middle| \frac{1}{r^3}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2) \middle| n, \ell, j, m_j \right\rangle.$$

Using that the vectors in the coupled basis are eigenvectors for $(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$, we can have that term act on the ket to give us

$$= \frac{e^2\hbar^2}{4m^2c^2}\left(j(j+1)-\ell(\ell+1)-\frac{3}{4}\right)\left\langle n,\ell,j,m_j\left|\frac{1}{r^3}\right|n,\ell,j,m_j\right\rangle.$$

We now just need to compute the expectation value of $\frac{1}{r^3}$, and to do that, it's easier to do so in the uncoupled basis first: it turns out (see Griffiths problems 7.43 and 7.44, for example)

$$\left\langle \psi_{n,\ell,m_\ell}\left|\frac{1}{r^3}\right|\psi_{n,\ell,m_\ell}\right\rangle = \frac{1}{n^3a_0^3\ell(\ell+1)(\ell+\frac{1}{2})}.$$

(This expression does not depend on m_ℓ, because it is a rotationally-invariant operator.) We'll call this expression $g(n,\ell)$, and now we claim the full matrix elements are

$$\left\langle n,\ell,m_\ell,m_s\left|\frac{1}{r^3}\right|n,\ell',m'_\ell,m'_s\right\rangle = g(n,\ell)\delta_{\ell,\ell'}\delta_{m_\ell}$$

(similarly to our argument above, the off-diagonal entries vanish because $\frac{1}{r^3}$ commutes with the various spin operators $L_z, \vec{L}^2, S_z$, and n needs to be the same so that the states have the same energy). So now to get things into the coupled basis, if we fix n and ℓ, the expression $g(n,\ell)$ is a constant, and the rest of the expression is the identity matrix. So making the matrix transformation from the coupled basis to the uncoupled basis doesn't change that part of the matrix, and thus **even in the coupled basis**,

$$\left\langle n,\ell,j,m_j\left|\frac{1}{r^3}\right|n,\ell',j',m'_j\right\rangle = g(n,\ell)\delta_{j,j'}\delta_{m_j,m'_j}.$$

(This is the same argument that was made last lecture!) So plugging everything back in and doing some arithmetic gives us

$$\boxed{E^{(1),\text{S-O}}_{n,\ell,j,m} = \frac{\alpha^4mc^2}{4n^3}\left(\frac{j(j+1)-\ell(\ell+1)-\frac{3}{4}}{\ell(\ell+1)(\ell+\frac{1}{2})}\right)}.$$

So now we can add up the energy shifts from the different parts of the Hamiltonian (noting that all of the energy shifts are diagonal in the coupled basis, making calculations easier). In the $\ell = 0$ case, the Darwin term has no effect, and thus

$$E^{(1),\text{fs}}_{n,\ell,j,m_j} = \langle n,\ell,j,m_j|\delta H_{\text{rel}}+\delta H_{\text{S-O}}|n,\ell,j,m_j\rangle = \frac{\alpha^4mc^2}{8n^4}\left(3+2n\left[\frac{j(j+1)-3\ell(\ell+1)-\frac{3}{4}}{\ell(\ell+1)(\ell+\frac{1}{2})}\right]\right)$$

We'll call the bracketed term $f(j,\ell)$. It turns out that this expression actually simplifies nicely: because j can only be $\ell+\frac{1}{2}$ or $\ell-\frac{1}{2}$, meaning that for any fixed j, we have $\ell = j+\frac{1}{2}$ or $\ell = j-\frac{1}{2}$. And what we find is that

$$f\left(j,\ell=j+\frac{1}{2}\right) = -\frac{2}{j+\frac{1}{2}} = f\left(j,\ell=j-\frac{1}{2}\right).$$

So for the two allowed values of ℓ, we have a much simpler form of $f(j,\ell)$ – there isn't actually any ℓ-dependence at all! So this gives us our final fine-structure correction:

$$\boxed{E^{(1),\text{fs}}_{n,\ell,j,m_j} = -\alpha^4mc^2\frac{1}{2n^4}\left(\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right)}.$$

And if we try plugging in $\ell = 0$, it turns out that this formula still works when we add in the Darwin term. To understand this, notice that the spin-orbit contribution is 0 for $\ell = 0$ (because we have a $\vec{L}$ term in the Hamiltonian), but we get a nonzero contribution from the Darwin term. And if we look again at the first boxed expression for spin-orbit energy shift, we have an ℓ in the denominator – it turns out that taking the limit

$$\lim_{\ell \to 0} E^{(1),\text{S-O}}\left(j = \ell + \frac{1}{2}, \ell\right) = E^{(1),\text{D}}$$

exactly reproduces the Darwin term for $\ell = 0$. So because of certain "magic" calculations, we get a nice expression for the fine-structure energy shift at the end of the day!

Some of the most important takeaways from this calculation are below:

- **The coupled basis is a good basis** for the fine-structure calculation (but the uncoupled basis is not). This is because $\vec{J}$, the total angular momentum, is conserved in relativistic physics, but $\vec{L}$ and $\vec{S}$ are not conserved because of the spin-orbit coupling term. (One way to understand this comes from the Heisenberg equation $\frac{\partial A}{\partial t} = -\frac{i}{\hbar}[A, H]$ for operators A – in other words, A and H commuting means that A is conserved.)
- Because the angular momentum $\vec{J}$ commutes with the Hamiltonian, all $2j+1$ states in a multiplet have the same energy. So the energy shifts do not depend on m_j.
- For a fixed n, j, the states with different ℓ have the same energy shift. (For example, $2S_{1/2}$ and $2P_{1/2}$ remain degenerate, and fine structure does not split them. Instead, these states only shift at a higher order in α, and this occurs because of the **Lamb shift** giving $O(\alpha^5 mc^2)$ energy splitting. But this is already a result from quantum electrodynamics.
- All energies are shifted down by fine-structure, but states with larger j shift less than states with smaller j. In other words, E_{nj} increases as a function of j for fixed n.

Fact 48

A quick logistical point about our our term paper: our topic and proposal is due on March 26, and there is a description that we should read on Canvas. A template will be posted shortly, but it should contain a topic, student peer editor (whose topic is different from yours), a brief plan for the paper, and a list of references.

Example 49

The next perturbation we'll look at is to place this hydrogen atom in an external magnetic field and examine the **Zeeman effect**. One application of this is to measure magnetic fields in interesting ways: for example, spectral lines in sunspots split compared to spectral lines in other places in the sun, and that's because of differences in the magnetic field (on the order of 3000 Gauss).

The leading-order correction due to a magnetic field is

$$\delta H = -\vec{\mu} \cdot \vec{B},$$

where we get a contribution to the magnetic moment from both the spin and the orbital angular momentum $\vec{\mu}_\ell$ and $\vec{\mu}_s$:

$$\delta H_Z = -(\vec{\mu}_\ell + \vec{\mu}_s) \cdot \vec{B} = \frac{e}{2mc}(\vec{L} + 2\vec{S}) \cdot \vec{B}_{\text{ext}}.$$

(The extra factor of 2 here comes from the g-factor of the electron.) We can choose our coordinates here so that the magnetic field points along the z-direction, and then our Zeeman perturbation is

$$\delta H_Z = \frac{eB_z}{2mc}(L_z + 2S_z).$$

So now we want to understand how the Zeeman effect affects the spectrum of hydrogen, but our Hamiltonian is now

$$H = H^{(0)} + \delta H_{\text{fs}} + \delta H_Z.$$

We now have **two different perturbations**, so in principle we need to calculate perturbations for the fine-structure term plus the Zeeman term. But there are two limits where the calculation is easier. The first is **weak field Zeeman**, where $\delta H_Z \ll \delta H_{\text{fs}}$, and thus we can treat the first two terms of the Hamiltonian as a single starting Hamiltonian $\tilde{H}^{(0)}$ and the Zeeman term is a perturbation. And the other is **strong field Zeeman**, where $\delta H_Z \gg \delta H_{\text{fs}}$, in which we treat $H^{(0)} + \delta H_Z$ as the unperturbed Hamiltonian and the fine-structure term as a perturbation.

Those two cases basically occur if B is very small or very large – let's understand where the cutoff lies. Recall that there's a typical magnitude in the spin-orbit coupling for the magnetic field due to proton motion (which we should think of as the **internal** magnetic field) – if the external magnetic field is much larger or much smaller than that internal field, it tells us that we're in the strong field or weak field Zeeman regime. There's also a case where the two are comparable, in which case we're in the **intermediate field Zeeman** regime (and then we need to consider the matrix elements of the combined perturbation $\delta H_{\text{fs}} + \delta H_Z$, and we need to do some hard work to diagonalize the matrix).

We'll do the weak field Zeeman calculation here, and the strong field Zeeman calculation is left for our problem set. We're trying to understand the Hamiltonian

$$H = \left(H^{(0)} + \delta H_{\text{fs}}\right) + \delta H_Z,$$

and the unperturbed states here of $H^{(0)} \tilde{+} \delta H_{\text{fs}}$ are labeled by $|n, \ell, j, m_j\rangle$ with known energies $E^{\text{fs}}(n, j)$. We must then do perturbation theory in δH_Z, and here we have a slight catch: we only have an **approximate solution** for the eigenstates and energies $H^{(0)} + \delta H_{\text{fs}}$ (to leading order). But that will turn out to be good enough for our purposes, as long as we have the weak-field limit.

Remembering that not all degeneracies were broken by the fine-structure, we're going to need to do degenerate perturbation theory. Each degenerate subspace is labeled by integers (n, j), and within the subspace we have $\ell = j \pm \frac{1}{2}$ and $m_j \in [-j, \cdots, j]$. Thus, we need to calculate matrix elements of $[\delta H_z]$ within each subspace, which means we need to find

$$\left\langle n, \ell, j, m_j \middle| \delta H_Z \middle| n, \ell', j, m_j' \right\rangle.$$

But we are actually pretty lucky – the off-diagonal entries vanish again! This is because δH_Z is proportional to $L_z + 2S_z$, and this expression does commute with $\vec{L}^2$, so using the same argument as above, we need ℓ and ℓ' to be the same to get a nonzero matrix element. Similarly, we can check that J_z commutes with δH_z, so $m_j = m_j'$ is also required. Therefore, we check again that **the coupled basis is a good basis**, and now we can calculate

$$E^{(1),Z}_{n,\ell,j,m_j} = \langle n, \ell, j, m_j | \delta H_z | n, \ell, j, m_j \rangle = \frac{eB}{2mc} \langle n, \ell, j, m_j | L_z + 2S_z | n, \ell, j, m_j \rangle.$$

Writing $L_z + 2S_z$ as $(L_z + S_z) + S_z = J_z + S_z$, the energy shift can be written as

$$= \frac{eB}{2mc} \langle n, \ell, j, m_j | J_z | n, \ell, j, m_j \rangle + \frac{eB}{2mc} \langle n, \ell, j, m_j | S_z | n, \ell, j, m_j \rangle.$$

The first term is just $\frac{eB}{2mc}\hbar m_j$ (because our states are eigenvectors of J_z), and in fact it turns out the second term is proportional to m_j as well with some extra constants! So each of these degenerate spaces split further into equidistant lines, and let's see how that plays out. The trick is to use the **projection lemma**, which states that

$$[J_i, S_j] = i\hbar\varepsilon_{ijk}S_k \implies \langle\vec{S}\rangle_j = \frac{\langle(\vec{S}\cdot\vec{J})\vec{J}\rangle_j}{\langle\vec{J}^2\rangle}.$$

where the j subscript indicates that we're in **any eigenstate** of $\vec{J}^2$. So we find that (we only care about the z-direction, not that expectation of the whole vector)

$$\langle n, \ell, j, m_j|S_z|n, \ell, j, m_j\rangle = \frac{\left\langle n, \ell, j, m_j\middle|(\vec{S}\cdot\vec{J})J_z\middle|n, \ell, j, m_j\right\rangle}{\hbar^2 j(j+1)} = \frac{\hbar m_j}{\hbar^2 j(j+1)}\left\langle n, \ell, j, m_j\middle|\vec{S}\cdot\vec{J}\middle|n, \ell, j, m_j\right\rangle.$$

But now we can simplify the dot product:

$$\vec{J} = \vec{L} + \vec{S} \implies \vec{S}\cdot\vec{J} = \vec{L}\cdot\vec{S} + \vec{S}^2 = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 + \vec{S}^2)$$

by using the same trick as we did for the spin-orbit term. But now our states are eigenstates for all of $\vec{J}^2, \vec{L}^2, \vec{S}^2$, so plugging things back in, we find that

$$\langle n, \ell, j, m_j|S_z|n, \ell, j, m_j\rangle = \frac{\hbar m_j}{j(j+1)}\frac{1}{2}\left(j(j+1) - \ell(\ell+1) + \frac{3}{4}\right),$$

and thus we've gotten our energy shifts for the weak field Zeeman effect:

$$E^{(1),Z}_{n,\ell,j,m_j} = \frac{eB}{2mc}\hbar m_j\left(1 + \frac{j(j+1) - \ell(\ell+1) + \frac{3}{4}}{2j(j+1)}\right).$$

We often call the term in parentheses $g_j(\ell)$, and that gives us our final answer

$$\boxed{E^{(1),Z}_{n,\ell,j,m_j} = \frac{e\hbar}{2mc}Bg_j(\ell)m_j}.$$

With this, all of the degeneracies of the hydrogen atom eigenstates are gone, because all of the multiplets split, and the splittings are different for different ℓs.

12 March 9, 2021 (Recitation)

We've been studying the fine structure of hydrogen for the past few lectures, and most recently we've been analyzing how the fine structure and Zeeman effect corrections compare to each other. Recall that the set up is as follows: we have the Bohr Hamiltonian H_{Bohr}, and we also add two correction terms H_{fs} and H_Z to that. And the reason this is interesting is that the different pieces of the Hamiltonian prefer different bases: for example, we can use the uncoupled basis $|n, \ell, m_\ell, m_s\rangle$ or the coupled basis $|n, \ell, j, m_j\rangle$. (Here, because this is hydrogen and the spin of the electron is $\frac{1}{2}$, we have $j = \ell \pm \frac{1}{2}$.)

Either of these are equally good bases for the Bohr Hamiltonian, since the energy levels really only depend on the principal number n. But we do have preferred bases for the other two terms, and that makes the analysis a little more complicated. If we just think about the fine structure term by itself, recall that the correction to the Bohr energy $E_n^{\text{Bohr}} = -\frac{mc^2\alpha^2}{2n^2}$ looks like

$$E^{\text{fs}}_{n,\ell,j,m_j} = -mc^2\alpha^4\frac{1}{2n^4}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)$$

(in other words, we now get a dependence on j but not directly ℓ). And on the other hand, if we think about the

Zeeman Hamiltonian terms, which looks like

$$H_Z = -(\vec{\mu}_L + \vec{\mu}_S) \cdot \vec{B}, \quad \vec{\mu}_L = -\frac{e\vec{L}}{2mc}, \quad \vec{\mu}_S = -\frac{e\vec{S}}{mc}.$$

If we plug in the magnetic moments and carry out the dot product, we find that

$$H_Z = \frac{eB}{2mc}(L_z + 2S_z),$$

which has a simple operation in the uncoupled basis but not the coupled basis:

$$H_Z \left| n, \ell, m_\ell, m_s \right\rangle = \frac{e\hbar}{2mc} B(m_\ell + 2m_s) \left| n, \ell, m_\ell, m_s \right\rangle,$$

where the $\frac{e\hbar}{2mc}$ term is the Bohr magneton (approximately 5.79×10^{-9}eV/Gauss).

Fact 50

The reason for these two different preferred bases is exactly why it's difficult to treat these two effects as a single Hamiltonian perturbation (we would need to find another good basis). This is particularly notable in the intermediate-field case where the fine-structure and Zeeman terms are on the same order of magnitude.

Remark 51. *Because we're not probing the quanta of the electromagnetic field (unlike something like the photoelectric effect, or transitions between hydrogen energy levels), we don't need to do quantization, and we can treat the (classical) magnetic field indeed as a regular vector.*

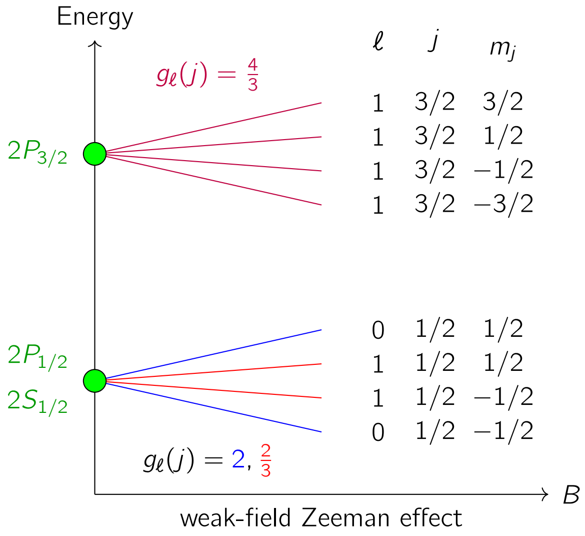
We analyze the Zeeman effect by thinking about it in three regimes: weak (where the fine-structure Hamiltonian is much larger than the Zeeman Hamiltonian, meaning the good basis is $|n, \ell, j, m_j\rangle$), strong (vice versa, and using the good basis $|n, \ell, m_\ell, m_s\rangle$), and intermediate (where we don't know as much). In each of these three situations, we have a different "zeroth order Hamiltonian" (Bohr plus fine-structure for the weak case, Bohr plus Zeeman for the strong case, and just Bohr for the intermediate case). We got the formula

$$E_Z^{(1)} = \langle n, \ell, j, m_j | H_Z | n, \ell, j, m_j \rangle = \mu_B B m_j g_\ell(j), \quad g_\ell(j) = 1 + \frac{j(j+1) - \ell(\ell+1) + \frac{3}{4}}{2j(j+1)}.$$

And remembering that $j = \ell \pm \frac{1}{2}$, we can simplify this expression a lot to see what the two cases yield, and a lot of cancellation happens: it turns out that

$$j = \ell \pm \frac{1}{2} \implies g_j(\ell) = 1 \pm \frac{1}{2\ell + 1}.$$

The most interesting case that we can talk about is the $n = 2$ energy level: recall that the $H^{(0)} = H_{\text{Bohr}} + H_{\text{fs}}$ unperturbed Hamiltonian leaves some states degenerate (since it only cares about n and j), so we have $2S_{1/2}$ and $2P_{1/2}$ at one energy level (for a degeneracy of $2 + 2 = 4$ because we can have $m_j = \pm 1/2$ in each case) and $2P_{3/2}$ at another energy level (degeneracy of 4 because $m_j \in \{-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}\}$). And now we can think about what happens as we turn on our magnetic field B and see the Zeeman effect at the weak level:



The top states split based on the value of m_j (notice that $g_\ell(j)$ is constant for all four states there), and then the bottom states split based on $g_\ell(j) = 2$ for $\ell = 0$ and $g_\ell(j) = \frac{2}{3}$ for $\ell = 1$ because $j = \frac{1}{2}$ and we want a negative sign. But as we increase the magnetic field, we can see that the differences in splitting will increase, and we need to start thinking about the intermediate regime (and toss this description of the energy splitting).

On the other hand, the picture looks very different for the strong-field Zeeman case (as we're doing on our problem set). In this case, our unperturbed energy levels are

$$E^{(0)} = E_{\text{Bohr}} + E_{\text{Z}} = -\frac{13.6 \text{ eV}}{n^2} + \mu_B B(m_\ell + 2m_s),$$

and then we need to compute the first-order energy shifts of the **fine-structure** Hamiltonian to understand the strong-field Zeeman effect. The answer turns out to be

$$E_{\text{fs}}^{(1)} = \frac{mc^2\alpha^4}{2n^3}\left(\frac{3}{4n} - \left\{\frac{\ell(\ell+1) - m_\ell m_s}{\ell(\ell+1/2)(\ell+1)}\right\}\right),$$

where the curly brace basically means that this expression is bad for $\ell = 0$, and instead we use 1 for the $\ell = 0$ case. Now that we know this formula, we can start thinking about degeneracy, and one way we can also think about what's going on is to switch bases from the uncoupled to the coupled basis, where the constants in the change-of-basis transformation are given by (using a resolution of the identity).

$$|n, \ell, m_\ell, m_s\rangle = \sum_{j,m_j} |n, \ell, j, m_j\rangle \langle n, \ell, j, m_j | n, \ell, m_\ell, m_s\rangle .$$

The bra-ket terms here are called **Clebsch-Gordan coefficients**, and they basically give the probabilities of being in various states when we switch bases. Remember that if we have a fixed m_ℓ and m_s, we know that we must have $m_j = m_\ell + m_s$ (because $\vec{J}$ is the sum of $\vec{L}$ and $\vec{S}$), and furthermore we know that j must be $\ell \pm \frac{1}{2}$. So the sum above really only has two terms, and what we end up calculating for our energy shifts is

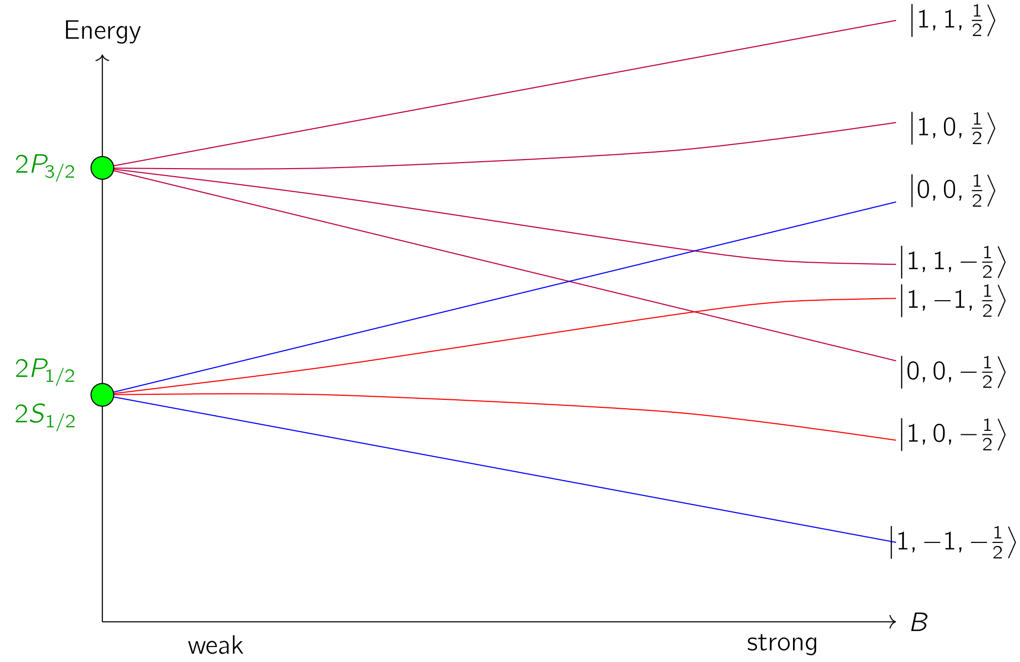
$$\langle n, \ell, m_\ell, m_s | H_{\text{fs}} | n, \ell, m_\ell, m_s\rangle = \sum_{j,j'} \langle n, \ell, m_\ell, m_s | n, \ell, j', m_j\rangle \langle n, \ell, j', m_j | H_{\text{fs}} | n, \ell, j, m_j\rangle \langle n, \ell, j, m_j | n, \ell, m_\ell, m_s\rangle .$$

And now notice from the matrix element of H_{fs}, and the other two bra-ket terms are basically giving us probabilities $P_\pm = |\langle n, \ell, m_\ell, m_s | n, \ell, j, m_j\rangle|^2$ of being in $j = \ell \pm \frac{1}{2}$: they are the squared Clebsch-Gordan coefficients.

Next time, we'll build on this and fill in more about what's happening in the intermediate and strong regimes for the Zeeman effect!

13 March 10, 2021 (Recitation)

We'll study the Zeeman effect a little bit more today. First of all, here's a general schematic of what happens as we increase the strength of the magnetic field in the Zeeman effect (not perfectly to scale, and also with states labeled by $|\ell, m_\ell, m_s\rangle$ in the limit, meaning that some change of basis is occurring in the middle):



Basically, we can label things in the strong limit with the (ℓ, m_ℓ, m_s) numbers, and we are asked to do the classification of states in our problem set. The idea is that some of the states come together because there is degeneracy, and the number that really matters most is the value of $m_\ell + 2m_s$. (Then the fine-structure term is a smaller splitting, but we need to work out what happens to each of those on our own.)

Right now, we'll talk about what's going on in the middle of this picture, which is the intermediate-field regime. Because each of the Hamiltonians H_Z and H_{fs} are not good bases on their own, we'll just start with the $|n, \ell, j, m_j\rangle$ basis to work in, and we'll diagonalize the matrix that comes up in doing degenerate perturbation theory. The types of matrix elements we then need to think about will look like

$$\left\langle n, \ell, j', m_j' \middle| H_{\text{fs}} + H_Z \middle| n, \ell, j, m_j \right\rangle .$$

The fine-structure part of this is easy, because the fine-structure Hamiltonian likes this basis. But we still need to think about the matrix elements of the Zeeman Hamiltonian, and in principle this means we need to compute an 8×8 matrix (for the $n = 2$ case) and diagonalize it to get the good states and the $E^{(1)}$ energy shifts. (And we would then be able to reproduce the answers in the weak- and strong-field cases by taking $B \to 0$ or $B \to \infty$.)

We won't go through all of the details here, but we can at least understand why a lot of the matrix elements are zero:

Problem 52

Take $n = 2$, and consider the change of basis that takes us from (n, ℓ, j, m_j) to (n, ℓ, m_ℓ, m_s). What linear combination of the uncoupled basis states are each of the coupled basis states?

First, we can try writing out all eight of the coupled basis states:

$$\left|2,1,\frac{3}{2},\frac{3}{2}\right\rangle_c, \left|2,1,\frac{3}{2},-\frac{3}{2}\right\rangle_c, \left|2,0,\frac{1}{2},\frac{1}{2}\right\rangle_c, \left|2,0,\frac{1}{2},-\frac{1}{2}\right\rangle_c,$$

$$\left|2,1,\frac{3}{2},\frac{1}{2}\right\rangle_c, \left|2,1,\frac{1}{2},\frac{1}{2}\right\rangle_c, \left|2,1,\frac{3}{2},-\frac{1}{2}\right\rangle_c, \left|2,1,\frac{1}{2},-\frac{1}{2}\right\rangle_c.$$

- The first two states are easy, because $m_j = \frac{3}{2}$ implies that we must have $m_\ell = 1$ and $m_s = \frac{1}{2}$ (there is no other way to get a total angular momentum large enough). Similarly, $m_j = -\frac{3}{2}$ implies $m_\ell = -1$ and $m_s = -\frac{1}{2}$. So

  $$\boxed{\left|2,1,\frac{3}{2},\frac{3}{2}\right\rangle_c = \left|2,1,1,\frac{1}{2}\right\rangle_{uc}, \quad \left|2,1,\frac{3}{2},-\frac{3}{2}\right\rangle_c = \left|2,1,-1,-\frac{1}{2}\right\rangle_{uc}}$$

  (constant is 1 because of normalization, and also ℓ is conserved).

- For the next two states, $\ell = 0$, so $m_\ell = 0$, and thus $m_s = m_j$. Therefore,

  $$\boxed{\left|2,0,\frac{1}{2},\frac{1}{2}\right\rangle_c = \left|2,0,0,\frac{1}{2}\right\rangle_{uc}, \quad \left|2,0,\frac{1}{2},-\frac{1}{2}\right\rangle_c = \left|2,0,0,-\frac{1}{2}\right\rangle_{uc}}.$$

  This is nice, because it means that for these first four (simpler) states, the matrix for H_Z looks the same in both bases, and thus the $[\delta H]$ matrix's top 4×4 component is diagonal.

- Next, notice that we can apply J_- to get from the first state $\left|2,1,\frac{3}{2},\frac{3}{2}\right\rangle_c$ to the fifth state $\left|2,1,\frac{3}{2},\frac{1}{2}\right\rangle_c$, and we know that $J_- = L_- + S_-$ (for working in the uncoupled basis). Computing in the coupled basis, we have

  $$J_-\left|2,1,\frac{3}{2},\frac{3}{2}\right\rangle_c = \hbar\sqrt{j(j+1)-m(m-1)}\left|2,1,\frac{3}{2},\frac{1}{2}\right\rangle_c = \hbar\sqrt{3}\left|2,1,\frac{3}{2},\frac{1}{2}\right\rangle_c,$$

  but computing in the uncoupled basis yields

  $$= (L_- + S_-)\left|2,1,1,\frac{1}{2}\right\rangle_{uc} = \hbar\sqrt{2}\left|2,1,0,\frac{1}{2}\right\rangle_{uc} + \hbar\left|2,1,1,-\frac{1}{2}\right\rangle_{uc},$$

  so comparing the two expressions yields

  $$\boxed{\left|2,1,\frac{3}{2},\frac{1}{2}\right\rangle_c = \frac{\sqrt{2}}{\sqrt{3}}\left|2,1,0,\frac{1}{2}\right\rangle_{uc} + \frac{1}{\sqrt{3}}\left|2,1,1,-\frac{1}{2}\right\rangle_{uc}}.$$

  We can get similar answers for the other states:

  $$\boxed{\left|2,1,\frac{1}{2},\frac{1}{2}\right\rangle_c = -\frac{1}{\sqrt{3}}\left|2,1,0,\frac{1}{2}\right\rangle_{uc} + \frac{\sqrt{2}}{\sqrt{3}}\left|2,1,1,-\frac{1}{2}\right\rangle_{uc}},$$

  $$\boxed{\left|2,1,\frac{3}{2},-\frac{1}{2}\right\rangle_c = \frac{1}{\sqrt{3}}\left|2,1,-1,\frac{1}{2}\right\rangle_{uc} + \frac{\sqrt{2}}{\sqrt{3}}\left|2,1,0,-\frac{1}{2}\right\rangle_{uc}},$$

  $$\boxed{\left|2,1,\frac{1}{2},-\frac{1}{2}\right\rangle_c = -\frac{\sqrt{2}}{\sqrt{3}}\left|2,1,-1,\frac{1}{2}\right\rangle_{uc} + \frac{1}{\sqrt{3}}\left|2,1,0,-\frac{1}{2}\right\rangle_{uc}}.$$

This is nice, because this means that the change-of-basis has blocks of size $1,1,1,1,2,2$: matrix elements between coupled basis states only interact if there are overlapping uncoupled basis states in the change of basis. So the only nonzero entries in this matrix look like

$$[\delta H] = \begin{bmatrix} * & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & * & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & * & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & * & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & * & * & 0 & 0 \\ 0 & 0 & 0 & 0 & * & * & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & * & * \\ 0 & 0 & 0 & 0 & 0 & 0 & * & * \end{bmatrix}$$

Diagonalizing this is now much easier (we only need to solve 2×2 problems), and that will give us a good basis. It turns out that the top four states have a term **linear in the magnetic field** B, while the other four states have a more complicated functional form (because we need to solve a quadratic equation). So there are indeed four straight lines in the figure above: the top and bottom lines in each group of 4 correspond to the diagonal terms in the matrix above.

14 March 11, 2021

We're ready to leave perturbation theory and the hydrogen atom behind for a bit (but we'll come back to them later): it's time to start a new topic, the **semiclassical approximation**, also known as the **WKB approximation** (credited to 1926 work by Wentzel, Kramers, and Brillouin). The idea is that we get approximations to solutions of differential equations with slowly varying coefficients, and in our applications to the Schrodinger equation, we'll see that classical behavior illuminates the quantum wavefunction behavior.

To start, recall that for a free particle with momentum p, we associate a de Broglie wavelength $\lambda = \frac{h}{p}$ (and this appears because the wavefunction of the particle $\psi(x) = e^{ipx/\hbar}$ has period λ). And classical physics is a good approximation to quantum physics when λ is **much smaller than relevant length scales** in the problem.

One formal way to access this classical regime is to take $h \to 0$ (because then the de Broglie wavelength is always small). We might object to this strategy because Planck's constant is a fixed number in our universe, but the point is that this is primarily a trick for studying the semiclassical regime.

Example 53

Suppose we have a particle that is moving in a potential $V(x)$, and consider some energy E. We know that the energy of a particle is given classically by

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

We can rearrange this equation to find that

$$\vec{p}^2(\vec{x}) = 2m(E - V(\vec{x})),$$

and this allows us to define a **position-dependent de Broglie wavelength**

$$\lambda(x) = \frac{h}{|p(\vec{x})|} = \frac{2\pi\hbar}{|\vec{p}(\vec{x})|}.$$

If we now look again at the time-independent Schrodinger equation

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

and now we can substitute in results from above:

$$\hat{p}^2\psi = p^2(\vec{x})\psi(x).$$

The left-hand side has a square operator, while the right-hand side has a position-dependent function. And while this is a suggestive way to write the equation, it is not an eigenvalue solution (because $p^2(\vec{x})$ is not a constant).

Before we get into the WKB approximation, let's take a closer look at our particle wavefunction: we can always write a complex-valued function in terms of its magnitude and phase as

$$\psi(\vec{x}, t) = \sqrt{\rho(\vec{x}, t)}e^{i\vec{S}(\vec{x},t)/\hbar},$$

where $\rho, \vec{S}$ are **real** quantities. The reason for writing the wavefunction in this way is that ρ is then the **probability density** (because $\rho(\vec{x}, t) = |\psi^2(\vec{x}, t)|^2$), and we know that the probability density satisfies a continuity equation

$$\frac{\partial\rho}{\partial t} = -\vec{\nabla}\cdot\vec{J},$$

where $\vec{J} = \frac{\hbar}{m}\text{Im}(\psi^*\vec{\nabla}\psi)$ is the **probability current**. And in this current form of ψ, we can write (using the product rule)

$$\vec{\nabla}\psi = \frac{1}{2}\frac{\nabla\rho}{\sqrt{\rho}}e^{i\mathcal{S}/\hbar} + \frac{i\sqrt{\rho}}{\hbar}\nabla\mathcal{S}e^{i\mathcal{S}/\hbar},$$

and then multiplying this by ψ^* cancels out the exponential term to get

$$= \frac{1}{2}\nabla\rho + \frac{i\rho}{\hbar}\vec{\nabla}\mathcal{S}.$$

But we want the imaginary part of this expression to get to the probability current, and because $\rho, \mathcal{S}$ are real, we can substitute in to find that

$$\boxed{\vec{J} = \rho\frac{\vec{\nabla}\mathcal{S}}{m}}.$$

In other words, **surfaces of constant phase $\vec{S}$ have probability current perpendicular to those surfaces**.

Fact 54

The reason of recalling this probability current story is that there is an analogy here with fluid flow, if we think of the probability as the density of a classical fluid.

We know that the current for a classical fluid looks like

$$\vec{J} = \rho\vec{v} = \rho\frac{\vec{p}}{m},$$

so classically the gradient $\vec{\nabla}\mathcal{S}$ should (maybe) look like our position-dependent momentum $\vec{p}(\vec{x})$. (And that is indeed what we'll find as we proceed on!

Example 55

Let's check this logic in the case for a free particle

$$\psi(\vec{x},t) = \exp\left(\frac{i\vec{p}\cdot\vec{x}}{\hbar} - \frac{iEt}{\hbar}\right).$$

Indeed, we have

$$S = \vec{p}\cdot\vec{x} - Et \implies \nabla\vec{S} = \vec{p} = \vec{p}(\vec{x}),$$

so our logic above at least checks out for this special case.

To start setting the WKB approximation now, we will first write

$$\psi(\vec{x},t) = \sqrt{\rho(\vec{x},t)}e^{i\vec{S}(\vec{x},t)/\hbar} = e^{iS(x)/\hbar},$$

where we define a new **complex** number

$$S(x) = \mathcal{S} - \frac{i\hbar}{2}\log\rho.$$

(Remember that because $\mathcal{S}$ is real and so is ρ, the first term on the right-hand side is real and the second is imaginary.) We'll be limiting ourselves to one-dimensional physics, and we'll also be thinking about solutions to the time-independent Schrodinger equation (so there is no t-dependence). We now want to plug this $e^{iS(x)/\hbar}$ into our Schrodinger equation $\hat{p}^2\psi = p^2(\vec{x})\psi(x)$, which can be rewritten as

$$-\hbar^2\frac{d^2\psi}{dx^2} = p^2(x)\psi(x),$$

where remember that $p^2(x)$ is the number $2m(E - V(x))$. To plug this in, we first compute the derivatives

$$\psi' = \frac{iS'}{\hbar}e^{iS/\hbar}, \quad \psi'' = \frac{iS''}{\hbar}e^{iS/\hbar} + \frac{(iS')^2}{\hbar^2}e^{iS/\hbar} = -\frac{1}{\hbar^2}(S'^2 - i\hbar S'')e^{iS/\hbar},$$

and then we can plug this in and simplify common terms on both sides to get

$$\boxed{S'(x)^2 - i\hbar S''(x) = p^2(x)}.$$

(At this point, we still have not made any approximations!) And the point is that we've converted the linear differential equation for ψ into a nonlinear differential equation for S. It might seem like we've made our lives harder, but the point is that this is a good starting point for the semiclassical approximation because of the factor of $\hbar$ (which will be used as an expansion parameter).

As we said at the beginning, we'll take $V(x)$ to be a **slowly varying** potential (on the scale of the de Broglie wavelength λ).

Proposition 56

The $i\hbar S''$ term in the above equation is small in the limit where $V(x)$ is slowly varying.

To get some intuition for this, first suppose that $V(x) = V_0$ is constant. Then $p^2(x) = 2m(E - V_0)$ is also constant, so we can define $p_0 = \sqrt{2m(E - V_0)}$, and we know that the solution to the Schrodinger equation is

$$\psi = e^{ip_0x/\hbar} = e^{iS/\hbar} \implies S = p_0x.$$

And indeed in this case, $S'' = 0$, so it's reasonable to believe that small variations will also lead to small values of S''. (Or alternatively, we can take $\hbar \to 0$ to make that term small as well.)

So now we're ready to do a power series expansion: much like in perturbation theory, we will write

$$S(x) = S_0(x) + \hbar S_1(x) + \hbar^2 S_2(x) + \cdots,$$

and we can plug this into the equation $S'^2 - i\hbar S'' = p^2(x)$, and we find (really only to first order) that

$$\left(S_0' + \hbar S_1' + O(\hbar^2)\right)^2 - i\hbar(S_0'' + \hbar S_1'' + O(\hbar^2)) = p^2(x).$$

Expanding this out and grouping in order in $\hbar$ yields

$$(S_0')^2 + \hbar(2S_0'S_1' - iS_0'') + O(\hbar^2) = p^2(x).$$

Here, we should be thinking of $p^2(x)$ as a **classical quantity** of order $1 = \hbar^0$, and now we can solve the equation order-by-order in $\hbar$. To order $\hbar^0, \hbar^1$, we find that

$$S_0'^2 = p^2(x), \quad S_1' = \frac{iS_0''}{2S_0'},$$

respectively. The first of these equations has solution

$$S_0' = \pm p(x) \implies \boxed{S_0(x) = \pm \int_{x_0}^{x} dx' p(x')},$$

where we should remember that $p(x') = \sqrt{2m(E - V(x')}$.

Remark 57. *We know that the wavefunction in quantum mechanics is continuous, and in fact if the potential is smooth, p is infinitely differentiable. So we won't switch between the two signs in this integral for $S_0(x)$. Also, we've combined the integration constant into the offset x_0 (so we can think of that as shifting the integration constant).*

And now that we have the solution to $S_0(x)$, we can find the next solution nicely:

$$S_1' = \frac{i}{2}\frac{\pm p'(x)}{\pm p(x)} = \frac{i}{2}\frac{d}{dx}\log p(x) \implies \boxed{S_1(x) = \frac{i}{2}\log p(x) + C'}.$$

So now we have an approximation to the wavefunction:

$$\psi(x) \approx e^{iS(x)/\hbar} = e^{i(S_0(x) + \hbar S_1(x))/\hbar} = \exp\left[i\left(\pm\int_{x_0}^{x} dx' \frac{p(x')}{\hbar} - \frac{1}{2}\log p(x) + C'\right)\right],$$

and now we can pull out the log from the exponential and the constant C' (turning it into a constant A in front) to get

$$\boxed{\psi(x) \approx \frac{A}{\sqrt{p(x)}}\exp\left[\pm\frac{i}{\hbar}\int_{x_0}^{x} dx' p(x')\right]}.$$

This is our WKB approximation, and we can notice a few things about it now. Because we like to write $\psi(x) = \sqrt{\rho(x)}e^{i\mathcal{S}(x)/\hbar}$ in terms of an amplitude and a phase, we can find that the amplitude is

$$\rho(x) = \frac{|A|^2}{p(x)} = \frac{|A|^2}{mv(x)}.$$

In other words, the probability density is large where the particle's classical velocity is small, which makes sense – particles linger in places where velocity is small. And the phase is

$$\mathcal{S} = \pm\int_{x_0}^{x} dx' p(x'),$$

which tells us that (by the fundamental theorem of calculus)

$$\vec{J} = \rho \frac{\nabla \mathcal{S}}{m} = \frac{|A|^2}{p(x)} \frac{1}{m} \cdot \pm p(x) = \pm \frac{|A|^2}{m}.$$

Notably, this probability current is a constant, and that's indeed necessary because the Schrodinger equation that we're solving is time-independent (so the probability density is time-independent, meaning that $\frac{\partial \rho}{\partial t} + \partial_x J = 0 \implies J$ is constant).

Fact 58

We can think of the $+$ solution in the $\pm$ above (with $J > 0$) as a particle moving to the right, and the $-$ solution (with $J < 0$) as a particle moving to the left.

But we've been ignoring some of the details here, which we'll address now. First of all, we've been implicitly saying that $E > V(x)$ (placing us in the **classically allowed region**), so that $p(x) = \sqrt{2m(E - V(x))}$ is a real number. (After all, a classical particle cannot ever be at positions where $V(x) > E$.) But we'll treat the other region later.

Often we will use the shorthand $p(x) = \hbar k(x)$, so that our solutions are of the form (renormalizing the factor of $\sqrt{\hbar}$ through A)

$$\psi(x) = \frac{A}{\sqrt{k(x)}} e^{\pm i \int_{x_0}^{x} dx' k(x')}.$$

But we know that two solutions to the time-independent Schrodinger equation with the same energy yield a general solution which is a linear combination of those two:

$$\psi(x) = \frac{A}{\sqrt{k(x)}} e^{i \int_{x_0}^{x} dx' k(x')} + \frac{B}{\sqrt{k(x)}} e^{-i \int_{x_0}^{x} dx' k(x')}$$

But in the **classically forbidden region** where $p(x)$ is imaginary (because $E < V(x)$), we can take a shortcut and "analytically continue" what we had from above: we use $p(x) = i\hbar\kappa(x)$, where $\kappa(x) = \frac{\sqrt{2m(V(x)-E)}}{\hbar}$ is a positive constant. We then find the general solution

$$\psi(x) = \frac{C}{\sqrt{\kappa(x)}} e^{\int_{x_0}^{x} dx' \kappa(x')} + \frac{D}{\sqrt{\kappa(x)}} e^{-\int_{x_0}^{x} dx' \kappa(x')}$$

(noticing that the i in the exponents are gone). And that means we get **real exponentials** instead of oscillating exponentials – the first term here is exponentially growing for large x, while the second term is exponentially decaying.

We should now be more formal about when this approximation is valid – in other words, how slowly does the potential V need to vanish? Recall that we derived these wavefunctions by formally expanding in $i\hbar$, which means that we need the order $\hbar^1$ terms to be smaller than the order $\hbar^0$ term.

Example 59

For illustration, we can compare S_0'' (one of the $\hbar^1$ terms) to $p^2(x)$ (one of the $\hbar^0$ terms).

The condition that needs to be satisfied is then

$$\hbar |S_0''(x)| \ll p^2(x)$$

for all real numbers x where the approximation is being applied. We know from previous work that $|S_0'| = |p(x)|$, and $|S_0''| = |p'(x)|$, so the condition that needs to be satisfied is

$$\hbar |p'(x)| \ll p^2(x) \implies \hbar \left| \frac{p'(x)}{p^2(x)} \right| = \left| \frac{d}{dx} \frac{\hbar}{p(x)} \right| \ll 1.$$

And remembering that the position-dependent de Broglie wavelength is $\frac{2\pi\hbar}{p(x)}$, our condition is really that

$$\boxed{\left|\frac{d(\lambda(x))}{dx}\right| \ll 1}$$

for our approximation to be valid. (And indeed, the left-hand side here is dimensionless, so everything makes sense!) We can alternatively get intuition for this by multiplying both sides by $\lambda(x)$ to find that

$$\left|\lambda\frac{d\lambda}{dx}\right| \ll \lambda,$$

and the left-hand side is basically the change in the de Broglie wavelength over one de Broglie wavelength. So if we are in the classically allowed region (for simplicity), and our wavefunction is oscillating but the period of oscillation is changing as a function of x, we need the period of oscillation to not change too much over a few wavelengths (so that the local period can be defined).

However, there is one generic place where this kind of reasoning breaks down: when we look at the **classical turning points** (meaning that $V(x)$ crosses from being below energy E to above energy E), we **always have** $p^2(x) \to 0$. More precisely, we can approximate $V(x)$ to be approximately linear around the turning point $x = a$, meaning that

$$V(x) - E = g(x - a)$$

for some $g > 0$. If we assume that x is still within the classical region, then

$$p^2 = 2m(E - V(x)) = 2mg(a - x) \implies \lambda(x) = \frac{2\pi\hbar}{p(x)} = \frac{2\pi\hbar}{\sqrt{2mg}}\frac{1}{\sqrt{a-x}}.$$

Then we can look at

$$\left|\frac{d\lambda}{dx}\right| = \frac{1}{2}\frac{2\pi\hbar}{\sqrt{2mg}}\frac{1}{(a-x)^{3/2}},$$

and clearly as $x \to a$, we cannot have $\left|\frac{d\lambda}{dx}\right| \ll 1$ because of divergence! So no matter how smooth our potential looks, we will always run into trouble with this semiclassical solution. To get around this, we know that we have a semiclassical solution in both the classically allowed and classically forbidden region (sufficiently far away from the turning point), and we'll stitch those together by solving the Schrodinger equation exactly near the turning point. Those **connection formulas** will help us connect the different solutions together!

15 March 15, 2021 (Recitation)

We'll start with a bit of review about the WKB approximation, giving some hints about where we're going next. Much like perturbation theory, this is an approximation for the Schrodinger equation, but this time the approximation has to do with how slowly the de Broglie wavelength is varying with position. Recall that if we write our wavefunction as $\psi(x) = e^{iS(x)/\hbar}$, then we get the differential equation

$$(S')^2 - i\hbar S'' = p^2(x),$$

where $p^2(x) = 2m(E - V(x))$. Then we expanded out this expression as a power series in $\hbar$, and we found the zeroth and first-order terms of the approximate solution. The result was that in the classically allowed regime $E > V(x)$, we have

$$\psi(x) = \frac{A}{\sqrt{K(x)}}e^{-i\int_{x_0}^{x} dx'\kappa(x')} + \frac{B}{\sqrt{K(x)}}e^{i\int_{x_0}^{x} dx'\kappa(x')},$$

where $K(x) = \frac{p(x)}{\hbar} = \frac{1}{\hbar}\sqrt{2m(E - V(x))}$. (These two terms correspond to a left-moving and a right-moving particle, respectively.) But we also have the classical forbidden region, in which we get

$$\psi(x) = \frac{C}{\sqrt{\kappa(x)}} e^{-\int_{x_0}^{x} dx' \kappa(x')} + \frac{D}{\sqrt{\kappa(x)}} e^{\int_{x_0}^{x} dx' \kappa(x')},$$

where this time $\kappa(x) = \frac{p(x)}{i\hbar} = \frac{1}{\hbar}\sqrt{2m(V(x) - E)}$. The four coefficients A, B, C, D are just generic numbers (since we can have linear combinations of our two original solutions to the differential equation).

And to tell whether this method is valid, we can check whether the second-order $\hbar$ term is small compared to the first two terms, or some other comparison of this type. And we find that the requirement is for $\left|\frac{d\lambda(x)}{dx}\right| \ll 1$, where $\lambda(x) = \frac{h}{p(x)}$ is the local de Broglie wavelength. Writing out the derivative, we have that $\left|\frac{d\lambda}{dx}\right| = \left|-\frac{hp'}{p^2}\right| = \lambda\frac{p'}{p}$, so another way to state our assumption is that

$$\left|\lambda(x)\frac{dp}{dx}\right| \ll |p(x)|.$$

In other words, we can talk about WKB's validity in terms of changes to the local momentum $p(x)$ over a distance of order λ. We can also look more carefully at the equation $p^2 = 2m(E - V(x))$ and take an x-derivative on both sides: we find

$$2p\frac{dp}{dx} = -2m\frac{dV}{dx}.$$

So we can write things in terms of the "force" now:

$$\left|\lambda(x)\frac{dV}{dx}\right| = \frac{1}{m}|\lambda(x)pp'| = \frac{h}{m}|p'|,$$

and then we can substitute this into the above expression: because $|hp'| \ll |p^2|$, what we find is that

$$\left|\lambda(x)\frac{dV}{dx}\right| \ll \frac{p^2}{2m}$$

(where we added a factor of 2 to make it look more familiar).

Proposition 60

The equation $\left|\lambda(x)\frac{dV}{dx}\right| \ll \frac{p^2}{2m}$ says that over a distance of λ, the change in potential energy should be much less than the kinetic energy.

So now that we have these two approximations: as mentioned at the end of lecture, we should try a WKB-type approximation for $E > V$ and also $E < V$, but then near $E = V$ we need something to stitch those two solutions together. That's because $E \approx V$ implies $p \approx 0$, and that means all of the approximations we've described above break down. So we need to figure out the **connection formulas**, and we'll do that in lecture.

But we'll write down the answers right now so we've at least seen them: suppose that $E = V$ at $x = a$ (and we have exponentially decaying solutions for $E < V$ and oscillatory for $E > V$). Suppose that our solution on the left is oscillatory, and the solution on the right is exponentially decaying. Then we find that the coefficients A, B, C, D are constrained by the wavefunctions

$$\frac{2}{\sqrt{K(x)}}\cos\left(\int_x^a K(x')dx' - \frac{\pi}{4}\right) \Longleftarrow \frac{1}{\sqrt{\kappa(x)}}\exp\left(-\int_a^x \kappa(x')dx'\right)$$

(in other words, if we know the form of the solution on the right, we know what the coefficients have to be on the left). Notice that the equation above relates C to a combination of A and B if $D = 0$. On the other hand, we also have that

$$-\frac{1}{\sqrt{K(x)}}\sin\left(\int_x^a K(x')dx' - \frac{\pi}{4}\right) \implies \frac{1}{\sqrt{\kappa(x)}}\exp\left(\int_a^x \kappa(x')dx'\right)$$

(which relates D to a combination of A and B). And the arrows are important – we can't apply the formulas in reverse, because an exponentially growing solution doesn't give us enough information to also learn about the exponentially falling solution (approximations break down).

Example 61

One of the applications of WKB is the tunneling phenomenon – we also need the connection formulas for a derivation here, but we'll just explain the answer right now.

Basically, a particle of energy E can get over a hump of energy larger than E, and the WKB approximation tells us that the transmission coefficient (ratios of probability currents $\frac{\psi_{\text{out}}}{\psi_{\text{in}}}$) is

$$T \approx \exp\left(-2\int_a^b \kappa(x')dx'\right),$$

where the hump in $V(x)$ goes from $x = a$ to $x = b$. (Imagine that there is an infinite potential for $x < 0$, so this means that usually the particle is stuck in the left region from 0 to a.) And because κ is proportional to $\sqrt{V(x) - E}$, indeed making the potential larger makes the exponential smaller, which gives us a smaller probability of tunneling.

If we know this T, we can then find the probability that our particle does **not** tunnel (that is, it remains trapped in the given region from $x = 0$ to a). If we know that the particle is trapped at some time t, then

$$P(t + dt) = P(t)(1 - \omega\, dt),$$

where $\omega = \frac{T}{\Delta t}$ is the **tunneling probability per unit time**. Here Δt is some characteristic time, which we can think of classically as "how long it takes for the particle to bounce off the potential at $x = a$," which motivates the definition

$$\Delta t = 2\int_a^b \frac{dx'}{v(x')},$$

where $v(x) = \frac{p(x)}{m}$. And now rearranging, we find that

$$P'(t) = \frac{P(t + dt) - P(t)}{dt} = -\omega P(t),$$

and thus $P(t) = P_0 \exp(-\omega t) = P_0 \exp\left(-\frac{t}{\tau}\right)$ (the probability of not tunneling is exponentially decaying). Here, $\tau = \frac{1}{\omega}$ is often called the **lifetime** of the particle in the well.

Example 62 (Gamow's α-decay)

In nuclear physics, a nucleus can decay via $N \to N' + \alpha$, where the α-particle has two protons and two neutrons (so N has two more protons than N'). Gamow's model accounts for the instability by thinking of a nucleus as having a potential well.

If N' has Z protons, then the potential takes the form

$$V(r) = \begin{cases} -V_0 & 0 < r < r_1 \\ \frac{2Ze^2}{r} & r > r_1 \end{cases},$$

where we basically have a Coulomb repulsion beyond $x > r_1$. To explain this, note that two protons and two neutrons almost form Helium-4 (without the electrons) and thus it is very stable. So once an alpha particle forms, there are two contributions to the potential – there is a Coulomb repulsion for $x > r_1$ and a strong nuclear binding force for $x < r_1$.

So if our particle is at some energy $E > 0$, so that we need to tunnel through the range $[r_1, r_2]$, where $\frac{2Ze^2}{r_2} = E$. Then we can use the above calculation to find the tunneling probability: we find that $T = e^{-2\gamma}$ for

$$\gamma = \frac{1}{\hbar}\int_{r_1}^{r_2} dr\sqrt{2m\left(\frac{2Ze^2}{r} - E\right)} = \frac{\sqrt{2mE}}{\hbar}\int_{r_1}^{r_2} dr\sqrt{\frac{r_2}{r} - 1}.$$

This integral is some arcsine term, but the limit for large $r_2 \gg r_1$ is that we have

$$\gamma = \frac{\sqrt{2mE}}{\hbar}\left(\frac{\pi}{2}r_2 + \cdots\right).$$

Since $r_2 \sim \frac{1}{E}$, this means that asymptotically, we have $\gamma \sim \frac{1}{\sqrt{E}}$. And for various different nuclei, we have different lifetimes, and indeed exactly like in this model, we can plot tunneling probabilities versus E. It turns out that this simple model does get the scaling model correctly! (And notice that even when γ changes by a little, the tunneling probability can change drastically, and thus we see the tunneling probability change significantly – order of 10^{25} – across different nuclei.)

Remark 63. *The effect of the $-V_0$ part does show up, but only as a prefactor in $\omega = \frac{T}{\Delta t}$ – it doesn't change the exponential behavior as a factor of E.*

16 March 16, 2021

Last time, we discussed the semi-classical or WKB approximation, which works well for slowly varying potentials $V(x)$. There are two main regimes – in the classically allowed regime $E > V(x)$, we have oscillating behavior, and in the classically forbidden regime $E < V(x)$, we get exponentially growing or decaying solutions. And we expect this WKB approximation to be good when $\left|\frac{d\lambda}{dx}\right| \ll 1$, where $\lambda = \frac{2\pi}{|k(x)|}$ is the position-dependent de Broglie wavelength. But no matter how smooth our potential is, that condition will break down near the classical turning point $E = V(x)$, so we'll discuss how to deal with that case today.

Suppose that our classical turning point occurs at some $x = a$, and our potential is such that $V(x) > E$ at $x > a$. Then for large enough $x \gg a$, we have

$$\psi(x) = \frac{A}{\sqrt{\kappa(x)}}\exp\left(-\int_a^x dx'\kappa(x')\right) + \frac{B}{\sqrt{\kappa(x)}}\exp\left(\int_a^x dx'\kappa(x')\right),$$

and for small enough $x \ll a$ in the region $V(x) < E$, we have

$$\psi(x) = \frac{C}{\sqrt{k(x)}}\cos\left(\int_x^a dx'\kappa(x') - \frac{\pi}{4}\right) + \frac{D}{\sqrt{k(x)}}\sin\left(\int_x^a dx'\kappa(x') - \frac{\pi}{4}\right)$$

(we've converted the exponentials to sines and cosines, and we can add the phase to make our lives easier later on). It may look like there are 4 independent coefficients here, but the Schrodinger equation is a second-order differential equation, so there should only be two unknown constants. And indeed, if we aren't making any approximations, we should be able to go from the solution on the left to the solution on the right (at least in principle), so we should be able to write C and D in terms of A and B, or vice versa.

Theorem 64 (Connection formula)

There is a relation between the coefficients of ψ above given by

$$C = 2A, D = -B.$$

We should note that if we plug in $x = a$ into the WKB solutions with those coefficients $C = 2A, D = -B$, we find

$$\psi_{\text{WKB}}(x = a^-) \neq \psi_{\text{WKB}}(x = a^+);$$

in fact, the WKB solutions will blow up. We would have continuity of the wavefunction and its derivative if we had an exact solution, but that's not what we have!

Additionally, there are some important caveats that we need to keep in mind when using the formulas, but we'll talk about that later.

Example 65

Suppose that we have a potential $V(x)$ such that $V(x) = \infty$ for all $x < 0$ (so there is an infinite hard wall that cannot be passed). We are looking for solutions to the Schrodinger equation with $E < V(\infty)$ (these are called **bound states**).

The boundary conditions we have here are that $\psi(0) = 0$ and $\psi(\infty) = 0$ (otherwise we won't have a normalizable state). Let $x = a$ be the classical turning point (so that $V(a) = E$), and for simplicity let's say that V is increasing (and smooth) for $x > 0$ Then the WKB approximation in the $x \gg a$ region tells us that

$$\psi(x) = \frac{A}{\sqrt{\kappa(x)}} \exp\left(-\int_a^x dx' \kappa(x')\right)$$

(we can only have the decaying exponential term here because the other term would make the wavefunction not normalizable), and $B = 0$. We'll now use the connection formulas to go across $x = a$ into the classically allowed region: we learn that $D = 0$ (so the sine term above is not present), and

$$\psi(x) = \frac{2A}{\sqrt{k(x)}} \cos\left(\int_x^a dx' \kappa(x') - \frac{\pi}{4}\right)$$

And now if we implement the boundary condition $\psi(0) = 0$, we find that

$$\cos\left(\int_0^a dx' k(x') - \frac{\pi}{4}\right) = 0 \implies \int_0^a dx' k(x') = \pi\left(n + \frac{3}{4}\right).$$

But here, $k(x) = \frac{1}{\hbar}\sqrt{2m(E - V(x))}$ is positive, meaning we must have $n = 0, 1, 2, \cdots$. And thus we have characterized the quantization condition for our bound states:

$$\boxed{\frac{1}{\hbar}\int_0^a dx \sqrt{2m(E - V(x))} = \pi\left(n + \frac{3}{4}\right), \quad n \in \mathbb{Z}_{\geq 0}}.$$

In other words, we indeed find that only discrete energy levels are allowed! And this calculation can in fact be generalized to smooth potentials $V(x)$ where $E < V(\infty), V(-\infty)$ (so that the particle is classically constrained to some region $[a, b]$, where a, b are the turning points). Then we analogously find that

$$\boxed{\int_a^b dx' k(x') = \pi\left(n + \frac{1}{2}\right), \quad n \in \mathbb{Z}_{\geq 0}}.$$

Proof of Theorem 64. To get around the fact that WKB only applies far away from the turning point, we will **solve the Schrodinger equation exactly** in the neighborhood of the $x = a$ turning point and then match coefficients from there. The idea is that if we're sufficiently close to $x = a$, we can approximate V by a linear potential, and there will be an area of **overlap** between our methods where the linearized V is valid, but so is the WKB approximation.

Explicitly, suppose that $V(x) - E = g(x - a)$, where g is the slope of the potential (the derivative $V'(a)$. We know that our WKB solutions look like (if g is positive)

$$\psi_R(x) = \frac{A}{\sqrt{\kappa(x)}} \exp\left(-\int_a^x \kappa(x')dx'\right) + \frac{B}{\sqrt{\kappa(x)}} \exp\left(\int_a^x \kappa(x')dx'\right).$$

Now turning to the region where the linearized potential is valid, note that

$$\kappa^2(x) = \frac{2m}{\hbar^2}(V(x) - E) = \frac{2mg}{\hbar^2}(x - a),$$

so that

$$\int_a^x \kappa(x')dx' = \sqrt{\frac{2mg}{\hbar^2}} \int_a^x dx'(x' - a)^{1/2} = \sqrt{\frac{2mg}{\hbar^2}}\frac{2}{3}(x - a)^{3/2}.$$

If we let $\eta = \left(\frac{2mg}{\hbar^2}\right)^{1/3}$ and introduce the dimensionless variable $u = \eta(x - a)$, then our integral above becomes $\frac{2}{3}u^{3/2}$, and $\kappa^2(x) = \eta^2 u$. And thus, our solution that is valid for both the linearized potential and the WKB forbidden-region solution is

$$\psi_R(x) = \frac{1}{\sqrt{\eta}} \frac{A}{|u|^{1/4}} \exp\left(-\frac{2}{3}u^{3/2}\right) + \frac{1}{\sqrt{\eta}} \frac{B}{|u|^{1/4}} \exp\left(\frac{2}{3}u^{3/2}\right).$$

On the other hand, the solution on the left is

$$\psi_L(x) = \frac{C}{\sqrt{k(x)}} \cos\left(\int_x^a dx' k(x') - \frac{\pi}{4}\right) + \frac{D}{\sqrt{k(x)}} \sin\left(\int_x^a dx' k(x') - \frac{\pi}{4}\right),$$

and we know that $k(x) = \frac{1}{\hbar}\sqrt{2m(E - V(x))}$, so employing a similar strategy with the linearized potential yields

$$\psi_L(x) = \frac{C}{\sqrt{\eta}|u|^{1/4}} \cos\left(\frac{2}{3}|u|^{3/2} - \frac{\pi}{4}\right) + \frac{D}{\sqrt{\eta}|u|^{1/4}} \sin\left(\frac{2}{3}|u|^{3/2} - \frac{\pi}{4}\right).$$

And we can now stitch these together with the Schrodinger equation:

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

Plugging in the linearized form of the potential yields

$$\frac{d^2\psi}{dx^2} = \frac{2mg}{\hbar^2}(x - a)\psi(x),$$

and we can rewrite this equation in terms of u to remove the constants: we find that the left and right sides become (evaluating ψ at u instead of x)

$$\frac{d^2\psi}{dx^2} = \eta^2\frac{d^2\psi}{du^2}, \quad \frac{2mg}{\hbar^2}(x - a)\psi(x) = \eta^2 u\psi,$$

and thus our solution simplifies to the **Airy equation**

$$\frac{d^2\psi}{du^2} = u\psi(u).$$

This is a second-order linear differential equation with two linearly independent solutions, which are denoted $\mathrm{Ai}(u)$ and $\mathrm{Bi}(u)$. (There are certain power series and integral representations for these functions which are good for us to know.) But from there, we can derive the asymptotic behavior of the two functions, and we want to match a linear combination of Ai and Bi with the WKB approximations, so we'll analyze those solutions at large u. It turns out that for $u \gg 1$,

$$\text{Ai}(u) \sim \frac{1}{2\sqrt{\pi}} \frac{1}{u^{1/4}} \exp\left(-\frac{2}{3}u^{3/2}\right),$$

and for $u \ll -1$,

$$\text{Ai}(u) \sim \frac{1}{\sqrt{\pi}} \frac{1}{u^{1/4}} \cos\left(\frac{2}{3}|u|^{3/2} - \frac{\pi}{4}\right).$$

But this has the same form as our WKB solutions – we have the same exponential term and the same $u^{1/4}$ in the denominator! And there is no ambiguity in these normalizations – the ratio of the coefficients in the positive and negative u regions for Ai will stay constant no matter what normalization factor we put in front of it – the coefficient of the cosine is twice the coefficient of the decaying exponential term, which indeed means $\boxed{C = 2A}$ as desired. And if we repeat this argument for Bi, we find that for $u \gg 1$,

$$\text{Bi}(u) \sim \frac{1}{\sqrt{\pi}} \frac{1}{u^{1/4}} \exp\left(\frac{2}{3}u^{3/2}\right),$$

and for $u \ll -1$,

$$\text{Bi}(u) = -\frac{1}{\sqrt{\pi}} \frac{1}{u^{1/4}} \sin\left(\frac{2}{3}u^{3/2} - \frac{\pi}{4}\right),$$

so indeed the ratio here tells us that $\boxed{D = -B}$, finishing our derivation. ☐

Fact 66

To understand why this **intersecting region** between the linearized $V(x)$ and WKB solutions does exist, we need to understand whether the deviation from linearity happens early or later than the $u \gg 1$ limit for Airy.

We know that

$$V(x) - E = g(x-a) + \frac{1}{2}V''(a)(x-a)^2,$$

where $g = V'(a)$, and thus in the intersecting region, we need to make sure the next-order correction is small compared to the linear term:

$$\frac{V''(a)}{g}(x-a) \ll 1.$$

Rewriting this in terms of $u = \eta(x-a)$, our condition becomes

$$\frac{V''(a)}{g}\frac{u}{\eta} \ll 1 \implies u \ll \frac{g\eta}{V''(a)} = \left(\frac{2mg^4}{\hbar^2}\right)^{1/3} \frac{1}{V''(a)} = \left(\frac{2mV'(a)^4}{\hbar^2}\right)^{1/3} \frac{1}{V''(a)}.$$

The other condition for our matching region is that we must have $u \gg 1$ (so that the Airy function asymptotics are valid). Therefore, the intersection region must satisfy

$$1 \ll u \ll \left(\frac{2mV'(a)^4}{\hbar^2}\right)^{1/3} \frac{1}{V''(a)},$$

which means that the condition for the connection formula to be valid is basically for $\boxed{V''(a) \ll \left(\frac{mV'(a)^4}{\hbar^2}\right)^{1/3}}$ (in other words, the second derivative is small with respect to the first derivative). And indeed, this condition is always satisfied when we take $\hbar \to 0$.

In summary, we can write down a relation like

$$\frac{2}{\sqrt{k(x)}}\cos\left(\int_x^a k(x')dx'-\frac{\pi}{4}\right) \Longleftarrow \frac{1}{\sqrt{\kappa(x)}}\exp\left(-\int_a^x dx'\kappa(x')\right),$$

$$-\frac{1}{\sqrt{k(x)}}\sin\left(\int_x^a k(x')dx'-\frac{\pi}{4}\right) \Longrightarrow \frac{1}{\sqrt{\kappa(x)}}\exp\left(\int_a^x dx'\kappa(x')\right).$$

But now notice the arrows: the caveat here is that all of our solutions are still approximate, and thus there are subleading terms in each of the solutions (in the expansion parameter $\frac{d\lambda}{dx}$). And when we have both a decaying and a growing exponential, the decaying term is very small compared to the growing exponential, so in particular the subleading terms from the growing exponential will be larger than the leading terms from the decaying one!

So if we start in the classically forbidden region, and we know that there is only a decaying exponential, then it is valid to use the connection formula and turn it into a cosine for the classically allowed region. But if we try to go the other way and we only have the cosine solution, it's still possible that subleading terms gives us a small amount of the sine solution, and that will give a growing exponential which will always overwhelm the decaying exponential term! So we can't use the arrow in reverse.

A similar argument works in reverse: the second arrow works in the forward direction, because a small cosine will be harmless when we start with a sine term in the classically allowed region. But it's possible that if we start with a growing exponential term, continuing to the classically allowed region could introduce a cosine term of the same magnitude (because the exponentially decaying term could be hiding with the same coefficient and still be of lower order).

We've been talking so far only about the case where the slope $g = V'(a)$ is positive, and indeed similar derivations can be made for $g < 0$ (the formulas look very similar):

$$\frac{1}{\sqrt{\kappa(x)}}\exp\left(-\int_x^b dx'\kappa(x')\right) \Longrightarrow \frac{2}{\sqrt{k(x)}}\cos\left(\int_b^x k(x')dx'-\frac{\pi}{4}\right)$$

$$-\frac{1}{\sqrt{\kappa(x)}}\exp\left(\int_x^b dx'\kappa(x')\right) \Longleftarrow \frac{1}{\sqrt{k(x)}}\sin\left(\int_b^x k(x')dx'-\frac{\pi}{4}\right)$$

Example 67 (Quantum tunneling)

Suppose that we have a potential barrier $V(x)$, and we shoot particles at the barrier with some energy E. We want to know whether particles are able to make it through the barrier, even when E is less than the height of the barrier.

We may have discussed this general type of scattering process in previous classes, and in principle this is a time-dependent problem (we have a wave packet going in and a wave packet coming out). But luckily, the time-dependent problem can be reduced to the time-independent problem with particular boundary conditions, and we'll see more of this later in 8.06.

At least for this one-dimensional problem, the boundary conditions are simple: if $V(x) \to 0$ as $x \to \pm\infty$, then we send an incident wave Ae^{ikx} into the potential barrier, and we have a reflected wave Be^{-ikx} and a transmitted wave Fe^{ikx}. We can then solve the Schrodinger equation with the boundary conditions $\psi(x) \to Fe^{ikx}$ as $x \to \infty$, and $\psi(x) \to Ae^{ikx} + Be^{-ikx}$ as $x \to -\infty$. Then we can extract the transmission probability via $T = \left(\frac{|F|}{|A|}\right)^2$, and the reflection probability is $R = \left(\frac{|B|}{|A|}\right)^2$. It's a fact that these coefficients satisfy $T + R = 1$, and we're going to find approximations for T and R using the WKB method next time!

17 March 17, 2021 (Recitation)

We'll focus some more on WKB today, particularly understanding how to use it to find quantization conditions for energy levels. Recall that the connection formulas can be used when searching for bound states, and our general strategy is to find the two points $x = a, b$ where $V(x) = E$ (assuming that $V(x) > E$ outside of the region $[a, b]$). Then we need to have exponentially decaying tails to have a normalizable state, and we found in lecture when we had an infinite wall at $x = a$ that we get an expression like

$$\psi(x) = \frac{2A}{\sqrt{k(x)}} \cos\left(\int_x^b k(x')dx' - \frac{\pi}{4}\right)$$

in the classically allowed value, and because we must have $\psi(a) = 0$ we know that the argument of the cosine must take on one of a discrete set of values:

$$\Delta = \int_a^b k(x')dx' - \frac{\pi}{4} = \left(n + \frac{1}{2}\right)\pi,$$

where $n \in \mathbb{Z}_{\geq 0}$. (After all, the integral $\int_a^b k(x')dx'$ is a function of energy, both in its integrand and in the bounds of integration.)

Proposition 68

One useful shift of the integral that we can make here (to change whether we're integrating from a or from b) is

$$\int_x^b k(x')dx' = \int_a^b k(x')dx' - \int_a^x k(x')dx'.$$

With this, we find that the wavefunction ψ is also proportional to $\cos\left(\Delta - \int_a^x dx' k(x')\right)$. Then we can use the cosine difference formula, noting that $\cos\Delta = 0$ when we have a bound state, and thus

$$\psi = \frac{2A}{\sqrt{k(x)}} \sin\Delta \sin\left(\int_a^x dx' k(x')\right) = \pm\frac{2A}{\sqrt{k(x)}} \sin\left(\int_a^x dx' k(x')\right).$$

And this way, it's built into the wavefunction that $\psi(0) = 0$, and also if we have a problem where we care about the nth excited state, we know that excited states will have more and more **nodes** in their wavefunctions. And it turns out that this formula gives us the right number of nodes in the nth excited state, because $\int_a^x dx' k(x')$ crosses multiples π the right number of times!

Proposition 69

We've mentioned before that WKB is a **large-**n approximation formula, and we can understand that by looking at the condition

$$\left|\lambda(x)\frac{dV}{dx}\right| \leq \frac{p^2(x)}{2m}.$$

Here, we can get a rough estimate for p because k and p are very closely related: if p is slowly varying, and we know that the integral is equal to

$$\frac{1}{\hbar}\int_a^b dx' p(x') = \left(n + \frac{3}{4}\right)\pi,$$

then we can estimate that p should be of order $\frac{n\pi\hbar}{b-a}$. And indeed, plugging this back into our condition puts an n^2 term on the right side, and thus we can eventually make our approximation good for a fixed potential $V(x)$.

Example 70

Suppose that we have a double-well potential, where there is a quadratic potential centered at $x = a$ for positive x and also another one centered at $x = -a$ for negative x: this can be encoded as

$$V(x) = \frac{m\omega^2}{2}(|x| - a)^2.$$

Notice that $V(0) = \frac{m\omega^2 a^2}{2}$. We want to think about the case where a is large (relative to the quantum scales), so that our well is deep and also steep. Specifically, we'll take $a \gg L_0 = \sqrt{\frac{\hbar}{m\omega}}$, the length scale for the quantum harmonic oscillator.

We have a parity symmetry here – we can take $x \mapsto -x$ and get the same $V(x)$, and the kinetic energy $\frac{p^2}{2m}$ also stays the same, meaning that the whole Hamiltonian stays the same. In other words, there is a **parity operator** P such that $[H, P] = 0$ and $P|x\rangle = |-x\rangle$. We can thus specify quantum numbers of the P operator simultaneously with energy eigenstates, and thus we will divide up the wavefunctions into even and odd parities: the even states have $\psi_n(x) = \psi_n(-x)$ (parity of $+1$), and the odd states have $\psi_n(x) = -\psi_n(-x)$ (parity of -1). And because we know that the jth excited state has j nodes, we must have the ground state be even, the first excited state be odd, the second excited state be even, and so on. Let's call the ground state ψ_+ and the first excited state ψ_-.

Remark 71. *In particular, it's important what happens at $x = 0$: even states will not have $\psi_+(0) = 0$, but (it turns out) they will have an exponentially small magnitude at 0, and the derivative at 0 will be 0. And the reverse is true for odd states, where $\psi_-(0) = 0$ but $\psi_-'(0) = 0$.*

A good zeroth order approximation for this problem is to say that the well in the middle is very tall, so we can just think about the single-well wavefunctions. If we let $\psi_0(x) = \frac{1}{\sqrt{\pi} L_0} \exp\left(-\frac{x^2}{2L_0^2}\right)$ be the ground-state wavefunction for the simple harmonic oscillator, then we can form even and odd combinations of this: perhaps we have

$$\psi_\pm(x) = \frac{\psi_0(x-a) \pm \psi_0(x+a)}{\sqrt{2}}.$$

If this were true, then the energies of the first and second excited states are the same, so what really causes the energy difference is the potential at $x = 0$. If the ground state and first excited state energies are $E_+ = \overline{E} - \Delta E$ and $E_- = \overline{E} + \Delta E$, it turns out that ΔE is exponentially small for $a \gg L_0$, and that's the quantity we'll be trying to compute right now.

We can show that for general symmetric potentials

$$\Delta E = \frac{\hbar^2}{m}\psi_+(0)\psi_-'(0)$$

(we can see Professor Zwiebach's textbook for this). We'll try doing this with WKB now: suppose that we're looking at some energy E which is smaller than $V(0)$, so that $V(x) = E$ occurs at some points $x = x_1, x_2$ and also $x = -x_1, -x_2$. We'll solve everything for just the positive x case by symmetry.

The regions (1) $x < x_1$ and (3) $x > x_2$ are forbidden, while the region (2) $x_1 < a < x_2$ is allowed. We'll start in the far-away region $x \gg x_2$: WKB tells us that the solution must take on the form

$$\psi_{(3)}(x) = \frac{A}{\sqrt{\kappa(x)}} \exp\left(-\int_{x_2}^{x} dx' \kappa(x')\right),$$

and there is no growing exponential for normalizability reasons. From this, we can infer from the connection formula that we must have a cosine wavefunction in the allowed region

$$\psi_{(2)}(x) = \frac{2A}{\sqrt{k(x)}} \cos\left(\int_x^{x_2} dx' k(x') - \frac{\pi}{4}\right).$$

We also need to do something at the other classical turning point, so we'll use the trick from above to introduce a new variable $\theta = \int_{x_1}^{x_2} dx' k(x')$, so that

$$\psi_{(2)}(x) = \frac{2A}{\sqrt{k(x)}} \cos\left(\theta - \int_{x_1}^{x} dx' k(x') - \frac{\pi}{4}\right) = \frac{2A}{\sqrt{k(x)}} \sin\left(\theta - \int_{x_1}^{x} dx' k(x') + \frac{\pi}{4}\right),$$

and it turns out that it's convenient to split this up with the sine difference formula as

$$= \frac{2A}{\sqrt{k(x)}} \left[\sin\theta \cos\left(\int_{x_1}^{x} dx' k(x') - \frac{\pi}{4}\right) - \cos\theta \sin\left(\int_{x_1}^{x} dx' k(x') - \frac{\pi}{4}\right)\right].$$

And now if we look at region (1), namely the x where $0 \le x \ll x_1$ (so that WKB is valid), it's reasonable to form the linear combinations

$$\psi_{(1)}(x) = \frac{D}{2\sqrt{\kappa(x)}} \left[\exp\left(\int_0^x dx' \kappa(x')\right) \pm \exp\left(-\int_0^x dx' \kappa(x')\right)\right],$$

and writing the integral from 0 to x in terms of the integral from x to a via

$$\frac{\phi}{2} = \int_0^{x_1} dx' \kappa(x') \implies \int_0^x dx' \kappa(x') = \frac{\phi}{2} - \int_x^{x_1} dx' \kappa(x').$$

Then we can plug those in and use the connection formula, and the cheat that we can do in this problem is to **not worry about the arrow**: usually we can only go one way with the connection formula, but here we're allowing ourselves to replace both exponentials with cosines and sines. We find that

$$\psi_{(2)}(x) = \frac{D}{2\sqrt{k(x)}} \left[2e^{\phi/2} \cos\left(\int_{x_1}^{x} dx' k(x') - \frac{\pi}{4}\right) \mp e^{-\phi/2} \sin\left(\int_{x_1}^{x} dx' k(x') - \frac{\pi}{4}\right)\right].$$

And once we've done the connection in both directions, we can compare the two formulas for $\psi_{(2)}$ and match up θs and ϕs: that gives us the desired formula $4A\sin\theta = 2De^{\phi/2}$ and $4A\cos\theta = \pm De^{-\phi/2}$, and the ratio of these tells us that $\tan\theta = \pm 2e^{\phi}$, which is the desired quantization condition. (And in the limit of large ϕ, we basically know to expand around $\theta = \frac{\pi}{2}$ to get the answer – it turns out that $E = \frac{\hbar\omega}{\pi}\theta$, and thus $\Delta E = \frac{\hbar\omega}{\pi}e^{-\phi}$.)

18 March 18, 2021

Last time, we talked about the WKB connection formulas, which allow us to stitch solutions in the classically allowed and forbidden regions together (but only in certain directions). We explored some applications of this method to bound states of potentials, and we'll continue our discussion of tunneling today.

Example 72

Recall that we're assuming that we're considering a system where we have a potential $V(x)$ with peak higher than the particle's energy E, and we're seeing whether a particle can go through it. (We assume that $V(x) \to 0$ as $x \to \pm\infty$.)

We said last time that to find such a tunneling probability, it suffices to solve the time-independent Schrodinger equation with certain **scattering boundary conditions**: we must have $\psi(x) \to Fe^{ikx}$ as $x \to \infty$, and we must have $\psi(x) = Ae^{ikx} + Be^{-ikx}$ as $x \to -\infty$. (Here, A, B, F correspond to the indicent, reflected, and transmitted waves, respectively.) If we can then solve the time-independent Schrodinger equation with energy E, the **transmission probability** (also transmission coefficient) is then $\left|\frac{F}{A}\right|^2$, and the reflection probability is $\left|\frac{B}{A}\right|^2$ (it is a theorem that we will find $T + R = 1$).

Before we apply WKB to this problem, we can notice a few things: if the barrier $V(x)$ is tall and wide, then $T \ll 1$ (the transmission probability is very small). And in this case, we expect that the solution mostly exponentially decays in the classically forbidden region (it would be strange if the wavefunction started to grow).

So now applying WKB, let's call the turning points into and out of the classically forbidden regions $x = a$ and $x = b$ (for $a < b$). We'll work right to left: in the range $x \gg b$, sufficiently far away from the turning point, we'll have

$$\psi(x) = \frac{F}{\sqrt{k(x)}} \exp\left(i \int_b^x k(x')dx' - \frac{i\pi}{4}\right).$$

(The point of the $\frac{i\pi}{4}$ phase is just to make the connection formulas easier later on.) In principle, there should also be a $-i\int_b^x k(x')dx'$ term, but remember that we have a boundary condition where there is only a right-moving wave! And we can to check that our wave is right-moving correctly in this case, because $V(x) \to 0$ as $x \to \infty$, so $k(x) = \frac{\sqrt{2m(E-V(x)}}{\hbar}$ goes to $\frac{\sqrt{2mE}}{\hbar} = k$. Therefore,

$$\int_b^x k(x')dx' \to kx + C$$

for some constant C as $x \to \infty$, and therefore we have

$$\psi(x) = \frac{F}{\sqrt{k}} e^{i(kx+\text{phase})},$$

which is of the desired form (we can incorporate the phase into the amplitude, and it doesn't matter because we care about the magnitude). So now by WKB, we can connect this to the solution in the barrier region $[a, b]$, but first we rewrite the complex exponential as a sum of cosines and sines

$$\psi(x) = \frac{F}{\sqrt{k(x)}} \cos\left(\int_b^x k(x')dx' - \frac{\pi}{4}\right) + \frac{iF}{\sqrt{k(x)}} \sin\left(\int_b^x k(x')dx' - \frac{\pi}{4}\right),$$

and the connection formulas (for a downward-sloping potential) tell us that a cosine becomes a decaying exponential (with a factor of $\frac{1}{2}$), and a sine becomes a growing exponential (with a factor of -1). If we apply those formulas blindly, we find that in the range $a \ll x \ll b$ (sufficiently far away from the turning points), we have

$$\psi(x) \approx \frac{F}{2\sqrt{\kappa(x)}} \exp\left(-\int_x^b \kappa(x')dx'\right) - \frac{iF}{\sqrt{\kappa(x)}} \exp\left(\int_x^b \kappa(x')dx'\right).$$

But now we can talk about the arrows and ask whether we are justified in keeping both pieces here. Notice that as x gets sufficiently far away from the classical turning point b, the growing exponential will overwhelm the decaying exponential (so the first term is much smaller than the second).

So it makes sense to just drop the first term, and that's indeed what the connection formula tells us: we can legitimately keep the growing exponential when we apply the connection formula in this direction, but not the decaying exponential. (If we kept the first term, we wouldn't get into real trouble, but we would be claiming higher accuracy than we actually have.) That means we just have the second term

$$\psi(x) \approx -\frac{iF}{\sqrt{\kappa(x)}} \exp\left(\int_x^b \kappa(x')dx'\right)$$

in the range $a \ll x \ll b$, and now if we use the connection formulas for an upward-sloping potential, we need our integral to be based at a instead of b. So we'll rewrite

$$\int_x^b \kappa(x')dx' = \int_a^b \kappa(x')dx' - \int_a^x \kappa(x')dx',$$

and the first term on the right-hand side is just some constant θ, so we can rewrite (still working in the $a \ll x \ll b$ region under the barrier)

$$\psi(x) \approx -\frac{iF}{\sqrt{\kappa(x)}} e^{\theta} \exp\left(-\int_a^x \kappa(x')dx'\right).$$

And indeed, this is what we expected at the beginning – there is mostly a decaying piece under the barrier as x increases from a to b. So this allows us to apply the connection formulas now: for an upward-sloping potential, a decaying exponential becomes twice a cosine, and the arrow points in the right direction (and a negative sine becomes a growing exponential, but we don't need that). So that tells us that in the classically allowed region $x \ll a$, we have

$$\psi(x) = -\frac{2iFe^{\theta}}{\sqrt{k(x)}} \cos\left(\int_x^a k(x')dx' - \frac{\pi}{4}\right),$$

which we can write in terms of an oscillating exponential as

$$= -\frac{iFe^{\theta}}{\sqrt{k(x)}}\left(\exp\left(i\int_x^a k(x')dx' - \frac{i\pi}{4}\right) + \exp\left(-i\int_x^a k(x')dx' + \frac{i\pi}{4}\right)\right).$$

Since we care about the coefficients of the right-moving and left-moving wave, we can take $x \to -\infty$ here, and because $k(x)$ again goes to the same $k = \frac{\sqrt{2mE}}{\hbar}$, we have again

$$\int_x^a k(x')dx \to -kx + C'$$

for some other constant C'. And thus the form of our solution for $x \to -\infty$ is

$$\psi(x) \approx -\frac{iFe^{\theta}}{\sqrt{k}}\left(e^{-i(kx+\text{phase})} + e^{i(kx-\text{phase})}\right),$$

and this gives us the desired form with the incident and reflected waves. We've now found an approximate solution, and if we read off the transmission coefficients, we find that the transmitted wave has amplitude $\frac{F}{\sqrt{k}}$, and the incident wave has amplitude $\frac{Fe^{\theta}}{\sqrt{k}}$, so

$$T_{\text{WKB}} = \left|\frac{F/\sqrt{k}}{Fe^{\theta}/\sqrt{k}}\right|^2 = e^{-2\theta},$$

or writing out the expression more explicitly,

$$\boxed{T_{\text{WKB}} = \exp\left(-2\int_a^b dx'\kappa(x')\right)}.$$

But notice that to the accuracy we're working with, the incident and reflected waves have the same magnitude, so $\boxed{R_{\text{WKB}} = 1}$. And because we want $R^2 + T^2 = 1$, this approximation is only valid when $T \ll 1$, and this happens indeed when we have a tall and wide barrier.

Fact 73

There are corrections (in principle) that come in the prefactor of the exponential, so the accuracy we have here is only in the exponent $-2\int_a^b dx'\kappa(x')$.

And notice that if we had blindly applied WKB without dropping the first exponential term, we would find that

$$T = \frac{e^{-2\theta}}{\left(1 + \frac{1}{4}e^{-2\theta}\right)^2}.$$

So as we said above, this isn't a huge change to the answer, but we would just be claiming higher accuracy than we actually have (since we really don't even know the prefactor at all).

Remark 74. *If we had a different k on the left and right, we would need to be more careful and define the transmission probability in terms of the flux or probability current instead of just the relative amplitudes, which depends on $\psi^* \nabla \psi$ (so it'll bring down a factor of k).*

Although we've computed the transmission or tunneling **probability** here, we're often more interested in the **tunneling rate**:

Example 75

Suppose we have a potential with a local (but not global) minimum, and we start with a particle localized inside that minimum. This is not a stationary or bound state, and the particle will eventually leak out – we are interested in how long it takes for this to happen.

We'll solve this with a combination of classical and quantum thinking, starting by imagining the particle inside the well as rattling back and forth with some energy E. Then every time it "hits the right wall," it has a probability of escaping through the barrier, and we'll use the WKB approximation for that number.

If we need to tunnel through a potential with turning points $x = a, b$, we know that the tunneling probability is $T = \exp\left(-2\int_a^b dx' \kappa(x')\right)$, and now we need to estimate how often it hits that wall. In the classical treatment, the time it takes to travel between turning points $x = c, a$ in the local minimum (that is, the time between escape attempts) is

$$\Delta t = 2\int_c^a \frac{dx}{v(x)} = 2m \int_c^a \frac{dx}{p(x)}$$

(because the particle needs to go from a to c, and then back to a). If we then let $P(t)$ be the probability that at time t, the particle is inside our local minimum well, we know that $P(0) = 1$, and we know that

$$P(t + \Delta t) - P(t) = -TP(t)$$

(there's an escape probability of T, as long as the particle is still in the well at time t). And if Δt is small enough, we can rewrite this equation as

$$\Delta t \frac{dP}{dt} = -TP(t) \implies \frac{dP}{dt} = -\frac{1}{\tau}P(t),$$

where $\tau = \frac{\Delta t}{T}$. We then find that we get the exponential decay

$$P(t) = e^{-t/\tau}$$

with the **lifetime** $\tau = \frac{\Delta t}{T}$ and **decay rate** $\frac{1}{\tau}$.

Remark 76. *Remember that we only know T to exponential accuracy – the calculation doesn't determine the prefactor. So the factor of 2 in the classical estimate for Δt really doesn't hold up, and we just have an order-of-magnitude estimate. But (as we discussed in recitation) applying this to Gamow's theory of α-decay of nuclei holds up well to experimental observations!*

Fact 77

If we want to think about the actual dynamics of tunneling, we have to solve the **time-dependent** Schrodinger equation, send in a wave packet, and understand how that evolves over time. That will give us, at large time, two wave packets moving to the left and right.

We'll now move on to our next topic – **motion of charged particles in electromagnetic fields**. The idea is that we'll be able to address how quantum particles move in electromagnetic fields, but we'll encounter the **gauge principle** along the way.

Example 78

Suppose that we have a particle of mass m and charge q moving in some electric field $\vec{E}(\vec{x}, t)$ and magnetic field $\vec{B}(\vec{x}, t)$.

First, let's treat the particle classically (we'll be treating the fields classically throughout). Then we know that the Lorentz force equation looks like

$$m\frac{d^2\vec{x}}{dt^2} = \vec{F}_{\text{Lorentz}} = q\vec{E}(\vec{x}, t) + \frac{q\vec{v}}{c} \times \vec{B}(\vec{x}, t),$$

and we want to now incorporate a quantum treatment of our particle and write down a Schrodinger equation. And the interesting thing is that quantum mechanically, we need to work with gauge potentials instead of the fields directly. Recall that the gauge potentials Φ and $\vec{A}$ are defined as follows: because $\vec{\nabla} \cdot \vec{B} = 0$, we can write (at least locally) $\boxed{\vec{B} = \vec{\nabla} \times \vec{A}}$ for some vector potential $\vec{A}$, and because $\vec{\nabla} \times \vec{E} = -\frac{1}{c}\frac{\partial \vec{B}}{\partial t}$, we have

$$\vec{\nabla} \times \left(\vec{E} + \frac{1}{c}\frac{\partial \vec{A}}{\partial t}\right) = 0,$$

and if the curl of something is zero, we can (at least locally) write

$$\vec{E} + \frac{1}{c}\frac{\partial \vec{A}}{\partial t} = -\nabla\Phi$$

for the scalar potential Φ, and thus $\boxed{\vec{E} = -\nabla\Phi - \frac{1}{c}\frac{\partial \vec{A}}{\partial t}}$.

Proposition 79

There are certain freedoms in how we pick Φ and $\vec{A}$, and these lead to the **gauge transformations**.

Notice that if we change

$$\vec{A'} = \vec{A} + \nabla\Lambda$$

(which doesn't change $\vec{B}$, because curl of gradient is zero), and we change

$$\Phi' = \Phi - \frac{1}{c}\frac{\partial \Lambda}{\partial t}$$

(which doesn't change $\vec{E}$ because the two contributions cancel out), we find that

$$\vec{E}(\vec{A'}, \Phi') = \vec{E}(\vec{A}, \Phi), \quad \vec{B}(\vec{A'}, \Phi') = \vec{B}(\vec{A}, \Phi)$$

(the transformed potentials and original transforms give us the same electric and magnetic field). So $(\Phi, \vec{A})$ should really be considered equivalent to $(\Phi', \vec{A}')$, and these gauge transformations endow the space of gauge potentials with an equivalence relation – an electromagnetic field is just an equivalence class under this relation.

Fact 80

It turns out that there are $(\phi, \vec{A})$ and $(\Phi', \vec{A}')$ that give the same electromagnetic fields, but aren't related by a gauge transformation.

So even though they look the same classically, they are different quantum mechanically (because they are in different equivalence classes!), and thus they will be treated as different electromagnetic configurations. In fact, we will see that there are **actual physical differences** in how the quantum particle is affected, and we can see this through the Aharonov-Bohm effect. These differences do not arise in infinite Minkowski space $\mathbb{R}^3 \times \mathbb{R}_t$, but they do arise if we have a nontrivial topology on the space (for example, particles confined to move on a ring).

Fact 81

It also turns out that there are electric and magnetic fields $\vec{E}, \vec{B}$ that satisfy Maxwell's equations but cannot be written in terms of the gauge potentials $\vec{A}$ and Φ.

Since the gauge potentials are the fundamental objects, those electromagnetic fields are actually illegal – those $\vec{E}, \vec{B}$ configurations won't be allowed in the quantum particle case. (And again, this only occurs on spaces with nontrivial topology – we'll see this in the case of a magnetic field on a torus.)

We're now ready to introduce the modified Schrodinger equation in the case of an electromagnetic potential: in free space, we have

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

where originally we have $H = \frac{p^2}{2m}$. To introduce Φ, we know that a particle has potential energy $q\Phi$ in a scalar potential, so we can replace $H \to H + q\Phi$ easily (for example, that's what we did for the $-\frac{e^2}{r}$ term in the hydrogen Hamiltonian). But $\vec{A}$ is more complicated: it turns out that we need to replace the momentum operator as

$$\vec{p} \to \vec{p} - \frac{q}{c}\vec{A}(\vec{x}, t).$$

This is called the **minimal coupling**, and it gives us the full Hamiltonian

$$H = \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A}(\vec{x}, t)\right)^2 + q\Phi.$$

This is already the form of the Hamiltonian in classical mechanics, but we'll also understand later on why this form makes a lot of sense – we'll in fact be able to derive the quantum analog of the Lorentz force law starting from this Hamiltonian.

Now that we're in the quantum world, we should replace $\vec{x}$ with the x operator, and thus $\vec{A}$ is also a quantum operator just like $\vec{p}$. And in the position-space representation, $\vec{A}$ acts by multiplication, but it can act more nontrivially in other representations. But the momentum operator p still satisfies $[\hat{p}_i, \hat{x}_j] = -i\hbar\delta_{ij}$, and we still have $\vec{p} = -i\hbar\vec{\nabla}$ in position space. So in other words, we can write the representation of H in position space as

$$H = \frac{1}{2m}\left(-i\hbar\vec{\nabla} - \frac{q}{c}\vec{A}(\vec{x}, t)\right)^2 + q\Phi(\vec{x}, t).$$

But it turns out the physical velocity now changes to

$$m\vec{v} = \vec{p} - \frac{q}{c}\vec{A},$$

so that the kinetic energy of the particle is still $\frac{1}{2}mv^2$, and we'll understand this a little more later on as well.

We can try to expand this square out and write (using repeated index notation)

$$H = \frac{1}{2m}\left(p_i - \frac{q}{c}A_i\right)\left(p_i - \frac{q}{c}A_i\right) + q\Phi = \frac{1}{2m}(p_i p_i - \frac{q}{c}A_i p_i - \frac{q}{c}p_i A_i + \frac{q^2}{c^2}A_i A_i) + q\Phi,$$

which can be rewritten as

$$= \frac{\vec{p}^2}{2m} - \frac{q}{2mc}\left(\vec{A}\cdot\vec{p} + \vec{p}\cdot\vec{A}\right) + \frac{q^2}{2mc^2}\vec{A}^2 + q\Phi.$$

(Remember that $\vec{A}$ and $\vec{p}$ do not commute, because $\vec{A}$ depends on $\vec{x}$.) We could then write

$$\vec{p}\cdot\vec{A} = p_i A_i = A_i p_i + [p_i, A_i(\vec{x}, t)] = A_i p_i - i\hbar\partial_i A_i = \vec{A}\cdot\vec{p} - i\hbar\vec{\nabla}\cdot\vec{A},$$

so substituting back in gives us

$$H = \frac{\vec{p}^2}{2m} - \frac{q}{mc}\vec{A}\cdot\vec{p} + \frac{iq\hbar}{2mc}\vec{\nabla}\cdot\vec{A} + \frac{q^2}{2mc^2}\vec{A}^2 + q\Phi.$$

So now we should have a feeling for how these kinds of calculations go, and the next issue we want to discuss is that of gauge-invariance – how does it manifest in the Schrodinger equation? Going back to the Schrodinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \left(\frac{1}{2m}\left(-i\hbar\vec{\nabla} - \frac{q}{c}\vec{A}(\vec{x}, t)\right)^2 + q\Phi(\vec{x}, t)\right)\psi,$$

if we replace the potentials with some gauge-transformed ones, we find that

$$i\hbar\frac{\partial\psi'}{\partial t} = \left(\frac{1}{2m}\left(-i\hbar\vec{\nabla} - \frac{q}{c}\vec{A}'(\vec{x}, t)\right)^2 + q\Phi'(\vec{x}, t)\right)\psi',$$

and we want to see whether a solution ψ to the original Schrodinger equation also solves the gauge-transformed Schrodinger equation. The answer turns out to be **no**, but there is a simple relation between the ψ and ψ', namely

$$\psi'(\vec{x}, t) = \exp\left(\frac{iq\Lambda(\vec{x}, t)}{\hbar c}\right)\psi(\vec{x}, t).$$

So we add a position- and time-dependent phase to ψ, but the amplitude does not change. We'll discuss the implications and derivation of this next time!

19 March 24, 2021 (Recitation)

Last lecture, we transitioned from WKB and tunneling to talking about quantum mechanics in the presence of electromagnetic fields (which comes up in the form of a vector and scalar potential in the Hamiltonian). We'll try to cover a little bit of each topic today.

Example 82

Consider the tunneling problem for a finite square barrier, meaning that

$$V(x) = \begin{cases} V_0 & 0 \le x \le a \\ 0 & \text{otherwise.} \end{cases}$$

If we send in a plane wave of energy E (where $0 < E < V_0$), then we can treat this problem with the WKB approximation, and the tunneling probability $T = e^{-2\theta}$ (as we derived in lecture) is only accurate if

$$\theta = \frac{1}{\hbar}\int_0^a dx \sqrt{2m(V_0 - E)}$$

is large. But we can evaluate this easily because the integral is a constant, so $\theta = \frac{a}{\hbar}\sqrt{2m(V_0 - E)}$, and thus this approximation is indeed accurate if a is large (wide barrier) and $V_0 - E$ is large (high barrier).

And we can actually solve this problem exactly without the need for WKB here! The idea is to solve the Schrodinger equation in each region whee the potential is constant: the solution is exponential or oscillatory in each region, so that (letting $k = \frac{1}{\hbar}\sqrt{2mE}$ and $\kappa = \frac{1}{\hbar}\sqrt{2m(V_0 - E)}$)

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{\kappa x} + De^{-\kappa x} & 0 < x < a \\ Fe^{ikx} & x > a \end{cases}$$

(we're only using an outgoing wave in the right region $x > a$, because we're treating this as a scattering problem like in lecture). And now we need to equate the coefficients A, B, C, D, F by using continuity of ψ and its derivative ψ' at $x = 0$ and $x = a$: those four conditions give us relative ratios of the five coefficients, and it turns out in particular that

$$\boxed{T = \left|\frac{F}{A}\right|^2 = \frac{1}{1 + \frac{V_0^2}{4E(V_0 - E)}\sinh^2(\theta)}}.$$

In the limit where θ is large, we have $\sinh\theta \approx \frac{e^\theta}{2}$, so plugging in $\frac{e^{2\theta}}{4}$ allows us to drop the 1 in the denominator and find $T = \frac{16E(V_0 - E)}{V_0^2}e^{-2\theta} + \cdots$. So the WKB solution does indeed emerge in the appropriate limit (with a more specific $O(1)$ prefactor).

Remark 83. *Any potential barriers that are piecewise constant are easy to do with the WKB approximation as well, because the integrand will also be piecewise constant. So we can try that ourselves if we want!*

Recall that we used the example of positronium a few recitations ago, and we mentioned that there was a lifetime for positronium because of potential decay to photons. And we can in fact connect this phenomenon to the probability to remain trapped inside a well, which takes the form $P(t) = e^{-t/\tau}$ for some lifetime $\tau = \frac{\Delta t}{T}$ (where Δt is the classical time spent between tunneling attempts, and T is the WKB transmission coefficient). Positronium was different because it doesn't have a physical potential in space, but the formula $P(t)$ applies again because we have one quantum state (positronium) which decays to a very different quantum state (photons). And it turns out that if we think about the probability by integrating the wavefunction for positronium over all space, we have

$$P(t) = \int dx\, |\psi_{e^+e^-}(x, t)|^2$$

instead of the usual 1. Basically, what's happening is that our photons $\gamma\gamma$ and $\gamma\gamma\gamma$ are left out of our Hilbert space, so we're losing some probability because of decay transitioning us out of the space. The idea is that probability conservation is connected with the unitary time evolution operator $U(t, t_0)$, because the Hamiltonian H is Hermitian.

Example 84

Let's think about some non-Hermitian effects: we replace our potential $V(x)$ with the potential $V(x) - \frac{i\Gamma}{2}$ (which is no longer Hermitian).

Then our Schrodinger equation becomes

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi - i\frac{\Gamma}{2}\psi,$$

and we want to understand how this affects the probabilities. Normally we have $\frac{\partial}{\partial t}\rho + \vec{\nabla}\cdot\vec{J} = 0$ (current conservation), but now that we added this $i\frac{\gamma}{2}$ term, we have

$$\frac{\partial\rho}{\partial t} = \frac{\partial}{\partial t}(\psi^*\psi) = \psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t},$$

and plugging in the Schrodinger equation and its conjugate via

$$\frac{\partial\psi}{\partial t} = \frac{i\hbar}{2m}\nabla^2\psi - \frac{i}{\hbar}V\psi - \frac{\Gamma}{2\hbar}\psi, \quad \frac{\partial\psi^*}{\partial t} = -\frac{i\hbar}{2m}\nabla^2\psi^* + \frac{i}{\hbar}V\psi^* - \frac{\Gamma}{2\hbar}\psi^*$$

yields an equation of

$$\boxed{\frac{\partial\rho}{\partial t}\frac{i\hbar}{2m}\left(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right) - \frac{\Gamma}{\hbar}\rho}$$

(the V terms cancel out because they have an i, but the Γ terms don't because they are real). And now this first term is usually $-\vec{\nabla}\cdot\vec{J}$, where we have the probability current

$$\vec{J} = \frac{\hbar}{m}\text{Im}(\psi^*\nabla\psi) = \frac{\hbar}{m}\frac{1}{2i}(\psi^*\nabla\psi - \psi\nabla\psi^*),$$

and we can confirm that taking another derivative of this gives us back the $\psi^*\nabla^2\psi - \psi\nabla^2\psi^*$ above. And yet another way to write this expression is

$$= \frac{1}{m}\text{Re}(\psi^*\hat{p}\psi),$$

because $\text{Im}(z) = \text{Re}(-iz)$. But returning to the extra term in the boxed equation above, we know that

$$\frac{d}{dt}P(t) = \frac{\partial}{\partial t}\int dx\rho(x, t),$$

and then we can push the partial derivative inside the integral and substitute in what we know to get

$$= \int dx\frac{\partial\rho}{\partial t} = -\int d^3x\vec{\nabla}\cdot\vec{J} - \frac{\Gamma}{\hbar}\int dx\rho.$$

And because we're assuming there's no flow of current at ∞, the first integral is just zero (here we're using the divergence theorem), and thus the equation simplifies to

$$\frac{d}{dt}P(t) = 0 - \frac{\Gamma}{\hbar}P(t).$$

So originally we had $\frac{dP}{dt} = 0$, and now we have the exponential decay differential equation, as expected! So indeed we get the probability $P(t) = P_0e^{-t/\tau}$, where $\tau = \frac{\hbar}{\Gamma}$.

Example 85

In the remaining time, we'll start talking about the Schrodinger equation and adding in the potentials $\Phi(\vec{x}, t)$ and $\vec{A}(\vec{x}, t)$.

Recall that we can recover the electric and magnetic fields via $\vec{E} = -\nabla\Phi - \frac{1}{c}\frac{\partial \vec{A}}{\partial t}$ and $\vec{B} = \vec{\nabla} \times \vec{A}$, and we found that the updated Hamiltonian for a charged particle of charge q is

$$\hat{H} = \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A}(x, t)\right)^2 + q\Phi(\hat{q}, t).$$

If we treat x, p as the classical position and momentum, we get back the Lorentz force equations, so this is a valid classical Hamiltonian (like we may have seen in 8.223). And now if we **canonically quantize** this by turning x and p into operators, that's a valid description of how to get to this quantum Hamiltonian. We expanded out the Hamiltonian in lecture and found that

$$\hat{H} = \frac{\vec{p}^2}{2m} - \frac{q}{mc}\vec{A} \cdot \vec{p} - \frac{q}{2mc}[p^i, A^i] + \frac{q^2}{2mc^2}\vec{A}^2 + q\Phi,$$

remembering that the order of the $\vec{A}$ and $\vec{p}$ operators matter. We can then write this Hamiltonian in a position basis to find

$$= -\frac{\hbar^2}{2m}\nabla^2 + \frac{iq\hbar}{mc}\vec{A} \cdot \vec{\nabla} + \frac{i\hbar q}{2mc}(\vec{\nabla} \cdot \vec{A}) + \frac{q^2}{2mc^2}\vec{A}^2 + q\Phi,$$

where we've replaced $\vec{p}$ by $-i\hbar\vec{\nabla}$. So we have our usual V potential term, and we have a modified kinetic energy term where it's useful to define a modified **velocity** via

$$m\vec{v} = \vec{p} - \frac{q}{c}\vec{A}$$

(it'll turn out that in this setup, the velocity is more fundamental than the momentum). And we'll close by talking a little about probability current: the probability density is still $\rho = |\psi(x, t)|^2$, and we still have the same equation $\frac{\partial}{\partial t}\rho + \vec{\nabla} \cdot \vec{J} = 0$, but this time the form of $\vec{J}$ is a bit different: doing the same product rule calculation $\frac{\partial(\psi^*\psi)}{\partial t}$ as above gives us

$$\frac{\partial \psi}{\partial t} = \frac{i\hbar}{2m}\nabla^2\psi + \frac{q}{mc}\vec{A} \cdot \vec{\nabla}\psi + \frac{q}{2mc}(\vec{\nabla} \cdot \vec{A})\psi - \frac{i}{\hbar}\left(\frac{q^2\vec{A}^2}{2mc^2} + q\Phi\right)\psi,$$

and the similar equation

$$\frac{\partial \psi^*}{\partial t} = -\frac{i\hbar}{2m}\nabla^2\psi^* + \frac{q}{mc}\vec{A} \cdot \vec{\nabla}\psi^* + \frac{q}{2mc}(\vec{\nabla} \cdot \vec{A})\psi^* + \frac{i}{\hbar}\left(\frac{q^2\vec{A}^2}{2mc^2} + q\Phi\right)\psi^*.$$

Adding together $\psi^*\frac{\partial \psi}{\partial t} + \psi\frac{\partial \psi^*}{\partial t}$ again gives us a few terms that don't cancel: we end up finding that (after some simplification)

$$\frac{\partial \rho}{\partial t} = \frac{i\hbar}{2m}\left(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right) + \frac{q}{mc}\vec{\nabla}(\vec{A}\psi^*\psi) = -\vec{\nabla} \cdot \vec{J}$$

So our new probability current is

$$\boxed{\vec{J} = \mathrm{Re}\left(\psi^*\vec{v}\psi\right)},$$

where $\vec{v} = \frac{\vec{p}}{m} - \frac{q\vec{A}}{mc}$ (possibly as we might expect from our definition of the modified velocity above)!

20 March 25, 2021

Last time, we started discussing motion in an electromagnetic field: we mentioned that we need to specify the vector potential $\vec{A}$ and the scalar potential Φ, and they enter the Hamiltonian in the manner

$$H = \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2 + q\Phi.$$

(Here, $\vec{A}$ and Φ are both functions of space and time.) We mentioned the principle of **gauge-invariance** last time: configurations of $\vec{E}$ and $\vec{B}$ correspond to choices of the potential, modulo certain **gauge transformations**. Specifically, we have the following:

Proposition 86

If ψ solves the Schrodinger equation, and then we do a gauge transformation

$$\vec{A'} = \vec{A} + \nabla\Lambda, \Phi' = \Phi - \frac{1}{c}\frac{\partial\Lambda}{\partial t},$$

then $\psi' = \exp\left(\frac{iq\Lambda}{\hbar c}\right)\psi$ (where this phase term does depend on space and time because Λ is a function of $\vec{x}$ and t) will solve the new Schrodinger equation.

We will denote $U(\vec{x}, t) = \exp\left(\frac{iq\Lambda}{\hbar c}\right)$ for convenience. Before we prove this result, we can do a quick intermediate calculation:

Lemma 87

We have the relation (for any wavefunction ψ)

$$\left(-i\hbar\vec{\nabla} - \frac{q}{c}\vec{A'}\right)U\psi = U\left(-i\hbar\vec{\nabla} - \frac{q}{c}\vec{A}\right)\psi.$$

Proof. The left-hand side can be written by the product rule as

$$-i\hbar(\vec{\nabla}U)\psi - i\hbar U(\vec{\nabla}\psi) - \frac{q}{c}U\vec{A}\psi - \frac{q}{c}U\vec{\nabla}\Lambda\psi$$

(remember that $\vec{A}$ and U are both just functions of $\vec{x}$ and t, so they can commute past each other). Since U is an exponential term, we can simplify this as

$$-i\hbar\frac{iq}{\hbar c}\nabla\Lambda U\psi + U\left(-i\hbar\vec{\nabla}\frac{q}{c}\vec{A}\right)\psi - \frac{q}{c}U\vec{\nabla}\Lambda\psi.$$

And in fact, the first and last terms here are actually the same, and we get the expression on the right-hand side, as desired. ☐

Proof of Proposition 86. Suppose that ψ' satisfies the Schrodinger equation

$$i\hbar\frac{\partial\psi'}{\partial t} = \frac{1}{2m}\left(-i\hbar\vec{\nabla} - \frac{q}{c}\vec{A'}\right)^2\psi' + q\Phi'\psi'.$$

Our goal is to show that ψ satisfies the Schrodinger equation with $\vec{A}$ and Φ. Because $\psi' = U\psi$, we can simplify our equation a bit to

$$i\hbar\frac{\partial}{\partial t}(U\psi) = \frac{1}{2m}\left(-i\hbar\vec{\nabla} - \frac{q}{c}\vec{A'}\right)^2 U\psi + q\left(\Phi - \frac{1}{c}\frac{\partial\Lambda}{\partial t}\right)U\psi.$$

Simplifying this by the product rule, we find that

$$i\hbar \frac{iq}{\hbar c}\frac{\partial \Lambda}{\partial t} U\psi + i\hbar U \frac{\partial \psi}{\partial t} = \frac{1}{2m} U \left(-i\hbar\vec{\nabla} - \frac{q}{c}\vec{A}\right)^2 \psi + qU\left(\Phi - \frac{1}{c}\frac{\partial \Lambda}{\partial t}\right)\psi.$$

where we've used Lemma 87 twice on the right-hand side to move U past both copies of $\left(-i\hbar\partial_i - \frac{q}{c}A_i'\right)$, turning both $\vec{A}'$s into $\vec{A}$s, and we've also used that U commutes past $\left(\Phi - \frac{1}{c}\frac{\partial \Lambda}{\partial t}\right)$ on the right-hand side. But now the first term on the left-hand side cancels with the last term on the right-hand side, and we end up with

$$i\hbar U\frac{\partial \psi}{\partial t} = \frac{1}{2m} U \left(-i\hbar\vec{\nabla} - \frac{q}{c}\vec{A}\right)^2 \psi + qU\Phi\psi,$$

which is the desired equation by multiplying by U^{-1} on the left, since U is a unitary operator. □

So now that we understand how our wavefunction changes under a gauge transformation $\psi' = U\psi$, we can ask **how the physics depends on the choice of gauge**. First of all, the probability density $\rho(\vec{x}, t) = |\psi(\vec{x}, t)|^2$ is definitely gauge-invariant, because the phase does not contribute to the magnitude. But we may also want to check other physical observables, like the position, and that motivates the following definition:

Definition 88

An observable $O[\vec{A}, \Phi]$ is a **gauge-covariant observable** if O is Hermitian (meaning $O^\dagger = O$), and

$$O' = O[\vec{A}', \Phi'] = UO[\vec{A}, \Phi]U^{-1}.$$

(Here, we're thinking of U and O as operators, and the right-hand side expression is a conjugation operation.) What's important is that **all physical observables in quantum mechanics are gauge-covariant** – this is a postulate that we're working with. And what this gauge covariance guarantees is that the outcome of the measurement will not depend on the gauge, because the eigenvalues (possible values of measurements) of conjugate operators $O' = UOU^{-1}$ and O are the same. To see this, notice that if $|\chi\rangle$ is an eigenvector of O, meaning that

$$O|\chi\rangle = \lambda|\chi\rangle,$$

then $U|\chi\rangle$ will be an eigenvector of O':

$$O'U|\chi\rangle = UOU^{-1}U|\chi\rangle = UO|\chi\rangle = U\lambda|\chi\rangle = \lambda U|\chi\rangle.$$

So the set of predictions will be the same, and the expectation value transforms as

$$\langle\psi|O|\psi\rangle \to \langle\psi'|O'|\psi'\rangle$$

(under a gauge transformation, both the operator and the wavefunction transform). And indeed,

$$\langle\psi'|O'|\psi'\rangle = \left\langle U\psi\middle|UOU^{-1}\middle|U\psi\right\rangle = \left\langle\psi\middle|U^\dagger UOU^{-1}U\middle|\psi\right\rangle = \langle\psi|O|\psi\rangle$$

because U is a unitary operator.

Example 89

The operator $\vec{x}$ is gauge-covariant. To show this, notice that $\vec{x}$ doesn't depend on $\vec{A}$ and Φ explicitly, so $\vec{x}'$ is just $\vec{x}$, and then

$$U\vec{x}U^{-1} = \vec{x}UU^{-1} = \vec{x} = \vec{x}',$$

since U is a function of $\vec{x}$ (and thus commutes with $\vec{x}$).

Example 90

The quantity $O = \vec{p} - \frac{q}{c}\vec{A}$ (which enters in the Hamiltonian) is also gauge-covariant, because $O' = \vec{p} - \frac{q}{c}\vec{A}'$ (replacing $\vec{A}$ with $\vec{A}'$), and then

$$O' = \vec{p} - \frac{q}{c}\vec{A}' \overset{?}{=} U\left(\vec{p} - \frac{q}{c}\vec{A}\right)U^{-1} = UOU^{-1}$$

is true, because after multiplying by U on the right-hand side, this identity is just Lemma 87.

We mentioned that we expect that the combination $m\vec{v} = \vec{p} - \frac{q}{c}\vec{A}$ should be the physical observable, so this fact should be reassuring to us.

Example 91

The canonical momentum operator $\vec{p}$ is **not** gauge covariant, because $\vec{A}$ does transform under gauge transformations, but the combination $\vec{p} - \frac{q}{c}\vec{A}'$ is gauge covariant.

Proposition 92

Sums of gauge covariant operators are also gauge covariant, and products of gauge covariant operators are gauge covariant if we don't require the Hermiticity assumption.

(We should try checking these facts from the definition on our own.)

Remark 93. *We're being very pedantic here about "gauge-covariant observables" and the outcome of the measurements being "gauge-invariant." Outside of this class, though, we may hear the observables as just being called gauge-invariant.*

And now that we have more justification for the velocity $\vec{v}$, we'll talk more about the Lorentz force law. Recall that **classically**, we just define $\vec{v} = \dot{\vec{x}}$ and $\vec{F} = m\ddot{\vec{x}}$, and we also know that $\vec{F} = q\vec{E}(\vec{x}, t) + q\frac{\vec{v}}{c} \times \vec{B}(\vec{x}, t)$. If we want a quantum analog for this, the analog to classical equations of motion are the **Heisenberg equations of motion** from 8.05: instead of thinking of the wavefunction time-evolving as

$$|\psi(t)\rangle = U(t)\,|\psi(0)\rangle\,,$$

where $U(t)$ is **not** the same gauge transform U that we've been talking about so far, and then we calculate expectations of observables via

$$\langle A\rangle(t) = \langle\psi(t)|A|\psi(t)\rangle\,.$$

But we can rewrite this expression as

$$= \left\langle\psi(0)\middle|U^\dagger(t)AU(t)\middle|\psi(0)\right\rangle,$$

and thus the combination $U^\dagger(t)AU(t)$ is defined as the **Heisenberg operator** $A_H(t)$ (so that the operator evolves, rather than the wavefunction). We then get the equation of motion

$$\boxed{\frac{dA_H}{dt} = \frac{i}{\hbar}[H_H(t), A_H(t)] + \left(\frac{\partial A_s}{\partial t}\right)_H}.$$

And notably, if our Schrodinger Hamiltonian $H = H_S$ is a function of $\vec{p}, \vec{x}$, and t, then the Heisenberg Hamiltonian is

$$H_H = H(\vec{p}_H, \vec{x}_H, t),$$

and we have the commutators (for any fixed time t)

$$\left[x_H^i(t), p_H^j(t)\right] = i\hbar\delta_{ij}.$$

If we now apply this formalism to our Hamiltonian for a charged particle in an electromagnetic field $H = \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2 + q\Phi$, we can think about how the individual components here transform: we have

$$\frac{dx_H^i}{dt} = \frac{i}{\hbar}[H_H(t), x_H(t)] = \frac{i}{\hbar}\left[\frac{1}{2m}\left(\vec{p}_H - \frac{q}{c}\vec{A}(\vec{x}_H, t)\right)^2 + q\Phi(\vec{x}_H, t), x_H^i\right]$$

(where we've replaced the positions and momenta in H with their Heisenberg equivalents). The second term $q\Phi(\vec{x}_H, t)$ commutes with x_H^i, and we'll rewrite the other term in Einstein notation (summing over j):

$$= \frac{i}{\hbar}\left[\frac{1}{2m}\left(p_H^j - \frac{q}{c}A^j(\vec{x}_H, t)\right)\left(p_H^j - \frac{q}{c}A^j(\vec{x}_H, t)\right), x_H^i\right].$$

We can now use the commutation relation $[BC, D] = B[C, D] + [B, D]C$ (we can check this ourselves) to find that this expression is equal to

$$= \frac{i}{\hbar}\frac{1}{2m}\left(\left(p_H^j - \frac{q}{c}A^j(\vec{x}_H, t)\right)\left[\left(p_H^j - \frac{q}{c}A^j(\vec{x}_H, t)\right), x_H^i\right] + \left[\left(p_H^j - \frac{q}{c}A^j(\vec{x}_H, t)\right), x_H^i\right]\left(p_H^j - \frac{q}{c}A^j(\vec{x}_H, t)\right)\right).$$

But now the commutators just evaluate to $-i\hbar\delta_{ij}$, because the A^j term commutes with x_H^i. So our final expression is

$$= \frac{1}{2m}\left(2\delta_{ij}\left(p_H^j - \frac{q}{c}A^j(\vec{x}_H, t)\right)\right) = \frac{1}{m}\left(p_H^i - \frac{q}{c}A^i(\vec{x}_H, t)\right).$$

So we now have an equation of motion if we move the m over to the other side:

$$\boxed{m\dot{\vec{x}}_H = \vec{p}_H - \frac{q}{c}\vec{A}(\vec{x}_H, t)}.$$

And indeed, this tells us that we make the definition we've been alluding to:

Definition 94

The (gauge-covariant) **velocity** operator $\vec{v}$ is given by

$$\vec{v} = \frac{1}{m}\left(\vec{p} - \frac{q}{c}\vec{A}\right).$$

And to get the Lorentz force law, we can apply the same technology, computing $m\dot{\vec{v}}_H = m\ddot{\vec{x}}_H$ through the Heisenberg equation of motion for the operator $A = \vec{p} - \frac{q}{c}\vec{A}$. It's a lengthy calculation, but the final result is that

$$\boxed{m\dot{\vec{v}}_H = q\vec{E}_H + \frac{q}{2}\left(\frac{\vec{v}_H}{c} \times \vec{B}_H - \vec{B}_H \times \frac{\vec{v}_H}{c}\right)}.$$

And indeed, if this were classical, the antisymmetry of the cross product would give us back the ordinary Lorentz force law. (And $\vec{E}$ and $\vec{B}$ become Heisenberg operators by replacing $\vec{x}$ with $\vec{x}_H$.)

Remark 95. *The main point is that we can only ever measure the kinematic momentum, not the canonical momentum $\vec{p}$, in experiments. And if we add additional forces to the picture, we'll need to add more terms to the momentum to get the thing that we actually measure in experiments! But then we usually get into quantum field theory because the expressions get much more complicated.*

Example 96

We'll now turn our attention to a specific problem, the **magnetic field on a two-dimensional torus**.

The results will imply that certain configurations of magnetic field that are okay in the classical world are not allowed in the quantum world. And this will show us the quantization of the magnetic flux, which will show that quantization of electric charge must be possible if we had magnetic monopoles!

As a geometer would say, a **torus** is the surface of a donut. But more algebraically, we can think of a circle (the one-dimensional analog of a torus) as a line segment with the endpoints identified, and then a torus as a rectangle with opposite sides identified. (We can imagine taking a sheet of paper, rolling it up along one direction to get a cylinder, and then rolling it up along the other direction to get a donut.) And this is equivalent to thinking about the entire two-dimensional plane and making an identification according to the equivalence relation

$$(x, y) \sim (x + L_x, y) \sim (x, y + L_y) \quad \text{for all } x, y.$$

(So for example, the point $(0, 0)$ would be identified with $(L_x, 0)$, but also $(0, L_y)$, and $(3L_x, 2L_y)$, and so on.) We want to study an electromagnetic field configuration, in which we have a constant magnetic field

$$\vec{B} = B_0\hat{z}$$

perpendicular to the surface of the torus, and there is no electric field (so $\vec{E} = 0$). We would then need our vector potential to satisfy

$$B_0 = \partial_x A_y - \partial_y A_x,$$

and one such choice that would work would be $A_y(x, y) = B_0 x$ and $A_x(x, y) = 0$. But remember that we're on a torus, so we have a **periodicity condition**, and here the y-component of the vector potential is not quite periodic (since shifting x by L_x changes A_y)!

It turns out that we don't need to assume the vector potential is periodic, because it's not a measurable quantity – instead, we only need periodicity up to gauge transformations. We'll implement this next time, and we'll see that this will give us the desired quantization.

21 March 29, 2021 (Recitation)

We've started understanding how charged particles behave in electromagnetic fields, and we'll see a lot of interesting examples of physical systems in lecture and our problem set. Today, we'll go over one particular example in detail:

Example 97

Consider a charged particle in a uniform magnetic field $\vec{B} = B\hat{z}$. Classically, if we translate our system in the xy-plane, nothing will change. But we'll see something interesting happen in the quantum mechanical case.

In this case, we can choose to have zero scalar potential Φ (because we have a magnetic field, but not an electric field), and we can set

$$H = \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2$$

for any vector potential where $\vec{\nabla} \times \vec{A} = B\hat{z}$. We get some freedom of choice here, and we'll pick

$$\vec{A} = \frac{B}{2}(-y, x, 0),$$

so that $(\vec{\nabla} \times \vec{A})_z = \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} = B$ as desired. (This is sometimes called the **symmetric gauge**.)

Classically, we know that this particle will do circular orbits in the xy-plane (or free motion in the z-direction, but for simplicity we can assume that doesn't happen). So the point is that we'll work with a 2-dimensional Hamiltonian, so that we have the operators $\hat{p}_1, \hat{p}_2 = \hat{p}_x, \hat{p}_y$ and $\hat{x}_1, \hat{x}_2 = \hat{x}, \hat{y}$. If we then plug in $\vec{A}$ into our Hamiltonian, we find that (ignoring the z-component and writing out the squared vector component-by-component)

$$H = \frac{1}{2m}\left(\hat{p}_1 + m\omega\hat{x}_2\right)^2 + \frac{1}{2m}\left(\hat{p}_2 - m\omega\hat{x}_1\right)^2,$$

where $\omega = \frac{qB}{2mc}$ is a characteristic frequency. And now if we want to do a translation (in quantum mechanics), we're going to notice that we don't have symmetry even though B is uniform, because we have the translation in the x_1-direction (for example)

$$T(b) = \exp\left(-\frac{i}{\hbar}b\hat{p}_1\right),$$

which is a unitary operator which translates in the x_1-direction by b. As a reminder, we can check that the operator acts on wavefunctions as

$$T^\dagger(b)\hat{x}_1T(b) = \hat{x}_1 + b \implies T(b)\psi(x_1) = \langle x_1|\hat{T}|\psi\rangle = \psi(x_1 - b).$$

But in this given problem, the momentum operators $\hat{p}_i$ do not commute with the Hamiltonian (because we see the $\hat{x}_i$ operators appearing explicitly), so we won't get a translation to an equivalent state. So we'll change variables a bit to make this Hamiltonian more tractable to work with: we'll change coordinates $\{x_1, x_2, p_1, p_2\} \to \{\pi, \phi, P_1, P_2\}$ such that

$$\pi = p_1 + m\omega x_2, \quad \phi = \frac{1}{2}\left(x_1 - \frac{p_2}{m\omega}\right), \quad P_1 = p_1 - m\omega x_1, \quad P_2 = p_2 + m\omega x_1.$$

Because of the convenient normalization that we chose, we then get a Hamiltonian that looks like

$$H = \frac{\pi^2}{2m} + \frac{m}{2}\omega_c^2\phi^2,$$

where $\omega_c = 2\omega = \frac{qB}{mc}$, and now this looks a lot like a harmonic oscillator Hamiltonian! (The frequency ω_c is called the **cyclotron frequency**.) But to make sure it actually is a harmonic oscillator, the two operators π and ϕ that appear should behave like x and p, in the sense that their commutator looks correct. And we can verify that directly:

$$[\phi, \pi] = \frac{1}{2}[x_1, p_1] - \frac{1}{2}\left[-\frac{p_2}{m\omega}, m\omega x_2\right] = \frac{1}{2}i\hbar + \frac{1}{2}i\hbar = i\hbar.$$

So the problem can now be solved by using the usual raising and lowering operators, and we know the energy eigenvalues of this system:

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

Therefore, a particle in a uniform magnetic field has quantized energies, and the ns here are called the **Landau levels**, which we'll discuss in lecture. But for now, we also want to think about why we picked the particular P_1 and P_2: we can compute the commutators

$$[P_2, \phi] = 0, \quad [P_1, \phi] = \frac{1}{2}[p_1, x_1] + \frac{1}{2}\left[-m\omega x_2, -\frac{p_2}{m\omega}\right] = -\frac{1}{2}i\hbar + \frac{1}{2}i\hbar = 0,$$

and we can also check that $[P_2, \pi] = [P_1, \pi] = 0$ with a similar calculation. And now because H is just quadratic in the two variables π and ϕ, the P_i operators are momentum-type operators that **commute with the Hamiltonian** – "momentum-type" coming from the fact that our new operators also have the familiar commutators $[x_i, P_j] = [x_i, p_j] = i\hbar\delta_{ij}$.

So the point is that these operators will be able to generate some kind of translations like p_1 and p_2 originally did, and we'll analogously define

$$T_1(b) = \exp\left(-\frac{i}{\hbar}bP_1\right) = \exp\left(-\frac{i}{\hbar}b\hat{p}_1 + \frac{ibm\omega}{\hbar}\hat{x}_2\right).$$

If we think about applying $T(b)$ on a two-dimensional wavefunction $\psi(x_1, x_2)$, we then get

$$T_1(b)\psi(x_1, x_2) = \exp\left(\frac{ibm\omega}{\hbar}x_2\right)\psi(x_1 - b, x_2),$$

(the exponential coming from the $\hat{x}_2$ part and the shift coming from the usual $\hat{p}_1$ part). So it may seem promising to look at the combination of operators $\{H, P_1, P_2\}$, and if we want to think about this as a complete set of commuting observables, we also need to consider the commutator $[P_1, P_2]$, and in fact those **do not commute**:

$$[P_1, P_2] = [p_1, m\omega x_1] + [-m\omega x_2, p_2] = -2im\hbar\omega.$$

Thus, what we should think about instead is the implication of this commutator on the translation operators $T_1(b_1) = \exp\left(-\frac{i}{\hbar}b_1P_1\right)$ and the analogous $T_2(b_2) = \exp\left(-\frac{i}{\hbar}b_2P_2\right)$. And now

$$[T_1(b_1), T_2(b_2)] = T_1(b_1)T_2(b_2) - T_2(b_2)T_1(b_1)$$

is going to encode the issue with how the two different translation paths differ (classically, doing the two translations shouldn't give us any difference). The trick for computing this expression is to first consider the function

$$f(b_1) = T_1^\dagger(b_1)P_2T_1(b_1) = \exp\left(\frac{i}{\hbar}b_1P_1\right)P_2\exp\left(-\frac{i}{\hbar}b_1P_1\right)$$

(which would be the "first term in the Taylor expansion" which we expand out the exponentials). And we can compute this with a trick: notice that by the product rule,

$$\frac{df}{db_1} = \frac{i}{\hbar}T_1^\dagger(b_1)P_1P_2T_1(b_1) - \frac{i}{\hbar}T_1^\dagger(b_1)P_2P_1T_1(b_1) = \frac{i}{\hbar}T_1^\dagger(b_1)[P_1, P_2]T_1(b_1) = \frac{i}{\hbar}(-2im\omega\hbar)T_1^\dagger(b_1)T_1(b_1) = 2m\omega,$$

which means that we have (by integration) $f(b_1) = 2m\omega b_1 + f(0) = 2m\omega b_1 + P_2$, by just plugging in $b_1 = 0$ into the definition. So this function f **shifts the operator** P_2, and now we can use this to solve our question by expanding out

$$T_1^\dagger(b_1)T_2(b_2)T_1(b_1) = T_1^\dagger\sum_{n=0}^{\infty}\left(-\frac{ib_2}{\hbar}\right)^n\frac{1}{n!}P_2^nT_1 = \sum_{n=0}^{\infty}\left(-\frac{ib_2}{\hbar}\right)^n\frac{1}{n!}\left(T_1^\dagger P_2T_1\right)^n,$$

and substituting in the values that we just got yields

$$= \sum_{n=0}^{\infty}\left(-\frac{ib_2}{\hbar}\right)^n\frac{1}{n!}\left(P_2 + 2m\omega b_1\right)^n = T_2(b_2)\exp\left(-2ib_1b_2\frac{m\omega}{\hbar}\right).$$

In other words, we have the relation

$$T_2(b_2)T_1(b_1) = T_1(b_1)T_2(b_2)e^{2-ib_1b_2m\omega/\hbar};$$

things almost commute up to an extra phase term! And now if we pick a particular value of b_1b_2 so that $b_1b_2\frac{m\omega_c}{\hbar} = 2\pi n$ for some integer n (remembering $\omega_c = 2\omega$), then the phase term just becomes 1. So for example, if we have $n' = 1$, then the relation is $b_1b_2 = 2\pi\frac{\hbar}{m\omega_c} = 2\pi\ell_B^2$ (where ℓ_B is the **magnetic length**, the length scale of the "harmonic oscillator" we've constructed) The magnetic flux Bb_1b_2 then turns out to be quantized in terms of fundamental constants via $\Phi_0 = \frac{hc}{q}$, and the point is that there are an infinite number of states (an infinite degeneracy) because of the different allowed values of n'.

22 March 30, 2021

We're continuing our discussion of motion of charged particles in electromagnetic fields today, looking more at a uniform magnetic field on a 2-dimensional torus. (And this problem is interesting because there are certain configurations of electric and magnetic fields that aren't allowed in quantum mechanics.)

Recall that the setup is as follows: we think of the torus as a rectangle with side lengths L_x and L_y with opposite sides identified, or equivalently as tiling the entire 2D plane and identifying two points which are L_x apart in the x-direction or L_y apart in the y-direction. (So we have the whole plane, modulo translations.) We then placed a constant uniform magnetic field $\vec{B} = B_0\hat{z}$ on this plane, and we then started thinking about how to define the potential $\vec{A}$ through the equation $\vec{B} = \vec{\nabla} \times \vec{A}$.

There are many choices for what $\vec{A}$ we can use, but one such solution we mentioned last time was to take $A_x = 0$ and $A_y = B_0x$. We now need to think about whether this is a suitable configuration on a torus – indeed, because A_y only depends on x, we do have periodicity in one direction:

$$A_y(x, y + L_y) = A_y(x, y).$$

However, along the translations in the other direction, we have

$$A_y(x + L_x, y) = A_y(x, y) + B_0L_x,$$

So we need to think about whether $\vec{A}$ needs to be periodic, especially because it is not a physical observable – it's not "gauge invariant." What we'll do is take the vector equation

$$\vec{A}(x + L_x, y) = \vec{A}(x, y) + (0, B_0L_x)$$

and try to write it **as a gauge transformation**, thinking of the second term as $\nabla\Lambda(x, y)$ for some Λ. And we can pick something like $\Lambda(x, y) = B_0L_xy$, and now that means our vector potential is periodic up to a gauge transformation:

$$\vec{A}(x + L_x, y) = \vec{A}(x, y) + \nabla\Lambda(x, y)$$

So the wavefunction of a charged particle living on this 2D plane is also periodic up to that gauge transformation:

$$\psi(x + L_x, y) = U(x, y)\psi(x, y),$$

where $U(x, y) = e^{\frac{iq\Lambda(x,y)}{\hbar c}} = e^{\frac{iqB_0L_xy}{\hbar c}}$. And under this particular choice of $\vec{A}$, we have $\vec{A}(x, y + L_y) = \vec{A}(x, y)$ and $\psi(x, y + L_y) = \psi(x, y)$, and therefore the boundary conditions seem to be properly satisfied.

Remark 98. *Remember that the wavefunction itself is not measurable, so adding a phase when we translate is okay. (Quantities that are actually gauge covariant, like $|\psi^2|$, indeed remain constant.)*

But we also need to figure out whether these boundary conditions are **consistent**: if we want to get from (x, y) to $(x + L_x, y + L_y)$, for example, we can translate first horizontally and then vertically, or first vertically and then horizontally. Let's check that those give us the same answer:

$$\psi(x + L_x, y + L_y) = \psi(x + L_x, y) = U(x, y)\psi(x, y),$$

and (translating in the other order)

$$\psi(x + L_x, y + L_y) = U(x, y + L_y)\psi(x, y + L_y) = U(x, y + L_y)\psi(x, y).$$

So we must have $U(x, y) = U(x, y + L_y)$, meaning that

$$\exp\left(\frac{iqB_0L_xy}{\hbar c}\right) = \exp\left(\frac{iqB_0L_x(y + L_y)}{\hbar c}\right) \implies \boxed{\exp\left(\frac{iqB_0L_xL_y}{\hbar c}\right) = 1}$$

is the requirement for our boundary conditions to be consistent! And since $B_0L_xL_y$ is the flux Φ of the magnetic field through the surface of the torus, we must have

$$\exp\left(\frac{iq\Phi}{\hbar c}\right) = 1 \implies \boxed{\Phi = \frac{2\pi\hbar c}{q}n}$$

for some integer n, meaning that we have **quantization of the magnetic flux**! We will define $\hat{\Phi}_0 = \frac{2\pi\hbar c}{q}$ to be the **flux quantum**, and this is the fundamental scale for our magnetic flux. For example, if we take the charge to be an electron, we have $\hat{\Phi}_0 = \frac{2\pi\hbar c}{e} \approx 4.134 \times 10^{-7}$ Gauss $\cdot$ cm^2, which is big enough to be measured.

Remark 99. *In the literature, we might find $\Phi_0 = \frac{2\pi\hbar c}{2e}$ with an extra factor of 2, because that constant plays a role in superconducting physics.*

Fact 100

We've been doing this problem very formally, treating the torus as a fundamental domain of the 2D plane. But in nature, we can think about a torus embedded in 3D space (like a bagel), and we want to ask if we can create a magnetic flux through the surface of that bagel.

We then know that in standard Maxwell electrodynamics,

$$\Phi = \int \vec{B} \cdot d\vec{s} = \int (\vec{\nabla} \cdot \vec{B})dV = 0$$

by the divergence theorem. So the flux through the surface will always be zero, which is not very interesting. But if we make an assumption that magnetic monopoles can actually exist, and one of strength Φ sits inside of our bagel (meaning that $\vec{\nabla} \cdot \vec{B} = \Phi\delta^3(\vec{x} - \vec{x}_0)$), we'll have a flux of Φ through the surface. Then a particle moving on the surface of the bagel of charge q will actually still satisfy the same quantization condition $\frac{q\Phi}{2\pi\hbar c} \in \mathbb{Z}$, even though our surface is no longer flat and the magnetic field is not necessarily uniform. Thus, we can turn the quantization statement around:

Proposition 101

If a single magnetic monopole exists in nature of strength ϕ exists in our universe, then charge must be quantized in units of $q = \frac{2\pi\hbar c}{\Phi}$.

Remark 102. *We chose a particular $A_x = 0$ and $A_y = B_0 x$ early on in this problem, and if we had chosen a different vector potential $\vec{A}$, we would still get the same quantization condition.*

And if we have a more general two-dimensional manifold and we want to try to find $\vec{A}$, we try to define it on small patches of the manifold so that the vector potentials (and wavefunctions) are related by gauge transformations Λ_{ij} when two patches i, j overlap.

If we then have a "triple intersection" of three such patches, we have a consistency condition required – if we go from patch 1 to 2 to 3 back to 1 using the three gauge transformations, we must get 1. This gives us the **cocycle condition** $e^{\frac{iq}{\hbar c}(\Lambda_{21}+\lambda_{32}+\Lambda_{13})} = 1$, and this in fact amounts to the equation

$$\int \vec{B} \cdot d\vec{S} = \frac{2\pi n\hbar c}{q}.$$

This is somewhat similar to the **Gauss-Bonnet theorem** in mathematics! And the point is that the condition that we're obtaining here is very general.

With this, we're ready to move on to the next (very related) topic, **Landau levels**.

Example 103

Consider an infinite xy-plane (this time without the periodic boundary conditions for a torus), where charges are bound to move, and there is again a magnetic field $\vec{B} = B\hat{z}$. We want to find the energy spectrum and wavefunctions for the problem.

We'll start with a classical description. A particle of charge q moving in this xy-plane will experience a Lorentz force $\vec{F} = q\frac{\vec{v}}{c} \times \vec{B}$ perpendicular both to the field and the direction of motion, and thus we get a centripetal force that makes the particle move in a circle. We can then figure out the frequency of the motion by equating forces:

$$\frac{qvB}{c} = \frac{mv^2}{r} \implies \omega_c = \frac{v}{r} = \frac{qB}{mc}$$

The particle then moves at this **cyclotron frequency** ω_c, regardless of the radius of the orbit.

We'll seem some features of this as we do the quantum problem as well. First, we start with the Hamiltonian

$$H = \frac{1}{2m}\left(\hat{p}_x - \frac{q}{c}A_x\right)^2 + \frac{1}{2m}\left(\hat{p}_y - \frac{q}{c}A_y\right)^2 + q\Phi,$$

and we need to figure out the scalar and vector potentials Φ and $\vec{A}$. We can again choose $\Phi = 0$, and much like before we choose $\vec{A}$ so that $B = \partial_x A_y - \partial_y A_x$ – this time, we will pick $\vec{A} = (-By, 0, 0)$, the **Landau gauge**. Plugging this into the above expression

$$H = \frac{1}{2m}\left(\hat{p}_x + \frac{qBy}{c}\right)^2 + \frac{1}{2m}\hat{p}_y^2,$$

and we want to find the spectrum for this Hamiltonian. To do that, first notice that $[H, \hat{p}_x] = 0$, so that we can simultaneously diagonalize H and $\hat{p}_x$. Recalling that eigenfunctions for $\hat{p}_x$ are plane waves along the x-direction

$$\psi(x, y) = \psi(y)e^{ik_x x}$$

(for some arbitrary function $\psi(y)$) with eigenvalue $\hbar k_x$, we can substitute this form of the solution into H and effectively get the one-dimensional problem describing motion along the y-direction:

$$H_{k_x}\psi(y) = E\psi(y),$$

where we now have a constant instead of the p_x operator:

$$H_{k_x} = \frac{1}{2m}\left(\hbar k_x + \frac{qBy}{c}\right)^2 + \frac{1}{2m}\hat{p}_y^2 = \frac{p_y^2}{2m} + \frac{1}{2}m\left(\frac{qB}{mc}\right)^2\left(y - \left(-\frac{\hbar k_x c}{qB}\right)\right)^2.$$

We call the blue quantity $-\frac{\hbar k_x c}{qB}$ to be y_0, and $\frac{qB}{mc}$ is the cyclotron frequency. So for **each** k_x, we have

$$H_{k_x} = \frac{p_y^2}{2m} + \frac{1}{2}m\omega_c^2(y - y_0)^2,$$

which means we have a harmonic oscillator centered around y_0, and thus the energy spectrum is $E_n = \hbar\omega_c\left(n + \frac{1}{2}\right)$ for n a nonnegative integer. Since those energies do not depend on k_x, that gives us the full spectrum of energies, and the wavefunctions will be related to the nth eigenfunction ϕ_n of the harmonic oscillator:

$$\psi_n(y) = \phi_n(y - y_0) \implies \boxed{\psi_{n,k_x}(x, y) = \phi_n(y - y_0)e^{ik_x x}},$$

where our states are labeled by both n and k_x, but the energies only depend on n (these different energy levels are called **Landau levels**). The key thing to notice is that because k_x can be any real number, we have an **infinite degeneracy** at each energy level. (But we'll talk more about this shortly.)

Visualizing these wavefunctions, we notice that $|\psi_{n,k_x}|^2$ is uniform along the x-coordinate (because the plane wave always have magnitude 1), and will be localized around y_0 with characteristic length scale $\ell_B = \sqrt{\frac{\hbar}{m\omega_c}} = \frac{\hbar c}{qB}$ in the y-direction, because of the harmonic oscillator localization. This quantity ℓ_B is called the **magnetic length**, and what this means is that we should imagine most of the wavefunction is localized within a horizontal strip of $y \in [y_0 - \ell_B, y_0 + \ell_B]$.

Fact 104

Remembering that the central y-coordinate y_0 is defined to be a constant times k_x, this means that the different ψ_{n,k_x} wavefunctions for a given energy n have similar probability density, just translated vertically from each other! And taking appropriate superpositions of different k_xs actually make it possible to create wavefunctions that are localized in both directions.

Example 105

Thinking more about the infinite degeneracy, it makes sense for us to try to look instead at just a finite domain of length L_x along the x-direction and L_y along the y-direction.

Then the degeneracy of each level actually becomes finite, as we will now see. For convenience, let's require periodic boundary conditions in the x-direction (though the qualititative features won't depend on these exact conditions). So then we must have $\psi(x + L_x, y) = \psi(x)$, and because

$$\psi_{n,k_x}(x, y) = \psi_n(y - y_0)e^{ik_x x},$$

we must have $k_x = \frac{2\pi m}{L_x}$ for some integer m. This is still an infinite degeneracy, but it's countable instead of uncountable now, and notice that this also means the vertical locations $y_0 = -\ell_B^2 k_x = -\frac{\ell_B^2 2\pi m}{L_x}$ are also discrete – as a consistency check, we notice that the spacing between these locations $\Delta y_0 = \frac{\ell_B^2 2\pi}{L_x}$ goes to 0 as $L_x \to \infty$.

We'll be a bit less precise about how things work in the y-direction now, but the idea is that if the vertical localization y_0 is far outside of the allowed range $[0, L_y]$, that won't be a valid wavefunction. (In real life, we'd have a significantly different potential outside $[0, L_y]$, which would change the wavefunctions.) So we'll say that we can only have $0 \leq y_0 \leq L_y$, and thus we have an N-fold degeneracy given by

$$N = \frac{L_y}{\Delta y_0} = \frac{L_x L_y}{2\pi \ell_B^2} = \frac{L_x L_y}{2\pi \frac{\hbar c}{qB}} = \frac{L_x L_y B}{\frac{2\pi\hbar c}{q}} = \frac{\Phi}{\hat{\Phi}_0},$$

and we see the magnetic flux appearing again! In fact, the degeneracy is (roughly) "how many flux quanta can fit inside our allowed rectangle," and if we want to make this more precise, we can use the torus boundary conditions in both cases (in which case the formula becomes exact).

Fact 106

If we take $L_x = L_y = 1$ cm and $B = 1$ Tesla, then it turns out $\frac{\Phi}{\hat{\Phi}_0} \approx \frac{1 \text{ Tesla}\cdot\text{cm}^2}{4\times 10^{-7} \text{ Gauss}\cdot\text{cm}^2} \approx 2.5 \times 10^{10}$. So the degeneracy of each Landau level is very large, and when degeneracy is large, we have high sensitivity to perturbations because of potential energy splittings.

Remark 107. *Physical realizations of this setup include graphene (a single atomic layer of carbon) and* **semiconductor heterostructures** *(where we take two different semiconductor structures and grow them on top of each other to get an interface).*

The idea of the latter is that some electrons will be stuck in the interface but free to move within it, which gives us a two-dimensional electron gas, and this led to the **quantum Hall effect** – effects of certain perturbations, such as disorder and the Coulomb interaction between electrons, lead to the **integer** and the **fractional** quantum Hall effect, respectively. Basically, as we cool a system down, we observe that the Ohm's law relation for the **Hall resistance** $R_H = \frac{V_H}{I}$ that we get when we have a current and magnetic field perpendicular to each other stops being completely linear in the magnetic field B, and it is instead quantized in terms of fundamental units of nature: we have

$$R_H = \frac{h}{e^2 \nu}$$

for some certain **integer** or **rational** numbers ν. And we've found that this effect holds up to very high experimental precision!

23 March 31, 2021 (Recitation)

We saw last recitation and lecture the concept of **Landau levels** (in two different gauges): basically, if we have a particle in a uniform magnetic field, the energies get quantized like a harmonic oscillator with cyclotron frequency $\omega_c = \frac{aB}{mc}$. We'll try to get a closer understanding of this concept, particularly the degeneracy of the different levels, today.

Recall that the degeneracy of a fundamental domain – a rectangle of length L_x and width L_y – has degeneracy factor $\frac{A}{2\pi\ell_B^2}$, where $\ell_b = \sqrt{\frac{\hbar c}{qB}}$ is the magnetic length. And if we move the factors of B to the numerator, we end up with the ratio $\frac{\Phi}{\Phi_0}$, where $\Phi = AB$ is the magnetic flux through the rectangle and Φ_0 is the fundamental flux quanta $\frac{2\pi\hbar c}{q} = \frac{hc}{q}$. So a larger magnetic field will increase the degeneracy levels, and for typical magnetic fields this is a very large degeneracy.

Remark 108. *Yet another way we can write this degeneracy factor is as* $\frac{Am\omega_c}{2\pi\hbar}$*, so that the dependence on charge is encoded in the cyclotron frequency.*

But we'll do an even simpler calculation now to get a sense of what this degeneracy calculation is really doing, by counting states for the free particle.

Example 109

Consider a free particle in a square box with $L_x = L_y = L$, and suppose that we impose periodic boundary conditions.

Solutions for this two-dimensional system look like plane waves

$$\psi = Ne^{ik_x x}e^{ik_y y},$$

where periodicity require us to have $k_x = \frac{2\pi}{L}n$ and $k_y = \frac{2\pi}{L}m$, where n, m are integers. So the spacing between different energy levels is given by $\frac{2\pi}{L}$, and if we think about the energy in this system, we just have the kinetic free energy of a free particle, which is

$$E = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2).$$

So we don't have the same kind of degeneracy, but we can still look at a range of energies and ask how many states are in that range. We'll think about this by counting how many states have energies in $0 < E < E_{\text{max}}$, and that's basically a condition constraining k_x, k_y to be within a circle centered at the origin. So that inequality can be rewritten as

$$k_x^2 + k_y^2 < \frac{2m}{\hbar^2}E_{\text{max}}$$

(where the right-hand side is sometimes written as k_F^2, where $k_F = \frac{\sqrt{2mE_{\text{max}}}}{\hbar}$ is the **Fermi wavenumber**). Then our counting estimate will be that the number of states with $E < E_{\text{max}}$ is the ratio of the circle area and the fundamental energy spacing area:

$$\text{number of states} \approx \frac{\pi k_F^2}{(2\pi/L)^2} = \frac{AmE_{\text{max}}}{2\pi\hbar^2}$$

(as long as the number of states is large so that the boundary corrections are not significant). And if we compare that to the result we had above, notice that this looks a little bit like the $\frac{Am\omega_c}{2\pi\hbar}$ that we had for the magnetic field! But the idea is that there are less Landau levels when we have a nonzero magnetic field than energy levels when we have a free particle: basically, the discrete levels that are originally spaced apart by $\frac{2\pi}{L}$ in wavenumber are being squished together into a single Landau level.

And to understand that statement, remember that the Landau levels are at energies $\frac{1}{2}\hbar\omega_c, \frac{3}{2}\hbar\omega_c, \frac{5}{2}\omega_c$, and so on. So what we claim is that the **degeneracy in the lowest Landau level is equal to the number of free particle states** in $0 < E < \hbar\omega_c$, and then the degeneracy of the Landau level $\frac{3}{2}\hbar\omega_c$ is the number of free particle states in $\hbar\omega_c < E < 2\hbar\omega_c$, and so on. That would mean that free particle states basically get "squished to the closest energy level," and indeed, the number of free particle states in the energy band $0 < E < \hbar\omega_c$ is

$$\frac{Am\hbar\omega_c}{2\pi\hbar^2} = \frac{Am\omega_c}{2\pi\hbar},$$

and similar calculations work for the higher Landau levels as well.

Remark 110. *Our approximations here only work for a significant magnetic field $\vec{B}$, because the area approximations only work in the high-degeneracy limit. So we don't need to worry about transitions in energy levels from $\vec{B} = 0$ to $\vec{B} \neq 0$ not behaving – our calculations are just not valid if Φ is on the same order as Φ_0, for example. Plus, ω_c depends on $\vec{B}$, so there really aren't any discontinuities at all – the spacing and degeneracy just increase along with $\vec{B}$.*

We'll talk next about something related to the **Aharonov-Bohm effect** and interference experiments:

Example 111

Consider a solenoid with radius a which causes a magnetic field B inside the solenoid, but zero magnetic field outside the solenoid. The idea is that even though there is no B outside the solenoid, quantum mechanically there can still be some effects.

To understand this, we'll take a circle C of radius $r > a$ wrapping outside the solenoid (so that $\vec{B}$ is pointing through the surface encompassed by C): Stokes' law tells us that the vector potential $\vec{A}$ satisfies

$$\int_C d\vec{\ell} \cdot \vec{A} = \int d\vec{S} \cdot (\vec{\nabla} \times \vec{A}),$$

and now $\vec{\nabla} \times \vec{A}$ is $\vec{B}$ inside the part of the surface that intersects the solenoid, so this is

$$= \pi a^2 B = \Phi$$

(the flux through the solenoid). But the left-hand side says that we're integrating $\vec{A}$ only along curve outside the solenoid, so even though $\vec{B} = 0$ everywhere along C, we still have a nonzero $\vec{A}$. And one way we can do that is to take

$$\vec{A} = \frac{\Phi}{2\pi r}\hat{\phi}$$

(in cylindrical coordinates (r, ϕ, z)) for all $r > a$, and then the curl formula in cylindrical coordinates gives us

$$\vec{B} = \vec{\nabla} \times \vec{A} = \hat{r}\left(-\frac{\partial A_\phi}{\partial z}\right) + \hat{z}\frac{1}{r}\frac{\partial}{\partial r}(rA_\phi),$$

and both of these terms are indeed zero. So the magnetic field is correctly zero outside the solenoid (for $r > a$), and now our job is to understand what this nonzero $\vec{A}$ does to our system. We can consider the **Aharanov-Bohm phase**

$$g(\vec{x}, C) = \frac{q}{\hbar c}\int_C d\vec{\ell} \cdot \vec{A},$$

where C is some curve from $\vec{0}$ to $\vec{x}$, where we can notice that $\vec{\nabla} g(\vec{x}, C) = \frac{q}{\hbar c}\vec{A}(\vec{x})$ by the fundamental theorem of calculus (so the derivative doesn't depend on the choice of path C). We'll use this to simplify the structure of our Schrodinger equation: we need to satisfy

$$\left[\frac{1}{2m}\left(-i\hbar\nabla - \frac{q}{c}\vec{A}\right)^2 + e\Phi\right]\Psi(x, t) = i\hbar\frac{\partial}{\partial t}\Psi(x, t),$$

and to solve this we'll use a change of variable

$$\Psi(\vec{x}, t) = e^{ig(\vec{x}, C)}\chi(\vec{x}, t).$$

We can then compute what happens when we substitute this in: the product rule gives us

$$\left(-i\hbar\nabla - \frac{q}{c}\vec{A}\right)\Psi = e^{ig(\vec{x}, C)}(-i\hbar\nabla\chi) + \frac{\hbar q}{\hbar c}\vec{A}\Psi - \frac{q}{c}\vec{A}\Psi,$$

and now we see that we substituted in this particular choice of g because it makes the last two terms cancel. So the equation that the χ obeys is the Schrodinger equation above, except setting $\vec{A} = 0$, so what we've done is split the wavefunction into two pieces – one that knows about $\vec{A}$, and one that doesn't!

Therefore, the impact of this vector potential is to add a **phase** $e^{ig(\vec{x}, C)}$ to the wavefunction, and we can now see how to use this.

Example 112

Consider a two-slit interference setup, where particles that pass through form an interference pattern on a far wall. We want to understand the impact of putting a solenoid of flux Φ between the two potential "paths" (close to the near wall with slits).

We know that superposition tells us that the wavefunction of the interference pattern at a point $\vec{x}$ on the wall is the sum of the contributions from the two potential paths, so

$$\Psi = \Psi_1 + \Psi_2 = e^{ig(\vec{x},C_1)}\chi_1(\vec{x},t) + e^{ig(\vec{x},C_2)}\chi_2(\vec{x},t) = e^{ig(\vec{x},C_1)}\left[\chi_1(\vec{x},t) + e^{ig(\vec{x},C)}\chi_2(\vec{x},t)\right],$$

where the path C can be thought of as going forward along C_2 and then coming back along C_1, which is a closed path! So then Stokes' law gives us

$$g(\vec{x},C) = \frac{q}{\hbar c}\oint d\vec{\ell}\cdot\vec{A} = \frac{q}{\hbar c}\Phi.$$

In other words, changing the magnetic field will actually change the interference pattern, because it changes how the two wavefunctions interfere with each other! But if we change B by the right amount to change the magnitude flux from Φ to $\Phi + \Phi_0$, that leaves the interference pattern unchanged. So that tells us what we can measure about Φ using physical experiments!

24 April 1, 2021

We'll start a new topic today, **time-dependent perturbation theory**. So far, we've been mostly solving problems where our Hamiltonian is time-independent, but there are many important problems in physics where the Hamiltonian is time-dependent:

Example 113

If we shine light at an atom, then the electromagnetic wave has electric and magnetic waves oscillating in time, so the Hamiltonian of the atom will be time-dependent.

So we need to be able to address such time-dependent problems, and we'll develop some new machinery for addressing them. And we'll be able to use this to understand systems like decay rates in excited atoms!

Recall that quantum mechanics is basically about solving the time-dependent Schrodinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = H(t)|\psi\rangle.$$

If the Hamiltonian $H(t) = H$ is time-independent, then we can simplify the problem, since we can find the eigenstates of H and write the time-evolution as

$$|\psi(t)\rangle = \sum_n c_n e^{-iE_nt/\hbar}|n\rangle.$$

But when the Hamiltonian is time-dependent, our life is more difficult, and it doesn't actually help very much to find the instantaneous eigenstates $|n\rangle_t$ of $H(t)$, because we no longer have a simple relation like $|\psi(t)\rangle \neq \sum_n c_n(t)|n\rangle_t$. (We will discuss a situation later in the class, where H is varying very slowly, where $|n\rangle_t$ is useful. But for general time-evolution, this is not a good approach.)

Example 114

We will often be interested in a setup where the Hamiltonian can be written as $H(t) = H^{(0)} + \delta H(t)$, where we know everything about the **time-independent** $H^{(0)}$ term, and $\delta H(t)$ is our time-dependent perturbation. And we will often take $\delta H(t)$ to be zero outside of a time interval $[t_0, t_f]$, where the perturbation is turned on.

Then if we know the spectrum of $H^{(0)}$, we know the evolution of the system at times up to t_0 and at times after t_f (given by the stationary state evolution that we described above). If we then assume that the system is in an eigenstate of $H^{(0)}$ for $t < t_0$, it makes sense to ask for the probability that it transitions to a different eigenstate at $t = t_f$:

Example 115

An example of such a $\delta H(t)$ is a laser that is focused on a hydrogen atom from time t_0 to t_f, and perhaps we're interested in the probability that the hydrogen atom has made a transition from the ground state (before t_0) to some excited state (after t_f).

To understand how to deal with these kinds of situations, it's good to first go over some formalism and talk about the **Schrodinger and Heisenberg pictures**. In the **Schrodinger picture**, we have states $|\psi(t)\rangle$ evolving in time, and the Schrodinger equation $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H(t)|\psi(t)\rangle$ tells us about the evolution of the system. Our observables $\hat{A}_S$ do not evolve in time: in particular, if we want to evaluate the expectation of any observable, we have

$$\langle \hat{A}_S\rangle(t) = \langle \psi(t)|A_s|\psi(t)\rangle .$$

But for any $\psi(t)$, we can define a **time-evolution operator** $U(t)$, defined by

$$|\psi(t)\rangle = U(t)|\psi(0)\rangle .$$

(This operator $U(t)$ should be unitary.) If the Hamiltonian is time-independent, then we have the simple form $U(t) = e^{-iHt/\hbar}$. But more generally, the expression is more complicated. And the **Heisenberg picture** starts by taking some of the equations above and reinterpreting them: we can write

$$\langle \hat{A}_s\rangle(t) = \langle \psi(t)|A_s|\psi(t)\rangle = \left\langle \psi(0)\middle|U^\dagger(t)A_sU(t)\middle|\psi(0)\right\rangle ,$$

and thus we can always work with the wavefunction at time 0 and evolve our operators instead! In other words, we measure the Heisenberg operator

$$A_H(t) = U^\dagger(t)A_SU(t),$$

and thus the operators are evolving instead of the wavefunctions. (We can then write down a Heisenberg equation of motion, but we won't do that now.)

These two pictures of quantum mechanics are completely equivalent, but we can now return to our Hamiltonian of the form

$$H(t) = H^{(0)} + \delta H(t).$$

We then want to see whether we can isolate the time-dependence coming from $\delta H(t)$, and that gives us the **interaction picture**, which is basically a cross between the Schrodinger and Heisenberg pictures.

Definition 116

The **interaction picture wavefunction** is given by

$$\left|\tilde{\psi}(t)\right\rangle = e^{iH^{(0)}t/\hbar}\left|\psi(t)\right\rangle .$$

The point of this definition is that if $\delta H(t) = 0$, then all of the time-evolution is due to the time-independent $H^{(0)}$:

$$\left|\psi(t)\right\rangle = e^{-iH^{(0)}t/\hbar}\left|\psi(0)\right\rangle ,$$

and thus the exponential factors cancel:

$$\left|\tilde{\psi(t)}\right\rangle = e^{iH^{(0)}t/\hbar}e^{-iH^{(0)}t/\hbar}\left|\psi(0)\right\rangle = \left|\psi(0)\right\rangle .$$

So $\left|\tilde{\psi(t)}\right\rangle$ doesn't change as a function of time when there is no perturbation, so any time-evolution of our system is due to δH. And if we know $\left|\tilde{\psi}(t)\right\rangle$, we can also recover our original wavefunction by multiplying by $e^{-iH^{(0)}t/\hbar}$.

So now if we turn on our δH, we can derive something similar to the Schrodinger equation: notice that by the product rule, we have

$$\boxed{i\hbar\frac{\partial}{\partial t}\left|\tilde{\psi}(t)\right\rangle} = e^{iH^{(0)}t/\hbar}(-H^{(0)})\left|\psi(t)\right\rangle + e^{iH^{(0)}t/\hbar}i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle ,$$

which simplifies by the Schrodinger equation to

$$= e^{iH^{(0)}t/\hbar}(-H^{(0)} + H(t))\left|\psi(t)\right\rangle = e^{iH^{(0)}t/\hbar}\delta H(t)\left|\psi(t)\right\rangle .$$

Since we want an equation in terms of $\tilde{\psi}(t)$, we can solve back for $\tilde{\psi}(t)$ and find that this is

$$= e^{iH(0)t/\hbar}\delta H(t)e^{-iH^{(0)}t/\hbar}\left|\tilde{\psi}(t)\right\rangle ,$$

where if we define the operator $\tilde{\delta H}(t) = e^{iH(0)t/\hbar}\delta H(t)e^{-iH^{(0)}t/\hbar}$, we have

$$\boxed{i\hbar\frac{\partial}{\partial t}\left|\tilde{\psi}(t)\right\rangle = \tilde{\delta H}(t)\left|\tilde{\psi}(t)\right\rangle}.$$

Here, $\tilde{\delta H}(t)$ is the **Heisenberg operator** for δH, with respect to $H^{(0)}$! So indeed, we have some aspects of both the Schrodinger and the Heisenberg picture here, and our goal will be to develop methods that help us solve for $\tilde{\psi}(t)$. (Everything is exact so far – we haven't made any assumptions about δH being small.)

It's also useful to discuss how these equations look in an orthonormal basis for concreteness: suppose that we have an orthonormal basis of $H^{(0)}$ given by $H^{(0)}\left|n\right\rangle = E_n\left|n\right\rangle$ (and we won't put (0) superscripts this time for the unperturbed states, just for brevity). Then any wavefunction can be expanded in the orthonormal basis, so we have

$$\left|\tilde{\psi}(t)\right\rangle = \sum_n c_n(t)\left|n\right\rangle$$

for some complex coefficients $c_n(t)$. Then we know that

$$\left|\psi(t)\right\rangle = e^{-iH^{(0)}t/\hbar}\left|\tilde{\psi}(t)\right\rangle = e^{-iH^{(0)}t/\hbar}\sum_n c_n(t)\left|n\right\rangle$$

and because $\left|n\right\rangle$ is an eigenstate of $H^{(0)}$, we just pick up a phase factor

$$= \sum_n c_n(t)e^{-iE_nt/\hbar}\left|n\right\rangle .$$

So we've separated the trivial phase factor $e^{-E_n t/\hbar}$ from the more complicated time-dependence of $c_n(t)$. And indeed, we recover the usual answer for time-independent Hamiltonians if $\delta H = 0$, and thus $c_n(t)$ are each constant in time.

But if we want to find the c_ns, we can try plugging the form of $\tilde{\psi}(t)$ into the interaction picture equation and get some differential equations. We find that

$$i\hbar \frac{\partial}{\partial t} \sum_m c_m(t) |m\rangle = \delta \tilde{H}(t) \sum_n c_n(t) |n\rangle ,$$

and now we can take the time-derivative inside the sum to get (relabeling m to m' because of the next step)

$$\sum_{m'} i\hbar \dot{c}_{m'}(t) |m'\rangle = \delta \tilde{H}(t) = \sum_n c_n(t) \delta \tilde{H}(t) |n\rangle .$$

This is a "vector equation" in the Hilbert space, so the equality must hold along each component, and we can check this by taking the inner product of both sides with some bra $\langle m|$. Then orthonormality on the left-hand side gives us

$$i\hbar \dot{c}_m = \sum_n c_n(t) \left\langle m \middle| \delta \tilde{H}(t) \middle| n \right\rangle ,$$

and now we will introduce the notation for the matrix element

$$\boxed{\delta \tilde{H}_{mn}(t)} = \left\langle m \middle| \delta \tilde{H}(t) \middle| n \right\rangle ,$$

which can be simplified in terms of the original δH as

$$= \left\langle m \middle| e^{iH^{(0)}t/\hbar} \delta H(t) e^{-iH^{(0)}t/\hbar} \middle| n \right\rangle = \left\langle m e^{-iE_m t/\hbar} \middle| \delta H(t) \middle| e^{-iE_n t/\hbar} \right\rangle ,$$

and now the constant phase factors come out to give us (remembering that bra has an extra complex conjugation term)

$$= e^{i(E_m - E_n)t/\hbar} \langle m | \delta H(t) | n \rangle = \boxed{e^{i\omega_{mn} t} \delta H_{mn}(t)},$$

where $\omega_{mn} = \frac{E_m - E_n}{\hbar}$ is related to the energy difference between energy levels (this is the **transition frequency**). So we now know that

$$\boxed{i\hbar \dot{c}_m = \sum_n e^{i\omega_{mn} t} \delta H_{mn}(t) c_n(t)},$$

and this gives us a **set of coupled first-order differential equations** for the coefficients $c_m(t)$.

Example 117 (Nuclear Magnetic Resonance)

Suppose that we have a spin 1/2 particle in a magnetic field, so that the Hamiltonian is given by

$$H = \vec{\omega} \cdot \vec{s}, \quad \vec{\omega} \propto \vec{B}.$$

Here, $\vec{\omega}$ has dimensions of frequency, and $\vec{s}$ has dimensions of $\hbar$, so the units work out. Now **if the magnetic field is constant**, the Hamiltonian is just the time-independent $H^{(0)} = -\omega_0 S_z = \frac{\hbar \omega_0}{2} \sigma^z$ – the eigenstates are then $|z;+\rangle$ and $|z;-\rangle$ with energy $\frac{\hbar\omega_0}{2}$, and in general a spin vector $\vec{s}$ will precess around the $\hat{z}$-axis with frequency ω_0.

But we can now consider perturbations to this system. First of all, we can consider a small additional magnetic field along the x-direction, so that we have the (still time-independent) Hamiltonian

$$H = (\Omega, 0, \omega_0) \cdot (S_x, S_y, S_z).$$

This then corresponds to a magnetic field that is slightly tilted off of the z-axis, and thus the spin precesses around this slightly tilted axis at a slightly modified frequency $|\vec{\omega}| = \sqrt{\omega_0^2 + \Omega^2}$. (So if the tilt is small, the modification of the motion will also be small, and we can find the new eigenstates as well – they will be spins aligned along the tilted axis with new energies $\frac{\hbar|\vec{\omega}|}{2}$.) The point is that this small constant perturbation doesn't change the motion much, because everything is still time-independent.

If we instead apply an additional rotating external magnetic field, though, things get more complicated. (Experimentally, this often comes from a large external magnetic field for the z-direction, plus some additional oscillating radiation.) And we will pick the perturbation to match the frequency of the natural precession, so that

$$\delta H(t) = \Omega \left(\hat{S}_x \cos \omega_0 t + \hat{S}_y \sin(\omega_0 t) \right).$$

We'll solve this problem by going into the interaction picture, which basically means we go into the frame of the unperturbed precession at frequency ω_0. To understand that, notice that

$$\tilde{\delta H}(t) = e^{iH^{(0)}t/\hbar} \delta H(t) e^{-iH^{(0)}t/\hbar}$$

can be simplified by plugging in the explicit expressions:

$$= \Omega e^{i\omega_0 t \sigma^z/2} \left(\hat{S}_x \cos \omega_0 t + \hat{S}_y \sin \omega_0 t \right) e^{-i\omega_0 t \sigma^z/2}.$$

And $e^{-i\omega_0 t \sigma^z/2}$ is a rotation around the z-axis, so indeed we are corotating with the unperturbed precession (and then the conjugation puts us back in our original frame)! Now we can use the fact that

$$e^{i\omega_0 t \sigma^z/2} \hat{S}_x e^{-i\omega_0 t \sigma^z/2} = \hat{S}_x \cos \omega_0 t - \hat{S}_y \sin \omega_0 t,$$

and we'll take $t \to -t$ so that

$$e^{-i\omega_0 t \sigma^z/2} \hat{S}_x e^{i\omega_0 t \sigma^z/2} = \hat{S}_x \cos \omega_0 t + \hat{S}_y \sin \omega_0 t.$$

Therefore, we have that

$$\hat{S}_x e^{i\omega_0 t \sigma^z/2} = e^{i\omega_0 t \sigma^z/2} \left(\hat{S}_x \cos \omega_0 t + \hat{S}_y \sin \omega_0 t \right),$$

so we can plug this back into $\tilde{\delta H}(t)$ to get

$$\tilde{\delta H}(t) = \Omega \hat{S}_x,$$

which is exactly what we expect: if we go into a frame rotating at ω_0, then we have a constant perturbation because we rotate along with the rotating magnetic field. So the interacting picture wavefunction satisfies

$$i\hbar \frac{\partial}{\partial t} \left| \tilde{\psi} \right\rangle = \tilde{\delta H}(t) \left| \tilde{\psi} \right\rangle = \Omega \hat{S}_x \left| \tilde{\psi} \right\rangle,$$

which is easy to solve: we have

$$\left| \tilde{\psi}(t) \right\rangle = e^{-i\Omega \hat{S}_x t/\hbar} \left| \tilde{\psi}(0) \right\rangle = e^{-i\Omega \hat{S}_x t/\hbar} \left| \psi(0) \right\rangle$$

(second equality by definition of $\tilde{\psi}$), so that

$$\left| \tilde{\psi}(t) \right\rangle = \exp\left(-\frac{i\Omega t}{2} \sigma^x \right) \left| \psi(0) \right\rangle.$$

Therefore, in the interaction picture, our spin is rotating at frequency Ω around the x-axis, so if we go to the Schrodinger picture, we have

$$\left| \psi(t) \right\rangle = e^{-iH^{(0)}t/\hbar} \left| \tilde{\psi}(t) \right\rangle = e^{-i\frac{\omega_0 t}{2}\sigma^z} e^{-i\frac{\Omega t}{2}\sigma^x} \left| \psi(0) \right\rangle.$$

So a spin that starts along the z-axis will gradually tilt into the xy-plane (and keep rotating around the x-axis), while still precessing around the z-axis at a faster rate. And the lesson here is that a constant perturbation with a small strength doesn't change the motion very much (because the unperturbed energy spectrum cannot supply any energy to the system, and it doesn't make transitions between systems effectively), but driving the system in a time-dependent way can cause **resonance** so that the motion will change dramatically.

We still haven't made any assumptions or approximations yet, but now we'll turn to perturbation theory, which is what the interaction picture is particularly good for. Just like at the beginning of the class, we'll now look at $H(t) = H^{(0)} + \lambda \delta H(t)$ for a dimensionless parameter $\lambda \in [0, 1]$. If we look at the interaction picture Schrodinger equation, we want to look for a perturbative solution which is a power series in λ:

$$\left|\tilde{\psi}(t)\right\rangle = \left|\tilde{\psi}^{(0)}(t)\right\rangle + \lambda \left|\tilde{\psi}^{(1)}(t)\right\rangle + \lambda^2 \left|\tilde{\psi}^{(2)}(t)\right\rangle + \cdots ,$$

where we're expanding the full time-dependent wavefunction in λ in the interaction picture. To understand how we find these terms, we integrate the interaction picture equation to find

$$\int_0^t dt' i\hbar \frac{\partial}{\partial t'} \left|\tilde{\psi}(t')\right\rangle = \lambda \int_0^t dt' \delta\tilde{H}(t') \left|\tilde{\psi}(t')\right\rangle .$$

Dividing through by $i\hbar$ and noticing that the left-hand side is an integral of a derivative, ew have

$$\left|\tilde{\psi}(t)\right\rangle - \left|\tilde{\psi}(0)\right\rangle = \lambda \int_0^t dt' \frac{\delta\tilde{H}(t')}{i\hbar} \left|\tilde{\psi}(t')\right\rangle .$$

Since $\left|\tilde{\psi}(0)\right\rangle = |\psi(0)\rangle$, we can rearrange this as

$$\boxed{\left|\tilde{\psi}(t)\right\rangle = |\psi(0)\rangle + \lambda \int_0^t dt' \frac{\delta\tilde{H}(t')}{i\hbar} \left|\tilde{\psi}(t')\right\rangle}.$$

So we now have an integral equation, and the reason we wrote things this way is that it is convenient for a perturbative expansion in λ (since $\left|\tilde{\psi}(t)\right\rangle$ appears on both sides). We'll substitute in this equation back into itself to get

$$\left|\tilde{\psi}(t)\right\rangle = |\psi(0)\rangle + \lambda \int_0^t dt' \frac{\delta\tilde{H}(t')}{i\hbar} \left(|\psi(0)\rangle + \lambda \int_0^{t'} dt'' \frac{\delta\tilde{H}(t'')}{i\hbar} \left|\tilde{\psi}(t'')\right\rangle \right),$$

which simplifies out as

$$= |\psi(0)\rangle + \lambda \int_0^t dt' \frac{\delta\tilde{H}(t')}{i\hbar} |\psi(0)\rangle + \lambda^2 \int_0^t dt' \int_0^{t'} dt'' \frac{\delta\tilde{H}(t')}{i\hbar} \frac{\delta\tilde{H}(t'')}{i\hbar} \left|\tilde{\psi}(t'')\right\rangle .$$

And now we again have a $\tilde{\psi}$ on the right-hand side, so we can plug in again to find

$$= |\psi(0)\rangle + \lambda \int_0^t dt' \frac{\delta\tilde{H}(t')}{i\hbar} |\psi(0)\rangle + \lambda^2 \int_0^t dt' \int_0^{t'} dt'' \frac{\delta\tilde{H}(t')}{i\hbar} \frac{\delta\tilde{H}(t'')}{i\hbar} \left(|\psi(0)\rangle + O(\lambda) \right)$$

(the $O(\lambda)$ part gives us a λ^3 term, which would then be a triple integral, but we can probably predict the form of the solution from here on). And now, we can read off the zeroth, first, and second order terms, but we'll discuss the structure of this more next time!

25 April 5, 2021 (Recitation)

We'll talk about magnetic monopoles and the interaction picture today – we'll save the perturbation theory for next week recitation. Recall that in electromagnetism, we know that we have $\vec{\nabla} \cdot \vec{B} = 0$, but $\vec{\nabla} \cdot \vec{E} = 4\pi\rho$ for some charge distribution given by ρ. And this fact is encoding the idea that there are no magnetic monopoles: otherwise, Gauss's divergence theorem tells us that

$$\int_S \vec{B} \cdot d\vec{s} = \int_V (\vec{\nabla} \cdot \vec{B}) dV = 0$$

(where the integral on the left is over a surface, and the integral over the right is over a volume). But it seems like we might want more symmetry in Maxwell's equations between $\vec{E}$ and $\vec{B}$.

Example 118

Suppose that we modify Maxwell's equations so that we have a magnetic charge density ρ_M and $\vec{\nabla} \cdot \vec{B} = 4\pi\rho_m$. (We can also introduce other analogous quantities to make Maxwell's equations completely symmetric in $\vec{E}$ and $\vec{B}$.)

Now if we have a magnetic monopole at a point so that

$$\vec{B} = \frac{e_m}{r^2}\hat{r},$$

we would find only a nonzero divergence at the origin:

$$\vec{\nabla} \cdot \vec{B} = \delta^3(\vec{r}).$$

We then want to construct a quantum mechanical $\vec{A}$ that is consistent with $\vec{B} = \vec{\nabla} \times \vec{A}$. Since this problem is spherically symmetric, we should use spherical coordinates (r, θ, ϕ), and it turns out one result that works is

$$\vec{A} = \frac{e_m(-\cos\theta)}{r\sin\theta}\hat{\phi} = A_\phi(\theta, r)\hat{\phi}$$

(we just need a component in the $\hat{\phi}$ direction). We then find that (looking up the formula for curl in spherical coordinates and only keeping the terms corresponding to A_ϕ)

$$\vec{\nabla} \times \vec{A} = \hat{r}\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(A_\phi \sin\theta) + \hat{\theta}\frac{1}{r}\left(-\frac{\partial}{\partial r}\right)(rA_\phi).$$

And we can indeed check that this indeed gives us the $\hat{r}\frac{e_m}{r^2}$ that we want, so this is a valid vector potential! (There are different $\vec{A}$s that also work, but we'll work with this one.)

So now that we're doing quantum mechanics, we can imagine substituting this $\vec{A}$ into the Hamiltonian. But we have a problem – as $\theta \to 0$ or $\theta \to \pi$, this potential $\vec{A}$ diverges. If we instead think about

$$\vec{A}_I = \frac{e_m(1 - \cos\theta)}{r\sin\theta}\hat{\phi},$$

this solution also satisfies $\vec{\nabla} \times \vec{A} = \vec{B}$, and as $\theta \to 0$ this solution no longer diverges. But this solution still doesn't work for $\theta = \pi$ – we can also instead get a solution that doesn't diverge at π if we write down

$$\vec{A}_{II} = \frac{e_m(-1 - \cos\theta)}{r\sin\theta}\hat{\phi},$$

basically replacing the 1 with the -1, but this time our solution will diverge at 0. So in other words, we can get $\vec{A}$ to be fine for all $\theta < \pi - \varepsilon$ or all $\theta > \varepsilon$, but not both at the same time.

Proposition 119

Because what physically matters is $\vec{B}$ rather than $\vec{A}$, the idea is to patch together our two solutions from the different $\vec{A}$s to describe $\vec{B}$ in both cases. And in this way, we are able to cut out the singularities and start doing quantum mechanics.

The idea is that because we have two different $\vec{A}$s that both give us the same $\vec{B}$, we need things to agree in the overlapping region. In other words, we should be able to write the difference

$$\vec{A}_{II} - \vec{A}_I = -\frac{2e_m}{r\sin\theta}\hat{\phi}$$

in terms of a pure gauge transformation $\nabla\Lambda$. And because the gradient in spherical coordinates for the $\hat{\phi}$ term is $\frac{\hat{\phi}}{r\sin\theta}\frac{\partial}{\partial\phi}\Lambda$, we find that $\Lambda = -2e_m\phi$ gives us what we want.

So we'll now understand what this magnetic monopole implies for the quantum mechanics: suppose that we have an electron of charge q in this potential $\vec{A}$. The two different $\vec{A}$s will give us two wavefunctions that are related by a $U = \exp\left(\frac{iq}{\hbar c}\Lambda\right)$ term:

$$\psi_{II} = \exp\left(\frac{2iqe_m\phi}{\hbar c}\right)\psi_I.$$

If we look at the "overlap" region, for example at $\theta = \frac{\pi}{2}$ (in the xy-plane), then we get a condition because we know that the wavefunction for the electron needs to be single-valued. In other words,

$$\psi_I(r,\theta,\phi+2\pi) = \psi_I(r,\theta,\phi), \quad \psi_{II}(r,\theta,\phi+2\pi) = \psi_{II}(r,\theta,\phi),$$

and then substituting in the U term gives us a condition

$$\boxed{\frac{2qe_m}{\hbar c} \in \mathbb{Z}}.$$

In other words, we have quantization of our magnetic monopoles – if q comes in discrete amounts, then that gives us a one-to-one correspondence with the quantization of the magnetic charge!

We'll finish this recitation with some discussion of the interaction picture: recall that we started **time-dependent perturbation theory** last lecture, where we have a Hamiltonian of the form

$$H(t) = H_0 + \delta H(t).$$

Note that these two pieces of the Hamiltonian both generate time-dependence for our wavefunction – for an energy eigenstate, we get a phase even if the energy is constant. And the point of the **interaction picture** is to separate out the phase contribution from the other time-dependence: specifically, we cancel out the H_0 phase contribution via

$$|\tilde{\psi}(t)\rangle = e^{iH_0t/\hbar}|\psi(t)\rangle.$$

We then get the interaction picture Schrodinger equation

$$i\hbar\frac{d}{dt}|\tilde{\psi}(t)\rangle = \delta\tilde{H}(t)|\tilde{\psi}(t)\rangle$$

for the **interaction picture operator** $\delta\tilde{H}(t) = e^{iH_0t/\hbar}\delta H(t)e^{-iH_0t/\hbar}$. And this is similar to the Heisenberg picture, in which we conjugate by $e^{iHt/\hbar}$ instead so that the states are completely fixed – here, we're only moving some of the time-dependence to the operators, not all of it.

So if we take a basis of the H_0 unperturbed Hamiltonian satisfying $H_0 |n\rangle = E_n |n\rangle$, then recall that we have

$$\left\langle m \middle| \tilde{\delta H}(t) \middle| n \right\rangle = e^{i\omega_{mn}t} \delta H_{mn}(t).$$

And the idea from here is to look at the representation of our interaction picture wavefunction in terms of the unperturbed basis: we write

$$|\tilde{\psi}\rangle (t) = \sum_n c_n(t) |n\rangle ,$$

where the $c_n(t)$ coefficients basically only encode time dependence due to δH. And recalling that the probability of observing a state $|m\rangle$ at time t is

$$\mathbb{P}_m(t) = |\langle m|\psi(t)\rangle|^2 = \left| \left\langle m \middle| e^{-iH_0 t/\hbar} \middle| \tilde{\psi} \right\rangle \right|^2 = \left|\langle m|\tilde{\psi}(t)\rangle\right|^2$$

(in the last step, we have the $e^{-iH_0 t/\hbar}$ act on the bra, and then the phase cancels and doesn't affect the squared magnitude). And this last expression is exactly $|c_m(t)|^2$, so if we can find those $c_m(t)$ coefficients, that's often the most relevant thing we want to find.

We then get a Schrodinger equation for c given by

$$i\hbar \dot{c}_m(t) = \sum_n c_n(t) e^{i\omega_{mn}t} \delta H_{mn}(t),$$

and we'll see an example of this how to use this on Wednesday where we don't need perturbation theory! (Basically, we'll be looking at **Rabi oscillations**, where we have two-state systems and a solvable Hamiltonian of the form

$$H_0 = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix}, \quad \delta H(t) = \begin{bmatrix} 0 & \gamma e^{i\omega t} \\ \gamma e^{-i\omega t} & 0 \end{bmatrix}.$$

And the point will be to understand how this time-dependent phase affects the evolution of the system.)

26 April 6, 2021

Our paper draft will be due on Wednesday, April 21 – if we haven't heard back from our writing assistant, we should email the course staff. And once our paper is in a reasonable form, we should exchange drafts with our peer editor and make comments!

Last time, we started discussing time-dependent perturbation theory for Hamiltonians of the form $H(t) = H^{(0)} + \delta H(t)$, where $H^{(0)}$ doesn't depend on time and the perturbation $\delta H(t)$ is often only turned on during a time interval $[t_0, t_f]$. It then makes sense to ask for the probability of starting in a particular eigenstate before t_0 and trying to understand the different probabilities of ending up in other eigenstates after t_f.

We separate the trivial time-dependence from $H^{(0)}$ from the nontrivial time-dependence from $\delta H(t)$ using the **interaction picture**: if we define $\left|\tilde{\psi}(t)\right\rangle = e^{iH^{(0)}t/\hbar} |\psi(t)\rangle$, then we get a Schrodinger-like equation $i\hbar \frac{\partial}{\partial t} \left|\tilde{\psi}(t)\right\rangle = \tilde{\delta H}(t) \left|\tilde{\psi}(t)\right\rangle$, but instead of the Hamiltonian, we have the operator

$$\tilde{\delta H}(t) = e^{iH^{(0)}t/\hbar} \delta H(t) e^{-iH^{(0)}t/\hbar}.$$

At the end of last lecture, we started treating δH as a perturbation, and (just like in the first class of 8.06) introduce a dimensionless parameter λ which we use for expansion in a power series

$$\left|\tilde{\psi}(t)\right\rangle = \left|\tilde{\psi}^{(0)}(t)\right\rangle + \lambda \left|\tilde{\psi}^{(1)}(t)\right\rangle + \lambda^2 \left|\tilde{\psi}^{(2)}(t)\right\rangle + \cdots .$$

We found that the zeroth order term for $\left|\tilde{\psi}(t)\right\rangle$ is just the constant $|\psi(0)\rangle$, the first order term is the integral

$$\left|\tilde{\psi}^{(1)}(t)\right\rangle = \int_0^t dt' \frac{\delta\tilde{H}(t')}{i\hbar} |\psi(0)\rangle ,$$

and then higher-order terms have a "nesting" of integrals:

$$\left|\tilde{\psi}^{(2)}(t)\right\rangle = \int_0^t dt' \int_0^{t'} dt'' \frac{\delta\tilde{H}(t')}{i\hbar} \frac{\delta\tilde{H}(t'')}{i\hbar} |\psi(0)\rangle .$$

Basically, everything always acts on the wavefunction $|\psi(0)\rangle$ at time zero, and then we integrate over all times $0 < t'' < t' < t$, and having the operators $\delta\tilde{H}$ at times t'' and then at t' act on our wavefunction.

Fact 120

We can think of time as progressing forward (from 0 to t), and we always have $\delta\tilde{H}$ at an earlier time acting before $\delta\tilde{H}$ at a later time. That's why we often talk about **time-ordered operators**, and this is important because the operators at different times do not usually commute.

(The analogous expression for $\left|\tilde{\psi}^{(n)}(t)\right\rangle$ has n nested integrals, looking over all possible $0 < t_n < t_{n-1} < \cdots < t_1 < t$ and having the $\delta\tilde{H}$s at these different times act on $|\psi(0)\rangle$. But we won't need it for what we're talking about.)

If we write this expression in basis form, where we're using the eigenstates $|n\rangle$ of the unperturbed Hamiltonian, remember that we get an equation

$$\left|\tilde{\psi}(t)\right\rangle = \sum_n c_n(t) |n\rangle ,$$

and we can expand out each term of the power series for $\left|\tilde{\psi}(t)\right\rangle$ in this same way as

$$\left|\tilde{\psi}^{(k)}(t)\right\rangle = \sum_n c_n^{(k)}(t) |n\rangle ,$$

where the superscript k refers to the order in perturbation theory. If we plug this into the power series, we find that each c_n is then also a power series:

$$c_n(t) = \sum_k \lambda^k c_n^{(k)}(t).$$

And now we can start doing order-by-order calculations, equating the two forms for $\left|\tilde{\psi}(t)\right\rangle$.For order 0, since $\left|\tilde{\psi}^{(0)}(t)\right\rangle = \left|\tilde{\psi}(0)\right\rangle$, we know that $c_n^{(0)}(t) = c_n(0)$ is just a constant. Next, for order 1, we know that

$$\left|\tilde{\psi}^{(1)}(t)\right\rangle = \int_0^t dt' \frac{\delta\tilde{H}(t')}{i\hbar} |\psi(0)\rangle = \sum_n c_n^{(1)}(t) |n\rangle ,$$

and $|\psi(0)\rangle$ can be rewritten as $\sum_n c_n(0) |n\rangle$, so that we have

$$\int_0^t dt' \frac{\delta\tilde{H}(t')}{i\hbar} \sum_n c_n(0) |n\rangle = \sum_n c_n^{(1)}(t) |n\rangle .$$

Since this is a vector equality, we put a bra $\langle m|$ on both sides, and we find (by orthogonality on the left and moving integrals and sums outside the inner product)

$$c_m^{(1)}(t) = \int_0^t \frac{dt'}{i\hbar} \sum_n c_n(0) \left\langle m \middle| \delta\tilde{H}(t') \middle| n \right\rangle .$$

The matrix on the right is defined to be $\delta\tilde{H}_{mn}(t')$, so that we get the equality

$$c_m^{(1)}(t) = \sum_n \int_0^t dt' \frac{\delta\tilde{H}_{mn}(t')}{i\hbar} c_n(0).$$

(we assume everything converges so we can freely swap sums and integrals). And now because $\delta\tilde{H}_{mn}$ and δH_{mn} are just related by a phase $e^{i\omega_{mn}(t)}$, where $\omega_{mn} = \frac{E_m - E_n}{\hbar}$, we can write down our answer:

Proposition 121

We have the first-order correction to our coefficients

$$c_m^{(1)}(t) = \sum_n \int_0^t dt' e^{i\omega_{mn}t'} \frac{\delta H_{mn}(t')}{i\hbar} c_n(0).$$

So we can now calculate the probability of being in eigenstate m at time t, which is

$$P_m(t) = |\langle m|\psi(t)\rangle|^2 = \left|\left\langle m\middle|e^{-iH^{(0)}t/\hbar}\middle|\tilde{\psi}(t)\right\rangle\right|^2$$

(trying to write things in terms of the interaction picture). Again we have the $e^{-iH^{(0)}t/\hbar}$ act on the bra, which gives us a phase (because $|m\rangle$ is an eigenstate of $H^{(0)}$, and that phase goes away since we're looking at the squared magnitude. So then we have

$$P_m(t) = \left|\left\langle m\middle|\tilde{\psi}(t)\right\rangle\right|^2 = |c_m(t)|^2.$$

And since we have a perturbative expansion for this, we can write it out as

$$= \left|c_m^{(0)}(t) + c_m^{(1)}(t) + \cdots\right|^2$$

(we're going to set $\lambda = 1$ from now on).

Example 122

As described above, suppose that at time 0, our system is in eigenstate $|n\rangle$ – we wish to find the probability (to first order) $P_{m\leftarrow n}(t)$ that the state will be in state $|m\rangle$ at time t.

In other words, we're told that $\left|\tilde{\psi}(0)\right\rangle = |n\rangle$, so we have coefficients $c_\ell(0) = \delta_{\ell n}$ (the only component we have at the beginning is along the $|n\rangle$-direction), and thus the zeroth-order coefficients are simple: $c_m^{(0)}(t) = c_m(0) = \delta_{mn}$. For the first-order correction $c_m^{(1)}(t)$, notice that we're summing

$$c_m^{(1)}(t) = \sum_\ell \int_0^t dt' e^{i\omega_{m\ell}t'} \frac{\delta H_{m\ell}(t')}{i\hbar} c_\ell(0),$$

and all of the $c_\ell(0)$ vanish except $\ell = n$, so

$$c_m^{(1)}(t) = \frac{1}{i\hbar}\int_0^t dt' e^{i\omega mnt'} \delta H_{mn}(t').$$

So now when we look at the probability

$$P_{m\leftarrow n}(t) = \left|\delta_{mn} + c_m^{(1)}(t) + c_m^{(2)}(t) + \cdots\right|^2,$$

there's two cases: when $m \neq n$, the leading term is given by

$$P_{m\leftarrow n}(t) = |c_m^{(1)}(t)|^2 = \boxed{\frac{1}{\hbar^2}\left|\int_0^t dt' e^{i\omega_{mn}t'}\delta H_{mn}(t')\right|^2 + O(\delta H)^3}$$

(since the $c_m^{(1)}(t)$ coefficient is first-order in δH, its square is second-order in δH, and the largest corrections come from cross-terms between the first and second order corrections). But for $m = n$, we then find

$$P_{n\leftarrow n}(t) = |1 + c_n^{(1)}(t) + c_n^{(2)}(t)|^2 = (1 + c_n^{(1)}(t) + c_n^{(2)}(t) + \cdots)(1 + c_n^{(1)}(t)^* + c_n^{(2)}(t)^* + \cdots)$$

and then expand order-by-order to find

$$= 1 + \left(c_n^{(1)}(t) + c_n^{(1)}(t)^*\right) + \left(|c_n^{(1)}|^2 + c_n^{(2)}(t) + c_n^{(2)}(t)^*\right) + O(\delta H)^3.$$

It turns out that $\left(c_n^{(1)}(t) + c_n^{(1)}(t)^*\right) = 0$, because $\delta H_{nn}(t')$ is always real, $\omega_{nn} = 0$, and thus we have a real integral divided by $i\hbar$, meaning that $c_n^{(1)}(t)$ is purely imaginary. So our first-order term vanishes, and then the next term $\left(|c_n^{(1)}|^2 + c_n^{(2)}(t) + c_n^{(2)}(t)^*\right)$ seems to have terms $c_n^{(2)}(t)$ that we haven't calculated yet, so it seems like we might be stuck. But instead, we can just calculate

$$P_{n\leftarrow n}(t) = 1 - \sum_{m\neq n} P_{m\leftarrow n}(t),$$

since we know each of those probabilities to order $(\delta H)^2$, and that gives us

$$P_{n\leftarrow n}(t) = \boxed{1 - \frac{1}{\hbar^2}\sum_{m\neq n}\left|\int_0^t dt' e^{i\omega_{mn}t'}\delta H_{mn}(t')\right|^2 + O(\delta H)^3}.$$

And noticing that $|c_n^{(1)}(t)|^2$ in the expression we tried originally is positive, so the contributions from $c_n^{(2)}(t)$ and $c_n^{(2)}(t)^*$ are important to make sure the probability $P_{n\leftarrow n}(t)$ is less than 1!

Remark 123. *Notice that the issue with normalization factors from time-independent perturbation theory does not arise in time-dependent perturbation theory, because using the interaction picture keeps our states normalized. So as long as we work consistently to some order k, there will not be any need to renormalize the wavefunction, since our expressions for the perturbed eigenstates will always be normalized.*

Example 124

Consider the case where $\delta H = V$ is time-independent, so that we have a constant perturbation, turned on from time 0 until some time t_0. The perturbation can also be on outside of this interval, but the point is that we start in an eigenstate $|i\rangle$ of the original Hamiltonian $H^{(0)}$ at time $t = 0$ and want to find the probability we're in some eigenstate $|f\rangle$ at time $t = t_0$.

We could use time-independent perturbation theory for this by finding eigenstates of $H^{(0)} + V$ and evolving each of those separately from time 0 to t_0. But it turns out to be more convenient to use the time-dependent formulation: our goal is to find (for all $f \neq i$)

$$P_{f\leftarrow i}(t_0) \approx |c_f^{(1)}(t_0)|^2,$$

where we know the expression for the necessary coefficient:

$$c_f^{(1)}(t_0) = \frac{1}{i\hbar}\int_0^{t_0} dt' = e^{i\omega_{fi}t'}V_{fi}.$$

Now V_{fi} is a time-independent term, and the remaining integral is the integral of an exponential:

$$= \frac{V_{fi}}{i\hbar}\left.\frac{e^{i\omega_{fi}}(t')}{i\omega_{fi}}\right|_{t'=0}^{t_0} = \frac{V_{fi}}{E_f - E_i}\left(1 - e^{i\omega_{fi}t_0}\right),$$

which we can further simplify as

$$= \frac{V_{fi}}{E_f - E_i}e^{i\omega_{fi}t_0/2}\left(-2i\sin\left(\frac{\omega_{fi}t_0}{2}\right)\right),$$

because the phase terms go away when we take the squared magnitude:

$$\boxed{P_{f\leftarrow i}(t_0) \approx \frac{4|V_{fi}|^2}{(E_f - E_i)^2}\sin^2\left(\frac{\omega_{fi}t_0}{2}\right)}.$$

There are two main cases to consider here: we can make transitions to other energies of $H^{(0)}$ (because the Hamiltonian changes when we turn on the perturbation, so energy doesn't need to be conserved), meaning $E_f \neq E_i$, or we could end up in states with the same energy, meaning $E_f = E_i$. (The subtlety here is that during the range from 0 to t_0, we have energy conservation if we're in an energy eigenstate of $H^{(0)} + V$, but we can't say anything about $H^{(0)}$ in general.)

- When $E_f \neq E_i$, we see that the probability of making a transition is proportional to $\sin^2\left(\frac{\omega_{fi}t_0}{2}\right)$, and it oscillates with period $\frac{2\pi}{|\omega_{fi}|}$ and amplitude $\frac{4|V_{fi}|^2}{(E_f - E_i)^2}$. But remember that perturbation theory is only valid when this amplitude (the probability of making a transition) is small, meaning that we must have $\frac{|V_{fi}|^2}{|E_f - E_i|^2} \ll 1$. But this kind of expression should look familiar from time-independent perturbation theory – it is in fact the same criterion! And because we're doing a constant (time-independent) perturbation in this example, we shouldn't be too surprised that the validity criterion is the same.

  But as long as this criterion is satisfied, perturbation theory remains valid at all times, which won't be true in the next case:

- When $E_f = E_i$, the expression $E_f - E_i$ in the denominator does not make sense: we can go back to the integral and do it properly, or we can take the limit $E_f \to E_i$ in our answer. The two procedures give the same answer, so we'll do the limit here, and we find that (expanding $\sin x \approx x$)

  $$P_{f\leftarrow i}^{(1)}(t_0) \approx \frac{4|V_{fi}|^2}{(E_f - E_i)^2}\cdot\left(\frac{\omega_{fi}t_0}{2}\right)^2 = \frac{|V_{fi}|^2t_0^2}{\hbar^2}.$$

  So the probability of making a transition actually **grows quadratically** with t_0, instead of oscillating like it did in the first case! So perturbation theory will break down here at large times because the probability must always be at most 1, but it will always work for sufficiently small times. (And this lines up with the fact that degeneracies require us to be more careful in time-independent perturbation theory.) In fact, the quadratic curve will be a good approximation of the $\sin^2$ expression from the first case for small t_0.

Example 125

Next, consider harmonic perturbations of the form

$$\delta H(t) = \begin{cases} 2H' \cos \omega t & 0 < t < t_0 \\ 0 & \text{otherwise} \end{cases},$$

where H' is a time-independent operator.

(A common example of this kind of Hamiltonian is where we shine electromagnetic radiation on a system, since the electric and magnetic fields oscillate.) We again care about the probability of transitioning to a final state $|f\rangle$ if we start in $|i\rangle$, recalling that the formula is

$$c_f^{(1)}(t_0) = \frac{1}{i\hbar} \int_0^{t_0} dt' e^{i\omega_{fi}t'} \delta H_{fi}(t').$$

Plugging in the form of δH that we have here, this becomes

$$= \frac{1}{i\hbar} \int_0^{t_0} dt' e^{i\omega_{fi}t'} 2\cos(\omega t') H'_{fi},$$

where H'_{fi} is time-independent so it can be taken out of the integral. We can also write the cosine as a sum of two complex exponentials, so that this becomes

$$= \frac{H'_{fi}}{i\hbar} \int_0^{t_0} dt' \left(e^{i(\omega_{fi}+\omega)t'} + e^{i(\omega_{fi}-\omega)t'} \right),$$

and now we can just evaluate the integral: we find that

$$c_f^{(1)}(t_0) = -\frac{H'_{fi}}{\hbar} \left[\frac{e^{i(\omega_{fi}-\omega)t_0} - 1}{\omega_{fi} - \omega} + \frac{e^{i(\omega_{fi}+\omega)t_0} - 1}{\omega_{fi} + \omega} \right].$$

This time, the special cases are the regimes where ω is close to $\pm\omega_{fi}$ – in those cases, the transition probability will be enhanced.

- If $\omega \approx \omega_{fi}$, that basically means the perturbation is tuned to gives us enough drive to make a transition up by $\hbar\omega$ (we almost have resonance in the system). In particular, if $|\omega - \omega_{fi}| \ll \omega$, then the first term of $c_f^{(1)}(t_0)$ dominates, and the probability of a transition is (remembering to take the square)

  $$P_{f \leftarrow i}(t_0) = \frac{4|H'_{fi}|^2}{\hbar^2} \frac{\sin^2\left(\frac{(\omega_{fi}-\omega)t_0}{2}\right)}{(\omega_{fi} - \omega)^2}.$$

  So again we see the probability oscillating, with period $\frac{2\pi}{|\omega_{fi}-\omega|}$ and amplitude $\frac{4|H'_{fi}|^2}{(E_f - E_i - \hbar\omega)^2}$. And if we are exactly on resonance, we get the quadratic behavior that we saw in the constant case also, and this is the case of **absorption** where the system energy very effectively.

- On the other hand, when $\omega \approx -\omega_{fi}$, the system undergoes **stimulated emission**, where $E_f \approx E_i - \hbar\omega$ (so the system is tuned for a downward transition). We'll talk more about this later on when discussing interactions of atoms with light!

27 April 7, 2021 (Recitation)

Today, we'll work out the example that we mentioned at the end of last recitation as an example of a solvable time-dependent Hamiltonian:

Example 126

Suppose that we have a Hamiltonian given by $H(t) = H_0 + \delta H(t)$ for

$$H_0 = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix}, \quad \delta H(t) = \begin{bmatrix} 0 & \gamma e^{i\omega t} \\ \gamma e^{-i\omega t} & 0 \end{bmatrix}.$$

For this particular problem, we have two time-dependent coefficeints $c_1(t)$ and $c_2(t)$, and the equation that we must satisfy is

$$i\hbar \dot{c}_1(t) = \sum_n c_n(t) e^{i\omega_{mn}t} \delta H_{mn}(t),$$

and the only terms with a nonzero δH_{mn} are the off-diagonals, and thus the actual equation is

$$\boxed{i\hbar \dot{c}_1(t) = c_2(t) e^{-i\omega_{21}t} \gamma e^{i\omega t} = \gamma c_2(t) e^{i(\omega - \omega_{21})t}}.$$

(where recall that $\omega_{21} = \frac{E_2 - E_1}{\hbar} = -\omega_{12}$, so we have an extra negative sign in the exponential). Similarly, the equation for the other variable is

$$\boxed{i\hbar \dot{c}_2(t) = c_1(t) e^{i\omega_{21}t} \gamma e^{-i\omega t} = \gamma c_1(t) e^{-i(\omega - \omega_{21})t}}.$$

Again, these are exact differential equations, and we can actually solve the problem exactly for this two-state system (we'll think about the perturbative solution soon).

Suppose that we set up the initial conditions so that $c_1(0) = 1, c_2(0) = 0$ (meaning that we're in state 1 at the start). We can combine the two boxed equations by taking another derivative: by the product rule,

$$i\hbar \ddot{c}_2(t) = \gamma \dot{c}_1(t) e^{-i(\omega - \omega_{21})t} - i(\omega - \omega_{21}) \gamma c_1(t) e^{-i(\omega - \omega_{21})t},$$

and now we can plug in our boxed equations above to simplify this to an equation just involving c_2:

$$i\hbar \ddot{c}_2 = \frac{\gamma}{i\hbar} c_2 - i(\omega - \omega_{21})(i\hbar \dot{c}_2) \implies \ddot{c}_2 + i(\omega - \omega_{21})\dot{c}_2 + \frac{\gamma^2}{\hbar^2} c_2 = 0.$$

Since this differential equation has constant coefficients, we can try $c_2 = e^{\lambda t}$ and we get

$$\lambda^2 + i(\omega - \omega_{21})\lambda + \frac{\gamma^2}{\hbar^2} = 0$$

(since the exponential cancels in all three terms), and by the quadratic formula we have

$$\lambda = i\left(-\frac{1}{2}(\omega - \omega_{21}) \pm \Omega\right), \quad \Omega = \left[\frac{\gamma^2}{\hbar^2} + \frac{(\omega - \omega_{21})^2}{4}\right]^{1/2}.$$

So our general solution looks like (either writing as exponentials or sines and cosines)

$$c_2(t) = e^{-i/2(\omega - \omega_{21})t}\left[A' e^{i\Omega t} + B' e^{-i\Omega t}\right] = e^{-i/2(\omega - \omega_{21})t}\left[A\cos(\Omega t) + B\sin(\Omega t)\right].$$

(And once we know the solution for c_2, we also know the one for c_1, but we'll just work with the former.) Plugging in the initial condition $c_2(0) = 0$ tells us that $A = 0$, and plugging in $c_1(0) = 1 \implies \dot{c}_2 = \frac{\gamma}{i\hbar}$ (from our second boxed equation above) tells us that

$$\Omega B\cos(0) = \frac{\gamma}{i\hbar} \implies B = \frac{-\gamma}{\hbar\Omega}.$$

(the term where we differentiate the phase instead of the cosine is 0 at $t = 0$). In other words, we now have the solution

$$\boxed{c_2(t) = -\frac{i\gamma}{\hbar\Omega}e^{-i/2(\omega-\omega_{21})t}\sin(\Omega t)}.$$

This tells us that the transition probability from 1 to 2 (from time 0 to t) is

$$\boxed{P_{2\leftarrow 1}(t) = |c_2(t)|^2 = \frac{\frac{\gamma^2}{\hbar^2}}{\frac{\gamma^2}{\hbar^2}+\frac{(\omega-\omega_{21})^2}{4}}\sin^2\left(\left[\frac{\gamma^2}{\hbar^2}+\frac{(\omega-\omega_{21})^2}{4}\right]^{1/2}t\right)},$$

and then if we want the probability of staying in state 1, we can just use $|c_1(t)|^2 + |c_2(t)|^2 = 1$. What's interesting about this result is that there are two intrinsic frequencies in the problem, and we can notice that the amplitude of the probability is largest at the resonant condition $\omega = \omega_{21}$ where the two frequencies are tuned to be equal. (The width at which the amplitude becomes smaller than $\frac{1}{2}$ is $\frac{4\gamma}{\hbar}$.)

Fact 127

Because $\sin^2$ oscillates between 0 and its maximum amplitude, the probabilities of transitions will keep changing, and this is related to a phenomenon for the ammonia molecule that we might remember from 8.05.

Example 128

But now we can think about this problem from the perturbation theory perspective, so that $\delta H_{12} = \gamma e^{i\omega t}$ is small. This means we will effectively want to do a power series expansion in γ, and we want to make sure $\frac{\gamma^2}{\hbar^2(\omega-\omega_{21})^2} = 1$.

If we approximate our exact result above with this limiting situation, we find that

$$P_{2\leftarrow 1}(t) = \frac{4\gamma^2}{(\omega-\omega_{21})^2}\sin^2\left(\frac{(\omega-\omega_{21})t}{2}\right).$$

Let's see if we arrive at the same answer through perturbation theory! The first-order correction to the coefficient $c_2(t)$ is (according to lecture)

$$c_2^{(1)}(t) = \int_0^t dt'\frac{e^{i\omega_{21}t}}{i\hbar}\delta H_{21}(t)c_1(0).$$

Plugging in what we know, this simplifies by integration to

$$= \frac{\gamma}{i\hbar}\frac{1}{i(\omega_{21}-\omega)}\left[e^{i(\omega_{21}-\omega)t}-1\right] = -\frac{\gamma}{\hbar(\omega_{21}-\omega)}e^{i(\omega_{21}-\omega)t/2}\cdot 2i\sin\left(\frac{(\omega-\omega_{21})t}{2}\right).$$

And indeed, if we square this result (meaning the phases go away), we indeed get the same answer as we expect.

More generally, returning more to the material we've been covering in lecture, remember that we're doing a perturbative expansion of the form

$$c_n(t) = c_n(0) + c_n^{(1)}(t) + c_n^{(2)}(t) + \cdots,$$

where we have the relation

$$c_m^{(1)}(t) = \sum_n \int_0^t dt' e^{i\omega_{mn}t'}\frac{\delta H_{mn}(t')}{i\hbar}c_n(0).$$

This can be compared to the differential equation $i\hbar \dot{c}_m = \sum_n c_n(t) e^{i\omega_{mn}t} \delta H_{mn}(t)$, and we're basically solving this differential equation perturbatively above by successively getting more integrals. Drawing more parallels with our example above, we have the initial condition for the kth derivative $c_n^{(k)}(t = 0) = 0$ for any positive k, and if we want to calculate the transition probability $P_{m \leftarrow i}(t)$, we compute $|c_m^{(1)}(t)|^2$ with the initial condition $c_n(0) = \delta_{ni}$.

Example 129 (Constant perturbation)

Consider a one-dimensional square well of length a which is usually an infinite well ($V(x) = 0$ for $0 \le x \le a$ and $V(x) = \infty$ otherwise). But from time $0 \le t \le t_0$, we add a constant perturbation to the well so that

$$V(x) = \begin{cases} V_0 & 0 \le x \le a/2 \\ 0 & a/2 \le x \le a \\ \infty & \text{otherwise.} \end{cases}$$

In other words, we raise half of the square well from time 0 to t_0, and we've derived using first-order perturbation theory in lecture that the transition probability is

$$P_{f \leftarrow i}(t_0) = \frac{4|V_{fi}|^2}{(E_f - E_i)^2} \sin^2\left(\frac{\omega_{fi} t_0}{2}\right).$$

For example, if we start off in the ground state $|i\rangle = |1\rangle$, we can calculate the probability that we are in state $|f\rangle = |2\rangle$ at some later time t, and what we care about is the matrix element

$$V_{21} = \langle 2|V|1\rangle = \int_0^{a/2} dx V_0 \frac{2}{a} \sin\left(\frac{2\pi x}{a}\right) \sin\left(\frac{\pi x}{a}\right)$$

(since we know the wavefunctions for the square well). And plugging this back in gives us the answer for the transition probability without too much work! Generally, we find that $\langle n|V|1\rangle = \frac{2n}{1-n^2} \frac{(-1)^{n/2}}{\pi} V_0$ when n is even and 0 when n is odd, and we'll see that transitions to higher energy levels n fall off as $\frac{1}{n}$. (But the assumption we do need to make for perturbation theory to be valid is that this coefficient is small to begin with, so V_0 must be smaller than the ground state energy E_1.)

28 April 8, 2021

Last time, we started discussing some applications of time-dependent perturbation theory, concentrating on two kinds of perturbations (the cases where $\delta H(t) = V$ doesn't depend on time, and where $\delta H(t) = 2H' \cos(\omega t)$ oscillates harmonically). We cared about the value of $P_{f \leftarrow i}(t_0)$, the probability of transitioning from state i to f in the time interval $[0, t_0]$, and the answers were that

$$P_{f \leftarrow i}(t_0) \approx \frac{|V_{fi}|^2}{\hbar^2} \frac{4 \sin^2\left(\frac{\omega_{fi} t_0}{2}\right)}{\omega_{fi}^2}$$

for a constant perturbation (in which the probability is enhanced for ω_{fi} small, meaning that the difference between energies is small), and

$$P_{f \leftarrow i}(t_0) \approx |H'_{fi}|^2 \frac{4 \sin^2\left(\frac{(\omega_{fi} \pm \omega) t_0}{2}\right)}{(\omega_{fi} \pm \omega)^2}$$

for a harmonic perturbation where the energy difference is $E_f \approx E_i \mp \hbar\omega$, respectively (and in which we see the probability is enhanced for $\omega \approx \omega_{fi}$, leading to resonance).

Today, our next step is to start thinking about transitions to a **continuum** of states. We've been thinking about the transition probabilities for a fixed initial and final state $|i\rangle$ and $|f\rangle$, and we've been treating these as part of a discrete set of states. But there are two main situations that we might consider where we have a continuum of states instead:

Example 130

Recall that the hydrogen atom Hamiltonian has discrete bound states for $E < 0$ and continuum scattering states for $E > 0$. We may ask for the probability of transitioning from a bound state $|i\rangle$ to some state in the continuum: for example, if we shine light on a hydrogen atom, we want the probability that after some time, the electron becomes ejected and free.

Example 131

Another situation which comes up is where the spectrum of discrete states is embedded within the continuum of other states (for example, this comes up in autoionization). Then we may again want the probability that we go from a discrete state to the continuum.

The key is that we will not be asking about the probability of being in a **particular** state of the continuum, only the entire continuum as a whole, and the perturbations we'll be analyzing will be again those where $\delta H(t) = V$ or $\delta H(t) = 2H' \cos(\omega t)$ (constant or harmonic). Motivated by the calculations we did last lecture, we expect most transitions to happen where $E_f \approx E_i$ for a constant perturbation, and where $E_f \approx E_i \pm \hbar\omega$ (absorption or emission). And we'll find in both cases that the probability will grow **linear in time**, meaning that we can associate a finite transition rate (which was not something we could do in the settings before).

Before we get started with this calculation, we need a technical ingredient – we need to be able to describe our states in the continuum. The way that we'll do this is to restrict ourselves to a discretization first – we **place our system in a cubic box** of size L. For a situation like the hydrogen atom, we know that the discrete part of the spectrum will be largely unaffected if L is large enough, but the continuous part will **become discrete** (because we have a particle-in-a-box situation), with spacing between those discrete energy levels decreasing as $L \to \infty$. So we will begin with a modeling by this set of discrete levels, and taking the limit later lets us check that L indeed drops out of all relevant physical quantities.

Definition 132

The **density of states** $\rho(E)$ is defined so that

$$\text{number of states } dn \text{ in energy interval } dE \text{ around } E = \rho(E)dE.$$

This is a useful quantity because we need to be able to take sums over this continuous part of the spectrum (since we want, for example, to add up the probabilities that we make a transition from our initial state to any of the continuum states), and the density of states helps us change this sum to an integral. Although $\rho(E)$ as defined does depend on the size of our box, we will see that the L-dependence will cancel out eventually.

Example 133

Consider a free particle in three dimensions, so that $H_0 = \frac{p^2}{2m}$, so that our eigenstates are plane waves

$$\psi(x, y, z) = e^{i(k_x x + k_y y + k_z z)}.$$

with energy $E = \frac{\hbar^2 \vec{k}^2}{2m}$.

If the particle is completely free, k_x, k_y, k_z can be any real number, so the energy spectrum is indeed continuous. But now let's place the system in a box of length L: it turns out that the physics of the system in the middle of the box will be basically not dependent on the boundary of the box, so we should be able to use whatever boundary conditions are convenient for us. And the easiest ones to work with are often the **periodic boundary conditions** where

$$\psi(x, y, z) = \psi(x + L, y, z) = \psi(x, y + L, z) = \psi(x, y, z + L)$$

for all x, y, z. Plugging in our plane wave solutions, we find that $e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1$, so that we must have $k_x = \frac{2\pi}{L} n_x$ for some integer n_x and similar for k_y and k_z. So all states in our box will be labeled by these three integers (n_x, n_y, n_z), and our normalized states in a box will look like

$$\psi(x, y, z) = \frac{1}{\sqrt{L^3}} \exp\left(\frac{2\pi i}{L}(n_x x + n_y y + n_z z)\right).$$

We can now compute the density of states: we can look in momentum space at (k_x, k_y, k_z), in which our states occupy a cubic lattice with spacing $\frac{2\pi}{L}$. If we now think about a box of fixed side lengths dk_x, dk_y, dk_z in momentum space, the **number** of states inside that box will be roughly

$$\frac{dk_x dk_y dk_z}{\left(\frac{2\pi}{L}\right)^3} = \frac{L^3}{(2\pi)^3} d^3k.$$

This is indeed a dimensionless number, because k has units of inverse length, and it diverges as $L \to \infty$ (because our spacing continues to get smaller). And now we need to convert between energy and momentum, since we care about $dn = \rho(E)dE$. But because we have the energy relation

$$E = \frac{\hbar^2 \vec{k}^2}{2m},$$

we know that the contours of constant energy are spheres in momentum space of fixed $|\vec{k}|$, so that states in an energy interval $[E, E + dE]$ live in a spherical shell which has some width dk in momentum space, where we can relate dE and dk via

$$dE = \frac{\hbar^2}{m} k dk.$$

So putting everything together, we can divide our spherical shell into small boxes in momentum space, so that the number of states in the shell will then be

$$dn = d^3k \frac{L^3}{(2\pi)^3}.$$

We can convert to spherical coordinates (since the integrand is spherically symmetric) so that our box now has some radial width dk and some solid angle $d\Omega = sin\theta d\theta d\phi$. So the volume element is

$$d^3k = k^2 dk d\Omega,$$

meaning that we can substitute in

$$dn = \left(\frac{L}{2\pi}\right)^3 k^2 dk d\Omega = \left(\frac{L}{2\pi}\right)^3 k(kdk) d\Omega = \boxed{\left(\frac{L}{2\pi}\right)^3 \frac{mk}{\hbar^2} d\Omega} dE,$$

and now the boxed part looks exactly the density of states, except that we also have a "per solid angle" factor that will be useful for later calculations! And we can write our answer for $\rho(E)$ per solid angle explicitly in terms of E by substituting back in with $k = \frac{\sqrt{2mE}}{\hbar}$.

Example 134

Let's now consider the case where we have a constant perturbation $\delta H(t) = V$, our system starts at a discrete level $|i\rangle$, and this discrete level overlaps with the continuum of states labeled by $|f\rangle$ (where f labels over all continuum states). We want to find the probability that we transition from $|i\rangle$ to some $|f\rangle$.

The total transition probability here can be written as

$$P_{\text{trans}}(t_0) = \sum_f P_{f \leftarrow i}(t_0).$$

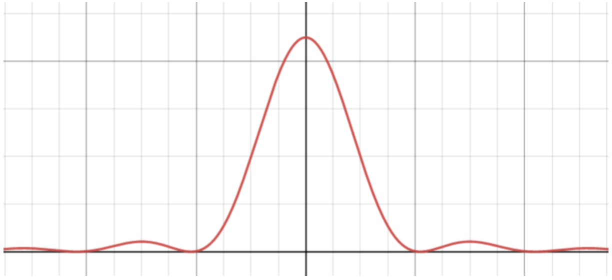
Since our setup here is to discretize our continuum spectrum, we can use the perturbation theory equation that we had above for the transition from some $|i\rangle$ to $|f\rangle$ under a constant perturbation! Substituting this in, we find that

$$P_{\text{trans}}(t_0) = \sum_f \frac{|V_{fi}|^2}{\hbar^2} \frac{4\sin^2\left(\frac{\omega_{fi} t_0}{2}\right)}{\omega_{fi}^2} = \sum_f \frac{|V_{fi}|^2}{\hbar^2} F(\omega_{fi}, t_0),$$

where we should again remember that $\omega_{fi} = \frac{E_f - E_i}{\hbar}$, V_{fi} is the matrix element between $|i\rangle$ and $|f\rangle$, and we define $F(\omega, t) = \frac{\sin^2(\omega t/2)}{(\omega/2)^2}$. And now the density of states comes in: we approximate the sum over f with an integral

$$= \int dE_f \rho(E_f) \frac{|V_{fi}|^2}{\hbar^2} F(\omega_{fi}, t_0),$$

where we're making the assumption that $|V_{fi}|^2$ doesn't change too much between nearby states so that we can actually evaluate this integral. And now at a fixed time t, we know that the function $F(\omega, t)$ has a central peak around $\omega = 0$ and some other peaks with amplitude decaying as $\frac{1}{\omega^2}$:



Furthermore, this function becomes narrower and narrower at time t and thus becomes more and more peaked. So the point is that we're integrating $|V_{fi}|^2 \rho(E_f)$, some smooth function of energy, against this sharply peaked function $F\left(\frac{E_f - E_i}{\hbar}, t_0\right)$ centered at E_i, so we can approximate $|V_{fi}|^2 \rho(E_f)$ with its value around E_i, and thus the transition probability for large enough t_0 can be written as

$$P_{\text{trans}}(t_0) \approx \frac{|V_{fi}|^2 \rho(E_i)}{\hbar^2} \int dE_f F\left(\frac{E_f - E_0}{\hbar}, t_0\right).$$

Fact 135

The way to understand the expression V_{fi} in the equation above when taken out of the integral is to think about

$$V_{fi} = \langle f|V|i\rangle$$

evaluated at the energy $E_f = E_i$. It's possible that the final states f may be labeled by both energy and other variables, so that this matrix element may depend on which of the state $|f\rangle$ we choose at energy E_f. So in those situations, we define the rate of transition for each specification of those variables, and then we can integrate over all specifications to get the total rate.

This integral is now easier to evaluate: changing variables, we can write the integral part as

$$\int_{-\infty}^{\infty} d(\hbar\omega_{fi})F(\omega_{fi}, t_0) = \hbar \int d\omega_{fi} \frac{\sin^2\left(\frac{\omega_{fi}t_0}{2}\right)}{(\omega_{fi}/2)^2},$$

and now if we make another change of variables $u = \frac{\omega_{fi}t_0}{2}$, we end up with

$$= \hbar \int_{-\infty}^{\infty} du \frac{2}{t_0} \frac{\sin^2 u}{(u/t_0)^2} = 2\hbar t_0 \int_{-\infty}^{\infty} du \frac{\sin^2 u}{u^2},$$

and this integral is just a constant which turns out to be π (we can do this by contour integration, for example). So notice that this is linear in t_0 (which we could have anticipated because $F(\omega, t)$ has largest peak proportional to t^2 and width proportional to $\frac{1}{t}$), and substituting this back into our transition probability gives us

$$P_{\text{trans}}(t_0) = \frac{2\pi}{\hbar}|V_{fi}|^2\rho(E_i)t_0,$$

and indeed, the probability of making a transition into one of the continuum state grows linearly with time! And this gives us the transition rate

$$\boxed{w = \frac{2\pi}{\hbar}|V_{fi}|^2\rho(E_i)},$$

and this is known as **Fermi's golden rule**. (What's interesting is that even though the different transition rates to states $|f\rangle$ oscillate in time, adding them all up gives us finite transition rate.)

Remark 136. *We can check that the dimensions of w are indeed inverse time (because V_{fi} has units of energy, so $|V_{fi}|^2\rho(E_i)$ has units of energy as well, and then dividing by $\hbar$ gives us the correct units. And we can also notice that the transitions are (increasingly narrowly) occurring mostly to states where $E_f \approx E_i$, specifically in the range*

$$E_i - \frac{2\pi m\hbar}{t_0} \le E_f \le E_i + \frac{2\pi m\hbar}{t_0}$$

for some constant m (which basically tells us how many "lobes" of the F function we want to include). In other words, the energy becomes "more and more conserved" as time goes on!

But we also need to discuss the conditions under which this expression actually applies: we've already mentioned that we need t_0 to be large enough so that we can approximate $|V_{fi}|^2\rho(E_f)$ by its value at E_i. But we also need t_0 to be short enough so that the probability of making a transition stays small, since time-dependent perturbation theory only applies if the wavefunction doesn't change much from its initial value. We'll discuss this more next time!

29 April 12, 2021 (Recitation)

We'll continue our discussion from last time, looking at harmonic time-dependent perturbations. First, a review: in first-order time-dependent perturbation theory, we want to solve for the mth state coefficient

$$c_m^{(1)}(t) = \frac{1}{i\hbar}\int_0^t dt' e^{i\omega_{mi}t'}\delta H_{mi}(t')$$

which tells us about the (approximate) probability of transitioning from our initial state i to a final state m (this is like substituting in $c_i(0) = 1$ and $c_n(0) = 0$ for all $n \neq i$), since $P_m(t) = |c_m^{(1)}(t)|^2$ to leading order. In the special case where we have a harmonic perturbation, we think about a particular kind of time-dependence $\delta H = 2H' \cos(\omega t)\theta(t)$ (the step function $\theta(t)$ meaning that we start the perturbation at 0), and we normalize it in this way because it makes it easier to substitute $2\cos x = e^{ix} + e^{-ix}$ in terms of exponentials.

Generically, both of those exponentials come into the picture, but we like to study the special cases where one term dominates over the other, meaning that the ω or $-\omega$ balances out with the ω_{mi} that is already in the exponential. We then found that if $\omega \approx \omega_{mi} > 0$, more specifically $|\omega - \omega_{mi}| \ll |\omega_{mi}|$, we had (from here, we're switching to using f instead of m to match lecture notation)

$$P_{f\leftarrow i}(\omega, t_0) = \frac{4|H'_{fi}|^2}{\hbar^2(\omega_{fi} - \omega)^2}\sin^2\left((\omega_{fi} - \omega)\frac{t_0}{2}\right).$$

We can think of this as an "absorption" situation, in which our state jumps up from $|i\rangle$ to $|f\rangle$ by an energy of $E_f - E_i = \hbar\omega_{fi}$, because our incoming perturbation has frequency $\omega \approx \omega_{fi}$. (So this is kind of an "energy conservation," where the energy $\hbar\omega$ is being taken out of the applied perturbation field and into our system. We don't actually have energy conservation here because our time-dependent field is inputting energ, though.y)

On the other hand, we also have a case where $\omega \approx -\omega_{fi} > 0$, and then we have

$$P_{f\leftarrow i}(\omega, t_0) = \frac{4|H'_{fi}|^2}{\hbar^2(\omega_{fi} + \omega)^2}\sin^2\left((\omega_{fi} + \omega)\frac{t_0}{2}\right).$$

This is known as "stimulated emission," and the idea is that the perturbation field causes our system to release energy externally.

Example 137

Consider an electromagnetic wave (a solution to Maxwell's equations with oscillating electric and magnetic fields) where we have $\vec{E} = E_0\hat{z}\cos(\omega t - ky)\theta(t)$. (This is a wave polarized in the $\hat{z}$ direction, traveling in the $\hat{z}$ direction, and we should remember that $\frac{\omega}{k} = c$ because waves travel at the speed of light.)

We consider a hydrogen atom at the origin, in the ground state $1s = |1, 0, 0\rangle$ at times $t \le 0$, and we want to find the probability of transitioning from $1s$ to $2p$ at time t_0. The approximation that is good to make here is that

$$\lambda_{\text{atom}} \approx a_0 \ll \lambda_{\text{wave}} = \frac{2\pi}{k} = \frac{2\pi c}{\omega}.$$

It turns out that the frequencies that are most likely to cause a transition do always satisfy this inequality. So we'll make that simplification, and it makes it a bit simpler to simplify the applied electric field in this case.

It does look like things are harmonically oscillating in this problem, but instead of a $\cos\omega t$, we have a $\cos(\omega t - ky)$ (meaning that we have a traveling wave). But the point is that our atom doesn't really see the spatial extent of this wave – it only sees a y-patch of length λ_{atom} centered at a single point. So in other words, we can just substitute

$y = 0$ into our electric field and find that

$$\vec{E} = E_0 \hat{z} \cos(\omega t - ky)\theta(t) = E_0 \hat{z} \cos(\omega t)\theta(t).$$

To get this into a perturbation, we need to write things in terms of the electromagnetic potentials, and here we can solve $\vec{E} = -\nabla\Phi \implies \Phi = -\vec{r} \cdot \vec{E}$ (we should check that this function Φ does indeed give us back our electric field), so then we find that the change to our Hamiltonian is

$$\delta H(t) = q\Phi = -q\vec{r} \cdot \vec{E} = qE_0 z \cos(\omega t)\theta(t).$$

So the coefficient we care about is $H' = -\frac{qE_0 z}{2}$ (the extra 2 because our perturbation should be $2H' \cos(\omega t)$), and now we go back to our formula above: we just need to find the matrix element between $1s$ and $2p$

$$H'_{fi} = \langle 21m|H'|100\rangle = -\frac{qE_0}{2} \langle 21m|z|100\rangle\,,$$

and the only nonzero matrix element is where $m = 0$ here, because L_z and z commute and thus $\langle 21m|[L_z, z]|100\rangle = 0$. (Alternatively, the matrix elements must all have even exponents of each of x, y, z, and we get a z from $m = 1$ but none from $m = 0$.) It turns out that this evaluates to

$$= -\frac{qE_0}{2}\delta_{m0} a_0 \frac{180\sqrt{2}}{243},$$

so plugging everything back in gives us our answer for the probability of going from the $1s$ to the $2p$ state

$$P_{1s\to 2p}(t_0) = \frac{4|H'_{fi}|^2}{\hbar^2(\omega_{fi} - \omega)^2} \sin^2\left((\omega_{fi} - \omega)\frac{t_0}{2}\right),$$

where this formula applies when $\omega \approx \frac{\omega_{fi}}{2} = \frac{E_2 - E_1}{2}$. (This is like "absorbing $\hbar\omega$ of energy to make a transition upwards in our hydrogen atom.) And we get a similar expression for the transition probability from $2s$ to $1p$, and everything would stay the same except that we use $\omega_{fi} + \omega$ instead of $\omega_{fi} - \omega$. And we should remember that in either case, our formulas are only valid when $|\omega - \omega_{fi}| \ll |\omega_{fi}|$ (otherwise we'd need to include contributions from both exponential terms and that gives us some cross-terms).

Fact 138

We may notice that our atom gained angular momentum when going from $1s$ to $2p$, but that's because "the electromagnetic field also has angular momentum" – photons have spin 1.

We can also tweak our problem setup a little bit:

Example 139

Now suppose that we replace the hydrogen atom by a 3-dimensional harmonic oscillator, which has Hamiltonian $H_0 = \frac{\vec{p}^2}{2m} + \frac{1}{2}m\omega_0^2\vec{x}^2$.

We again make the approximation where the typical wavelength of the oscillator satisfies $\lambda_0 = \sqrt{\frac{\hbar}{m\omega_0}} \ll \lambda_{\text{wave}}$, and we have energies $E_{\vec{n}} = (n_x + n_y + n_z + \frac{3}{2})\hbar\omega_0$. A lot of calculations like before look similar, but we have a different matrix element

$$\left\langle n_x n_y n_z \middle| z \middle| n'_x n'_y n'_z \right\rangle,$$

where $z \sim a_z + a_z^\dagger$. Then the selection rules tell us that we must have $n_x = n'_x$, $n_y = n'_y$, and $n_z = n'_z \pm 1$.

Example 140

Suppose that we have our hydrogen atom again, but we now replace our electric field to be a decaying exponential pulse $\vec{E}(t) = E_0 \hat{z} e^{-\gamma t}\theta(t)$.

This time, our perturbation will look like

$$\delta H(t) = -qE_0 z e^{-\gamma t},$$

and this is neither a constant perturbation nor a harmonic one. So we'll need to redo the time integral

$$c^{(1)}_{1s\to 2p}(t_0) = \int_0^{t_0} dt' e^{-\gamma t'} e^{i\omega_{21}t'} \frac{-qE_0 a_0 \frac{180\sqrt{2}}{243}}{i\hbar}$$

(the matrix element stays the same as before), and then the remaining time-integral is an easily evaluated integral $\frac{1}{i\omega_{21}-\gamma}\left(e^{(i\omega_{21}-\gamma)t_0} - 1\right)$. Squaring the result gives us the transition probability

$$P_{1s\to 2p}(t_0) = |c^{(1)}_{1s\to 2p}(t_0)|^2,$$

but we can do things easily in the case where $t_0 \to \infty$: the $e^{(i\omega_{21}-\gamma)t_0}$ term always goes to 0 because $\gamma > 0$, and thus we have

$$P_{1s\to 2p}(t_0) = \left(\frac{qE_0 a_0 \frac{180\sqrt{2}}{243}}{\hbar}\right)^2 \frac{1}{\omega_{21}^2 + \gamma^2}.$$

Indeed, if $\gamma \to \infty$, we see that the transition probability goes to zero, which makes sense – having an infinitesimally short pulse basically turns off the electric field.

30 April 13, 2021

Last time, we discussed Fermi's golden rule, which basically told us that when we want to make a transition into a continuum of states, we have (after some initial transient time) a constant transition rate

$$P_{\text{trans}}(t_0) = wt_0, \quad w = \frac{2\pi}{\hbar}|V_{fi}|^2 \rho(E_f)\bigg|_{E_f=E_i}.$$

We're now going to understand when this is a valid expression, and we will do so first by going back to the derivation. Recall that we discretized our system, wrote a transition probability over a sum of states, and then converted this to an integral

$$\int dE_f \rho(E_f) \frac{|V_{fi}|^2}{\hbar^2} F(\omega_{fi}, t_0),$$

where F is a sharply-peaked function which becomes more and more like a delta function as t_0 gets large. The approximation we made was that our F is thin enough that $\rho(E_f)\frac{|V_{fi}|^2}{\hbar^2}$ is approximately constant over the relevant part of the integral, and we'll now make that more precise. If we define the **band width** Δ to be the energy range around E_i so that $|V_{fi}|^2\rho(E_f)$ changes significantly, then our condition will be that Δ should be much bigger than the width of one of the lobes of F, which we can restate as

$$\Delta \gg \frac{\hbar}{t_0} \iff t_0 \gg \frac{\hbar}{\Delta}.$$

So this $\frac{\hbar}{\Delta}$ is the "transient time" before the finite-rate linear growth is apparent. But there is another term as well – the transition probability cannot keep growing linearly with time, and time-dependent perturbation theory only works when the changes of the wavefunction from the initial value are small. So the transition probability cannot be of order 1, and thus the other condition is

$$P_{\text{trans}}(t_0) \ll 1 \implies t_0 \ll \frac{1}{w}.$$

In particular, we can only have both of these conditions $\frac{\hbar}{\Delta} \ll t_0 \ll \frac{1}{w}$ hold if $\hbar w \ll \Delta$, and that's the same as saying that the "energy perturbation is weak."

We'll now turn our attention to the regime where t_0 gets larger than $O(\frac{1}{w})$ (but we still have $\hbar\omega \ll \Delta$). Our time-dependent perturbation theory does not work anymore, but with some care, we can still study the system. Defining $P_i(t) = 1 - P_{\text{trans}}(t)$ to be the probability of remaining in a state i, it turns out that we have the rate equation

$$\frac{dP_i}{dt} = -wP_i(t)$$

for all $t \gtrsim \frac{\hbar}{\Delta}$, and thus we have $P_i(t) = e^{-wt}$. (And here, we can see that for small times, $e^{-wt} \approx 1 - wt$ gives us the expected linear growth, and as t gets larger, the higher-order.)

Remark 141. *The reason we're ignoring the other discrete times here is that their probabilities oscillate in time and are thus smaller than the linearly-growing rate of transitioning to the continuum. But the continuum transition is dominating here because our energy E_i is already in the continuum and because our V is constant – if we do not have an overlap, Fermi's golden rule will not apply and we will not have a finite transition rate for constant perturbations.*

If we think about $t \gg \frac{1}{w}$, we see that $P_i(t) \to 0$, so the system transitions out of the initial state with high probability. To figure out where the states actually end up, we should think more about the function F again – the window of energies into which we make non-negligible transitions initially shrinks with time, but once the system has already decayed from the initial state (for $t \gg \frac{1}{w}$), it turns out the distribution of final-state probabilities will still be basically centered around E_i, but the width of the distribution will be roughly $\hbar w$, and in fact we have the precise formula

$$P_{f\leftarrow i}(t = \infty) = \frac{|V_{fi}|^2}{(E_f - E_i - \delta E)^2 + \frac{\hbar^2\omega^2}{4}},$$

and we have a Lorentzian distribution. Because of this, w here is called the **line width** (along with "decay rate"), and we measure the transition rate by looking at the final limiting distribution rather than trying to calculate the decay rate! (The δE term is a small constant shift due to the perturbation V, but we won't get into the details there.)

Remark 142. *The formula above is the probability of transitioning to a particular state, so if we wanted to sum up probabilities over all states, we would need to do an integral that involves $\rho(E_f)$, and we can indeed check that this integral is equal to* 1.

Example 143

We'll now discuss **autoionization of atoms** as an application of this formalism. Consider a helium atom, which has two protons and two electrons, so that the Hamiltonian is the kinetic energy terms plus the Coulomb interactions

$$H = \frac{\vec{p}_1^2}{2m} + \frac{\vec{p}_2^2}{2m} - \frac{Ze^2}{|\vec{r}_1|} - \frac{Ze^2}{|\vec{r}_2|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

(placing the nucleus fixed at the origin).

We'll treat the first four terms here as the unperturbed Hamiltonian $H^{(0)}$ and the last term as our constant perturbation V. Since $H^{(0)}$ describes two decoupled electrons in "hydrogenic atom" setups, the energy spectra of those two systems are being added together, and we have energy levels

$$E = E_1 + E_2 = (-13.6 \text{ eV})Z^2 \left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) = -54.4 \text{ eV} \left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)$$

(since $Z = 2$ for the helium atom), with ground state $E_{1,1} = -108.1$ eV, first excited state $E_{2,1}$ (or $E_{1,2}$), and then subsequent excited states are $E_{3,1}, E_{4,1}, \cdots$, up to $E_{\infty,1}$ (which has energy -54.4 eV. Up until this point, we've been requiring $n_2 = 1$, and that's because the lowest energy level where both atoms are excited is $E_{2,2} = -27.2$ eV. So the point is that because we can have one of the atoms in its continuum states and the other in the ground state and get a continuum of energies above -54.4 eV, at this approximation (without any hybridization), **the discrete level $E_{2,2}$ will be embedded in the continuum**.

So we'll start our system in the initial state $(2s)^2$ (two electrons in the 2s state), and we'll try to transition to a state of the form $1s+\text{free}$ (one electron decays to the ground state, and the other electron is ejected into a scattering state). We know that the final energy should be approximately equal to the initial energy for this Fermi's golden rule situation, so

$$E_f = -54.4 \text{ eV} + E_{\text{free}} \approx E_i = -27.2 \text{ eV},$$

and our ejected electron should have energy 27.2 eV. So in principle, we can calculate the probability of transitioning, and in fact the rate is pretty big because the perturbation V is not actually that small (so we're not even fully justified in using Fermi's golden rule)! So we might ask how such a transition might happen in practice, and this is known as the **Auger effect**:

Fact 144

If we imagine an atom like magnesium with many electrons, we can imagine shooting in an x-ray and exciting one of the core electrons into a higher level. (This is actual ionization, rather than autoionization.) From this point, the atom can autoionize, so that one of the electrons goes back to the inner shell and the other (called the Auger electron) is ejected.

We'll now turn our attention to the **harmonic perturbations** and how they cause transitions into the continuum. Recall that we use the perturbation

$$\delta H(t) = 2H' \cos(\omega t)$$

(where we should not confuse ω with the rate w), which is good at driving transitions from an initial state of energy E_i into states of energy approximately $E_i \pm \hbar\omega$ (with $+$ being absorption and $-$ being stimulated emission).

We'll find that we again get a constant transition rate in those regimes, and the formalism is very similar. We'll do the absorption case, where we want the probability of being in the continuum around $E_f = E_i + \hbar\omega$: we know that for a general state around this range, we have

$$P_{f\leftarrow i}(t_0) = \frac{4|H'_{fi}|^2}{\hbar^2} \frac{\sin^2\left(\frac{\omega_{fi}-\omega}{2} t_0\right)}{(\omega_{fi} - \omega)^2},$$

where $\omega_{fi} = \frac{E_f - E_i}{\hbar}$, so the probability of transitioning to any continuum state via this absorption can be approximated with an integral

$$= \int dE_f \rho(E_f) P_{f\leftarrow i}(t_0) = \int dE_f \rho(E_f) \frac{4|H'_{fi}|^2}{\hbar^2} \frac{\sin^2\left(\frac{\omega_{fi}-\omega}{2} t_0\right)}{(\omega_{fi} - \omega)^2}.$$

So this looks similar to the constant-perturbation case: we have a term that depends on the specific initial state, and then we have the blue term that looks like the $F(\omega_{fi}, t_0)$ we had before – the main difference is that

$$\omega_{fi} - \omega = \frac{E_f - E_i}{\hbar} - \omega,$$

so we get the same multi-lobe function but now centered at $E_i + \hbar\omega$ instead of E_i. And the result we end up with is similar to before (this is called Fermi's golden rule, too):

$$\boxed{P_{\text{trans}}(t_0) = wt_0, \quad w = \frac{2\pi}{\hbar}\left(\rho(E_f)|H'_{fi}|^2\right)_{E_f = E_i + \hbar\omega}}.$$

Basically, the only differences are that we look at H' instead of V, and we evaluate our ρ and H' at $E_f = E_i + \hbar\omega$ instead of E_i. And stimulated emission looks very similar, just with $E_f = E_i - \hbar\omega$ instead.

Example 145

We'll now study the **ionization of hydrogen**: suppose we shine light on a hydrogen atom, so that the electron goes from bound to free, flying away with some energy and momentum. We want to calculate the rate of this process.

In particular, we'll assume the light comes in with frequency ω high enough that it can ionize the hydrogen electron, which has ground state energy -13.6 eV $= -$Ry (Ry stands for Rydberg and is equal to $\frac{e^2}{2a_0} = \frac{\hbar^2}{2ma_0} = \frac{1}{2}\alpha^2 mc^2$). So the final energy will be $E_f = E_i + \hbar\omega$, and the ionization only happens if $\hbar\omega > \text{Ry}$. (We will think about this light as an electromagnetic wave, but we can also think about it in terms of incoming photons.) And because $E_f = \frac{\hbar^2 k^2}{2m}$, we can also find the outgoing momentum $\hbar k$ for our (free) electron.

We'll make a few approximations to make this calculation possible: first of all, we assume the wavelength of the light $\lambda = \frac{2\pi}{q} = \frac{2\pi c}{\omega}$ is much larger than the Bohr radius a_0. So the magnitude of the electric field does not vary much over the size of the atom, and it is roughly constant. For this approximation to work, we must have

$$\frac{\lambda}{a_0} = \frac{2\pi}{\hbar\omega}\frac{\hbar c}{a_0} = \frac{2\pi}{\alpha}\frac{1}{\hbar\omega}\frac{e^2}{a_0}.$$

Since $\frac{e^2}{2a_0}$ is the Rydberg, this can be further written as

$$= \frac{4\pi}{\alpha}\frac{\text{Ry}}{\hbar\omega},$$

and this is the quantity that we need to be large. That means we basically need $\hbar\omega \ll 1700\text{Ry} \approx 23$ keV, so the frequency cannot be **too** large.

We'll also impose the simplification that our electron is nearly free, so that it's not affected much by the attraction to the nucleus. This is basically saying that the energy of the outgoing electron should be much larger than the Rydberg (the characteristic energy of the hydrogen atom), meaning that $\hbar\omega - \text{Ry} \gg \text{Ry}$. Putting this together with the above condition, we see that the range we're looking at is

$$\text{Ry} \ll \hbar\omega \ll 1700 \text{ Ry}.$$

In particular, the ejected electron will be non-relativistic, so we won't need to worry about relativistic effects. And we can reformulate this condition into a condition on the wavevector $\vec{k}$ for our ejected electron as well: we have

$$E_f = \frac{\hbar^2 k^2}{2m} = \hbar\omega - \text{Ry} \approx \hbar\omega \implies \text{Ry} \ll \frac{\hbar^2 k^2}{2m} \ll 1700 \text{ Ry},$$

which further simplifies to

$$\frac{\hbar^2}{2ma_0^2} \ll \frac{\hbar^2 k^2}{2m} \ll 1700\frac{\hbar^2}{2ma_0^2} \implies 1 \ll (ka_0)^2 \ll 1700,$$

meaning that $1 \ll ka_0 \ll 40$. And this approximation $ka_0 \gg 1$ will be one that we will use in our calculation shortly – our job next time will be to figure out the (harmonic) perturbation from our incoming shining light, understanding how the Hamiltonian of our system is affected by understanding the vector and scalar potential, and then calculate matrix elements and the density of states to get our final answer.

Remark 146. *The reason for discussing the wavevector as well as the energy of the is that we may care about ionization rates in each direction of $\vec{k}$, and because we will be approximating our continuum states as plane waves. So $\vec{k}$ will explicitly enter the final state wavefunctions, and we need that to calculate the matrix element!*

31 April 14, 2021 (Recitation)

We'll discuss Fermi's golden rule today, doing calculations a slightly different way, and then derive a few of the results we found in lecture.

Today, we'll consider the probability of transitioning from a discrete to a continuous eigenstate under a constant perturbation $\delta H(t) = V$. We found in lecture that we have the transition rate

$$w = \frac{1}{t_0}\sum_f P_{i\to f}(t_0) = \frac{1}{t_0}\int dE_f \rho(E_f)\frac{|V_{fi}|^2}{\hbar^2}F(\omega_{fi}, t_0),$$

where we convert a sum over states to an integral $\rho(E_f)$ over the density of states, and $F(\omega, t_0) = \frac{\sin^2\left(\frac{\omega t_0}{2}\right)}{(\omega/2)^2}$ is the sharply peaked function with lobes that we discussed. This function F has bumps at a regular period $\frac{2\pi}{t_0}$ because of the $\sin^2$, but the heights of the bumps fall off as $\frac{1}{\omega^2}$ because of the denominator – the tallest one has height t_0^2.

So if we take large t_0, we claim that the function $\frac{F(\omega,t_0)}{t_0}$ behaves like $2\pi\delta(\omega)$. To understand this, we can collect some facts about the function:

- For any $\omega \neq 0$, the function goes to 0 – indeed, the off-diagonal peaks of F's oscillations have constant value $\frac{1}{(\omega/2)^2}$, and then as we divide by t_0, all of the peaks go to 0.
- The width of the central peak $\frac{2\pi}{t_0}$ also goes to 0.
- The central peak has height proportional to t_0 in the limit, in such a way that if we integrate the function over the central peak, we get 2π.

So the idea is that the $\frac{F(\omega,t_0)}{t_0}$ term in our above expression w can be substituted in, and that explains the alternative formula that we found in lecture: we have a delta function of ω_{fi}, which simplifies in to

$$w = \int dE_f \rho(E_f)\frac{|V_{fi}|^2}{\hbar^2}2\pi\delta\left(\frac{E_f - E_i}{\hbar}\right).$$

Doing this integral, the $\hbar$ in the delta function cancels out one of the $\hbar$s in the other denominator, and we end up with

$$= \frac{2\pi}{\hbar}|V_{fi}|^2\rho(E_f = E_i),$$

which is indeed Fermi's golden rule – the transition rate is linear when we transition to a state in the continuum with the same energy. (But still, this approximation only works when $t_0 w \ll 1$, so that perturbation theory works, and when t_0 is large enough so that $\frac{4\pi\hbar}{t_0}$ is smaller than the variation of the other terms in the integral $V_{fi}^2\rho(E)$.)

We'll now take more time to derive some results that we found from lecture:

Proposition 147

When $t \gg \frac{1}{w}$ (so perturbation theory is no longer valid), the probability of remaining in state i is $P_i(t) = e^{-\omega t}$, and the probability of transitioning to a final state $P_{i\to f}(t)$ is $\frac{|V_{fi}|^2}{(E_f - E_i - \delta E_i)^2 + \frac{\hbar^2}{4}\omega^2}$.

Proof. We'll use a simplified setup: suppose that there is a single discrete state $|i\rangle$ and a set of continuous states $|\alpha\rangle$ around it, so that our perturbation V (constant in time) satisfies $V_{i\alpha} = \langle i|V|\alpha\rangle \neq 0$, and also that $V_{i\alpha} \neq V_{\alpha i}^*$ because V is Hermitian.

Fact 148

Continuous eigenstates are normalized via $\langle\alpha|\alpha'|=\rangle\,\delta(\alpha-\alpha')$, and we'll also write $\langle\alpha|i\rangle = 0$ (orthogonality) and $I = |i\rangle\langle i| + \int d\alpha\,|\alpha\rangle\langle\alpha|$ (complete set of states). Writing a generic state as a linear combination of the continuous states would then look like

$$\left|\tilde{\psi}(t)\right\rangle = c_i(t)\,|i\rangle + \int d\alpha\; c_\alpha(t)\,|\alpha\rangle\,.$$

Since we're starting in state $|i\rangle$, our initial conditions are $c_i(0) = 1$ and $c_\alpha(0) = 0$. We had a differential equation for the c's before doing perturbation theory, which looked like

$$i\hbar\dot{c}_m(t) = \sum_n e^{i\omega_{mn}t}V_{mn}c_n(t),$$

but this was valid only for **discrete** states, and we need a slightly different version of the formula when we have both continuous and discrete states.

We'll now make the further assumption that $V_{ii} = 0$ and $V_{\alpha\alpha} = 0$, and then we end up with the equation

$$\boxed{i\hbar\dot{c}_i(t) = \int d\alpha e^{i\omega_{i\alpha}t}V_{i\alpha}c_\alpha(t)}$$

where we have no V_{ii} term because $V_{ii} = 0$. And meanwhile, our differential equation for c_α looks like

$$\boxed{i\hbar\dot{c}_\alpha(t) = e^{i\omega_{\alpha i}t}V_{\alpha i}c_i(t)}$$

where we're assuming that **the different continuous states do not connect with each other at all** (just to make the calculation easier and avoid more coupling in our differential equations). So now with these simplified equations, we want to get an equation for $c_i(t)$, and we'll do that by eliminating $c_\alpha(t)$ from the equation. Integrating the second boxed equation, we get

$$c_\alpha(t) = \frac{V_{\alpha i}}{i\hbar}\int_0^t dt' e^{i\omega_{\alpha i}t'}c_i(t'),$$

and plugging this into our first equation, we find

$$\dot{c}_i = -\frac{1}{\hbar^2}\int d\alpha|V_{\alpha i}|^2\int_0^t dt' e^{i\omega_{i\alpha}(t-t')}c_i(t'),$$

since $V_{\alpha i}, V_{i\alpha}$ are complex conjugates so their product is the magnitude squared, and $\omega_{i\alpha}$ and $\omega_{\alpha i}$ are negatives of each other. We will now convert the first piece $\int d\alpha|V_{\alpha i}|^2$ into an integral over energy $\int dE_\alpha\rho(E_\alpha)|V_{\alpha i}|^2$, and we'll make the assumption now that this changes slowly over energy (just like we have previously made), though the $e^{i\omega_{i\alpha}(t-t')}$ can rapidly oscillate with energy unless $t \approx t'$. The point is then that the rapid oscillations cancel out any contributions of that first $\rho(E_\alpha)|V_{\alpha i}|^2$ part unless $t \approx t'$, and thus we can approximate $c_i(t) = c_i(t')$.

So now we can just pull that factor out of the integral to get

$$\dot{c}_i(t) = c_i(t) \cdot -\frac{1}{\hbar^2} \int dE_\alpha \rho(E_\alpha)|V_{\alpha i}|^2 \int_0^t dt' e^{i\omega_{i\alpha}(t-t')},$$

and now in the large-t limit the integral here looks approximately like $\int_0^\infty dt'' e^{i\omega_{i\alpha}t''}$ (where $t'' = t - t'$). If we integrated this expression over all t'', we'd get 2π times a delta function, so it turns out that what we have here is

$$\int_0^\infty dt'' e^{i\omega_{i\alpha}t''} \approx \pi\delta(\omega_{i\alpha}) + iP(\omega_{i\alpha}),$$

giving us an extra imaginary part from the **principal value** in complex analysis. This can be rewritten in terms of energies as

$$= \pi\hbar\delta(E_i - E_\alpha) + \cdots$$

and thus if we plug this in and do the integral, we will find that (delta function picking out only energy E_i)

$$\frac{\dot{c}_i(t)}{c_i(t)} = -\frac{\pi}{\hbar}\rho(E_i)|V_{\alpha i}|^2 + \cdots = -\frac{w}{2} - \frac{i}{\hbar}\delta E_i$$

for some shift to the energy δE_i caused by the imaginary principal value term above. And the right-hand side is constant in time, so we can solve for $c_i(t)$ with a direct integration, and indeed this gives us

$$c_i(t) = \exp\left(-\frac{w}{2}t - \frac{i}{\hbar}\delta E_i(t)\right),$$

and the probability $|c_i(t)|^2$ of remaining in state i is indeed e^{-wt} as desired. And if we substitute in the form of c_i into

$$c_\alpha(t) = \frac{V_{\alpha i}}{i\hbar} \int_0^t dt' e^{i\omega_{\alpha i}t'} c_i(t'),$$

we find that the right-hand side is an exponential integral, and the result turns out to be

$$= \frac{V_{\alpha i}}{i\hbar} \frac{e^{\left(-\frac{w}{2} + \frac{i}{\hbar}(E_\alpha - E_i - \delta E_i)\right)t} - 1}{\left(-\frac{w}{2} + \frac{i}{\hbar}(E_\alpha - E_i - \delta E_i)\right)}.$$

In particular, in the large t limit (which is what we should be taking), the first term in the numerator decays away to 0 and thus we just have

$$\approx \frac{V_{\alpha i}}{\left(E_\alpha - E_i - \delta E_i + \frac{i\hbar w}{2}\right)}.$$

So the probability that we transition from state i to state α will be

$$P_{i\to\alpha}(t) = |c_\alpha(t)|^2 = \frac{|V_{\alpha i}|^2}{(E_\alpha - E_i - \delta E_i)^2 + \frac{\hbar^2\omega^2}{4}},$$

as desired. (And because we have an integral over αs, this is a probability density rather than an exact probability.) ☐

So far, we've always been doing first-order perturbation theory, and we'll take a quick minute to discuss how we might derive second-order perturbation theory. The idea is to look again at the $\dot{c}_m(t)$ differential equation

$$i\hbar\dot{c}_m(t) = \sum_n c_n(t) e^{i\omega_{mn}t} V_{mn}$$

and substitute in $c_m^{(2)}(t)$ for $\dot{c}_m$ and $c_n^{(1)}$ for $c_n(t)$ (since we're basically doing a perturbation in V). So the strategy would be to take

$$c_m^{(2)}(t) = \sum_n \int_0^t dt' e^{i\omega_{mn}t'} \frac{V_{mn}}{i\hbar} c_n^{(1)}(t')$$

and substitute in the expression we know for $c_n^{(1)}(t')$; we then end up with a double integral solution

$$= \sum_n \int_0^t dt' \int_0^{t'} dt'' e^{i\omega_{mn}t'} \frac{V_{mn}}{i\hbar} e^{i\omega_{ni}t''} \frac{V_{ni}}{i\hbar}$$

which then simplifies by doing one of the integrals to

$$= -\sum_n \frac{V_{mn}V_{ni}}{\hbar^2} \int_0^t dt' e^{i\omega_{mn}t'} \frac{e^{i\omega_{ni}t'} - 1}{\frac{i}{\hbar}(E_n - E_i)}.$$

So in this second-order calculation we see again the $\frac{V_{mn}V_{ni}}{(E_n - E_i)}$ term that we saw in time-independent perturbation theory! This can be thought of as a "virtual transition," in the sense that V_{ni} takes us from i to a "virtual state" n, and then V_{mn} takes us from that state back to the final state m that we're looking at, and we might see this kind of expression in quantum field theory as well.

32 April 15, 2021

Last time, we discussed Fermi's golden rule for harmonic perturbations, and we started a classic application of our formalism – ionization of hydrogen. Recall that the setup is that we have a hydrogen atom initially in its ground state, and then we shine light at it with frequency ω. It's possible that light will ionize the atom, kicking out the electron, and then the final energy of the electron will be $E_f = \hbar\omega - \text{Ry}$, which we can also write in terms of the wavevector as $\frac{\hbar^2 k^2}{2m}$.

We make the approximation that the wavelength of light is much larger than than the Bohr radius a_0, so that the incoming light wave doesn't vary much over the atom, and we also make the assumption that the Coulomb interaction between the nucleus and ejected electron does not affect the ejected electron. And we discussed last time that these two approximations together give us the range of allowed energies

$$13.6 \text{ eV} \ll \hbar\omega \ll 23 \text{ keV} \iff 1 \ll ka_0 \ll 40.$$

Our next step is to understand how the hydrogen atom couples to our perturbation due to the light. Since light is an electromagnetic wave, we can (**classically**) write the $\vec{E}$ and $\vec{B}$ fields as

$$\vec{E}(\vec{r}, t) = 2\vec{E}_0 \sin(\vec{q} \cdot \vec{r} - \omega t), \quad \vec{B}(\vec{r}, t) = 2\hat{q} \times \vec{E}_0 \sin(\vec{q} \cdot \vec{r} - \omega t)$$

where $\vec{q}$ is the vector of propagation with magnitude $q = \frac{2\pi}{\lambda} = \frac{\omega}{c}$. But electric and magnetic fields enter the Hamiltonian through the vector and scalar potentials

$$\vec{E} = -\nabla\Phi - \frac{1}{c}\frac{\partial \vec{A}}{\partial t}, \quad \vec{B} = \vec{\nabla} \times \vec{A},$$

so we need to find a Φ and $\vec{A}$ that work – one solution is

$$\Phi = 0, \vec{A}(\vec{r}, t) = -\frac{2c}{\omega}\vec{E}_0 \cos(\vec{q} \cdot \vec{r} - \omega t).$$

In particular, the divergence $\vec{\nabla} \cdot \vec{A}$ is zero, because it is proportional to $\vec{q} \cdot \vec{E}_0$ by the chain rule. (What we have here is the **Coulomb gauge**.) So our Hamiltonian now looks like

$$H = \frac{1}{2m}\left(\vec{p} + \frac{e}{c}\vec{A}\right)^2 - e\Phi - \frac{e^2}{r}$$

(remembering that the charge of an electron is $-e$), and plugging in the form of our solution gives us (after expanding the square and getting equal cross terms because the divergence of $\vec{A}$ is zero)

$$= \frac{\vec{p}^2}{2m} + \frac{e}{mc}\vec{p}\cdot\vec{A} + \frac{e^2}{2mc^2}\vec{A}^2 - \frac{e^2}{r}.$$

We'll work perturbatively in the magnitude $|\vec{E}_0|$ of the electric field – the third term proportional to $\vec{A}^2$ is then quadratic in $\vec{E}_0$, so to the order we're working in we can ignore it. This means we have (substituting in the expression for $\vec{A}$)

$$H = H^{(0)} + \delta H = \left(\frac{\vec{p}^2}{2m} - \frac{e^2}{r}\right) - \frac{2e}{m\omega}\vec{E}_0\cdot\vec{p}\cos(\vec{q}\cdot\vec{r} - \omega t).$$

We now place our proton at the origin, and remembering that we made the approximation that the wavelength of light is much bigger than the Bohr radius, that means that $\vec{q}\cdot\vec{r} \approx \vec{q}\cdot\vec{0} = 0$. So we'll ignore the spatial dependence of the cosine, and our perturbation looks like (remembering $\cos(-\omega t) = \cos(\omega t)$)

$$\delta H = -\frac{2e}{m\omega}\vec{E}_0\cdot\vec{p}\cos(\omega t) = 2H'\cos\omega t,$$

where $H' = -\frac{e}{m\omega}\vec{E}_0\cdot\vec{p}$ is our time-independent Hamiltonian.

Fact 149

If we go back to our electric field and make the approximation at the beginning, meaning $\vec{E}(\vec{r},t) = 2\vec{E}_0\sin(\vec{q}\cdot\vec{r} - \omega t) \approx -2\vec{E}_0\sin(\omega t)$, we can then use a different gauge and choose

$$\Phi = 2\vec{E}_0\cdot\vec{r}\sin\omega t, \quad \vec{A} = 0.$$

We then find that the perturbation ends up being

$$\delta H = -e\Phi = -2e\vec{E}_0\cdot\vec{r}\sin\omega t = 2\hat{H}'\sin\omega t, \quad \hat{H}' = -e\vec{E}_0\cdot\vec{r}.$$

So this time we have a sine instead of a cosine, but it doesn't matter in the derivation of Fermi's golden rule (since we write oscillations as a sum of exponentials, and also because the phase shift doesn't make a big difference over long periods of time). That means this is also a valid way to proceed.

This gives us $\vec{B} = 0$, but that turns out to not be a problem – the **effect of the magnetic field on the electron is much smaller** than the effect of the electric field for an electromagnetic wave like this, because the Lorentz force is $\vec{F} = -e\vec{E} - e\frac{\vec{v}}{c}\times\vec{B}$, and in the units that we used the magnitude of electric and magnetic fields are equal. (So the non-relativistic nature of the electron makes the effect of $\vec{B}$ suppressed.)

Proposition 150

The perturbations H' and $\hat{H}'$ lead to the same transition (that is, ionization) rate.

Proof. Recall that for harmonic perturbations, the rate of upward transitions takes the form

$$w = \frac{2\pi}{\hbar}\left|\langle f|H'|i\rangle\right|^2 \rho(E_f)\Big|_{E_f = E_i + \hbar\omega}.$$

So what we need to show is that the matrix elements $|H'_{fi}|^2$ and $|\tilde{H}'_{fi}|^2$ are equal, which means we need to compare $\langle f|\vec{p}|i\rangle$ to $\langle f|\vec{r}|i\rangle$. We can understand this by remembering that $|f\rangle$ and $|i\rangle$ are taken to be eigenstates of the **unperturbed** Hamiltonian

$$H^{(0)} = \frac{\vec{p}^2}{2m} - \frac{e^2}{r},$$

where we have the (verifiable by calculation) commutation relation

$$[H^{(0)}, \vec{r}] = -\frac{i\hbar}{m}\vec{p}.$$

So now we can get our answer by noting that

$$\frac{i\hbar}{m}\langle f|\vec{p}|i\rangle = \left\langle f\middle|[H^{(0)}, \vec{r}]\middle|i\right\rangle = \left\langle f\middle|H^{(0)}\vec{r} - \vec{r}H^{(0)}\middle|i\right\rangle,$$

and now we can apply $H^{(0)}$ on the bra and ket to find

$$= (E_f - E_i)\langle f|\vec{r}|i\rangle,$$

and thus we've found a relation between those matrix elements! And now we can just plug these in: we have

$$\langle f|H'|i\rangle = -\frac{e}{m\omega}\vec{E}_0 \cdot \langle f|\vec{p}|i\rangle = -\frac{ie}{\hbar\omega}(E_f - E_i)\vec{E}_0\langle f|\vec{r}|i\rangle,$$

and writing this in terms of the matrix element for $\hat{H}'$ gives us

$$= i\frac{E_f - E_i}{\hbar\omega}\left\langle f\middle|\hat{H}'\middle|i\right\rangle.$$

And because we evaluate this expression at $E_f = E_i + \hbar\omega<$ the prefactor is just i, and thus the squared magnitudes we get from H' and $\hat{H}'$ are indeed equal. So our Fermi's golden rule answers are the same in both cases, as desired. ☐

We'll often use the $\hat{H}'$ gauge in the future when doing computations – it's a bit weird because we're setting $\vec{B} = 0$, though. (In both cases, this sequence of approximations is called the **electric dipole approximation**.)

So now we need to actually find the transition rate w: to do that, we will calculate H'_{fi} and also $\rho(E_f)$. The form of the wavefunction for the initial and final state are

$$|i\rangle = \psi_{100}(\vec{r}) = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$$

(the ground state of the hydrogen atom), and

$$|f\rangle = \psi_{\vec{k}}(\vec{r}) \approx \frac{1}{\sqrt{L^3}}e^{i\vec{k}\cdot\vec{r}}$$

(approximating the scattering states as free electrons, which are in plane waves). Remember that we're using a cubic box of size L^3 so that we can calculate the density of states as well, and the energy of our final state is $\frac{\hbar^2\vec{k}^2}{2m}$ (in the approximation where $E_f \gg \text{Ry}$). So then the matrix element we want is

$$H'_{fi} = \langle f|H'|i\rangle = \left\langle \psi_{\vec{k}}\middle|-\frac{e}{m\omega}\vec{E}_0 \cdot \vec{p}\middle|\psi_{100}\right\rangle,$$

and now because the plane wave is actually an eigenstate for $\vec{p}$, we can apply $\vec{p}$ on the bra to get

$$= -\frac{e\hbar\vec{E}_0 \cdot \vec{k}}{m\omega}\langle \psi_{\vec{k}}|\psi_{100}|,\rangle$$

and then the remaining overlap can be computed with the integral

$$\langle \psi_{\vec{k}}|\psi_{100}|=\rangle \int d^3r \frac{1}{\sqrt{L^3}}e^{i\vec{k}\cdot\vec{r}}e^{-r/a_0}.$$

We can evaluate this by going to polar coordinates, and it turns out the answer is (the dimensionless)

$$= \sqrt{\frac{a_0^3}{L^3}} 8\sqrt{\pi} \frac{1}{(1 + (ka_0)^2)^2}.$$

Remembering that $ka_0 \gg 1$ in our "free electron" approximation, we can neglect the 1 in the denominator and rewrite this as

$$\approx \frac{8\sqrt{\pi}}{L^{3/2}} \frac{1}{k^4 a_0^{5/2}}.$$

Substituting this back in, we find that because $\hbar\omega \approx \hbar\omega - \text{Ry} = \frac{\hbar^2 k^2}{2m}$, we know that the $m\omega$ can be replaced by $\frac{\hbar k^2}{2}$ in our calculation for H'_{fi}. So

$$H'_{fi} \approx -2e \frac{\vec{E}_0 \cdot \vec{k}}{k^2} \frac{8\sqrt{\pi}}{L^{3/2}} \frac{1}{k^4 a_0^{5/2}}.$$

So the rate of transition here depends on the outgoing electron's wavevector – in particular, it depends both on the angle (because of the $\vec{E}_0 \cdot \vec{k}$ term) and on the magnitude (because of the $\frac{1}{k^2}$). If we write $\vec{E}_0 \cdot \vec{k} = E_0 k \cos\theta$, we can collect terms here to find that the matrix element is

$$H'_{fi} = -16\sqrt{\pi}(eE_0 a_0) \cos\theta \frac{1}{k^5 a_0^{7/2} L^{3/2}}.$$

Now $eE_0 a_0$ has dimensions of energy, and the rest is dimensionless – if we square this expression, we get one term in the transition rate w, and the other term we need to find is the density of states $\rho(E_f)$. But we calculated that for this kind of setting already – the density of states **per solid angle** for a free particle in a cubic box satisfies

$$\rho(E_f) = \left(\frac{L}{2\pi}\right)^3 \frac{m}{\hbar^2} k \, d\Omega.$$

So we can now take everything together and plug it into Fermi's golden rule: the rate **into a solid angle** $d\Omega$ looks like

$$dw = \frac{2\pi}{\hbar} |H'_{fi}|^2 \rho(E_f) = \frac{2\pi}{\hbar} \left(256\pi (eE_0 a_0)^2 \cos^2\theta \frac{1}{k^{10} a_0^7 L^3}\right) \cdot \left(\frac{L}{2\pi}\right)^3 \frac{m}{\hbar^2} k \, d\Omega,$$

and now (as expected) the L factors cancel out, and collecting all other terms gives us

$$= \frac{64}{\pi\hbar} \frac{(eE_0 a_0)^2}{\hbar^2/(m a_0^2)} \frac{1}{(ka_0)^9} \cos^2\theta \, d\Omega.$$

So we've now found the **partial ionization rate**

$$\frac{dw}{d\Omega} = \frac{64}{\pi\hbar} \frac{(eE_0 a_0)^2}{\hbar^2/(m a_0^2)} \frac{1}{(ka_0)^9} \cos^2\theta,$$

and in particular the $\cos^2\theta$ term tells us that the strongest ionization occurs parallel or antiparallel to $\vec{E}_0$. The units do indeed work out (the denominator $\frac{\hbar^2}{m a_0^2}$ is twice the Rydberg), and we can notice that as we increase the momentum of the final particle, there is a steep dropoff for the ionization rate. And if we only care about how many electrons are ejected per unit time, we have

$$w = \int \frac{dw}{d\Omega} d\Omega,$$

and since $\int d\Omega \cos^2\theta = \int \sin\theta d\theta \int d\phi \cos^2\theta = \frac{4\pi}{3}$, our full ionization rate is

$$\boxed{w = \frac{256}{3} \frac{(eE_0 a_0)^2}{\hbar^2/(m a_0^2)} \frac{1}{(ka_0)^9}}.$$

(We should remember that we've defined E_0 so that the electric field amplitude is $2E_0$, so we should be careful if we're consulting other references in the literature.)

Fact 151

If we do a similar calculation with $\hat{H}'_{fi}$ instead, using the same plane wave for our final state, it turns out that we actually get a difference by a factor of 4. The reason that we get this discrepancy is that the final state is an approximation and not an exact eigenstate of $H^{(0)}$, and it turns out that the correct answer comes up from H' but not from $\tilde{H}'$! So we need to include corrections to the scattering states due to Coulomb interaction if we want to use perturbations with $\vec{r}$ instead of $\vec{p}$.

We're now going to switch topics and discuss interactions of light with atoms that cause transitions between **discrete levels**, rather than from the discrete to the continuum.

Example 152

Suppose that we have an ensemble of atoms that are interacting with light, and there are two particular bound states $|a\rangle$ and $|b\rangle$ with energies $E_a < E_b$. We define $\omega_{ba} = \frac{E_b - E_a}{\hbar} > 0$, and we shine light on the atoms with frequency ω_{ba}.

As previously discussed, there are two processes that occur; we'll describe them using photons even though we'll be doing calculations with waves. In **absorption**, we shine a photon of frequency $\omega \approx \omega_{ba}$, which causes an upward transition for an atom from $|a\rangle$ to $|b\rangle$ – the atom then absorbs the photon. Meanwhile, in **stimulated emission**, we shine in a photon of frequency ω, and that stimulates the atom to transition down from $|b\rangle$ to $|a\rangle$, and then two photons are emitted (for conservation of energy).

Remark 153. *Lasers ("***l***ight* **a***mplification by* **s***timulated* **e***mission of* **r***adiation") work in this way. Basically, we have an ensemble of atoms that are initially prepared in the excited state $|b\rangle$, and we send in a single photon. Once that photon causes an atom to stimulate a downward transition, it releases more photons, and this causes a chain reaction of more and more photons. So the trick is to get the atoms initially in $|b\rangle$, and this is called* **population inversion** *– usually we do this with a third energy level.*

From here, we'll think about our ensemble of atoms as living in a furnace of some fixed temperature T – there is radiation inside the furnace, and we'll treat it as blackbody radiation. The idea is that after some interactions between light and atoms, we will achieve equilibrium, and we will see that **spontaneous emission** will also occur. But we'll discuss this in detail next time!

33 April 21, 2021 (Recitation)

Today's recitation is being taught by Cagin Yunus (the TA for this class). We'll cover three main topics today – we'll review the ionization of hydrogen, do a related problem, and understand the effect of electron spin on the transition rates between states.

Recall that the setup for ionization of hydrogen is that we have a hydrogen atom, in which we make two simplifications: first, we assume that the wavelength of the incoming light λ is much larger than the Bohr radius a_0, so that the magnitude of the electromagnetic wave does not vary considerably on the scale of the atom (and thus we don't need to worry about the spatial dependence of the EM wave). This is the condition that $\hbar\omega \ll 23$ keV ≈ 1722 Ry, or equivalently that $k_\gamma a_0 \gg 1$ (where k_γ is the wavenumber for the incoming light). But also, we assume that the ejected electron has high enough energy so that it is in a free-particle state, which implies that $\hbar\omega -$ Ry $\gg$ Ry; we often rephrase this as $\hbar\omega \gg$ Ry or that $k_e \gg 1$ (where k_e is the wavenumber for the outgoing electron). And thus we have the allowed range

$$\text{Ry} \ll \hbar\omega \ll 1722 \text{ Ry},$$

where we can say things like "$1 \ll 10$" for purposes of our approximation.

Our interaction picture Hamiltonian can then be obtained by taking the gauge where

$$\vec{A}(\vec{r}, t) = -\frac{c}{\omega} 2\vec{E}_0 \cos(\vec{k}_\gamma \cdot \vec{r} - \omega t), \quad \Phi(\vec{r}, t) = 0,$$

so that the perturbation is given by

$$\delta H = -\frac{e}{m\omega} 2\vec{E}_0 \cdot \vec{p} \cos(\vec{k}_\gamma \cdot \vec{r} - \omega t).$$

We now use the first assumption to say that the argument inside the cosine is essentially $\cos(-\omega t)$, since the first term $\vec{k}_\gamma \cdot \vec{r}$ is very small. So now our Hamiltonian takes the form $\delta H = 2H' \cos(\omega t)$, and in this case we have

$$H' = -\frac{e}{m\omega} \vec{E}_0 \cdot \vec{p}.$$

(Recall that the reason for the factor of 2 is that $\cos(\omega t) = \frac{1}{2}(e^{i\omega t} + e^{-i\omega t})$, and each exponential corresponds to a mode of emission or absorption.) And now we can use Fermi's golden rule, calculating the matrix element: if we assume that our electric field is $\vec{E} = E_0 \hat{z}$, so that $H' = -\frac{eE_0}{m\omega} p_z$, then we want to find the matrix element between the states

$$|i\rangle = |\psi_{100}\rangle = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}, \quad |f\rangle = \left|\psi_{\vec{k}_e}\right\rangle = \frac{1}{L^{3/2}} e^{i\vec{k}_e \cdot \vec{r}},$$

where L is the "large box" that we put our free box in and $\vec{k}_e$ is the outgoing wavenumber for the electron. The matrix element then looks like

$$H'_{fi} = \langle f | H' | i \rangle = -\frac{eE_0}{m\omega} \langle f | p_z | i \rangle,$$

and now because p_z is Hermitian, we can essentially apply it on the bra:

$$= -\frac{eE_0}{m\omega} \hbar k_e \cos\theta \langle f | i \rangle,$$

where θ is the angle between $\vec{k}_e$ and $\vec{E}$. We can then compute this matrix element by integration and use our other simplification:

$$\langle f | i \rangle = \frac{8\pi a_0^3}{(1 + k_e^2 a_0^2)^2} \approx 8\pi a_0^3,$$

so that the matrix element is

$$H'_{fi} = -16\sqrt{\pi}(eE_0 a_0) \frac{\cos\theta}{L^{3/2} a_0^{7/2} k_e^5}, \quad \hbar\omega = \frac{k_e^2 \hbar^2}{2m}.$$

Now because the density of states per solid angle is $\rho(E_e) = \frac{L^3}{8\pi^3} \frac{m}{\hbar^2} k_e d\Omega$, we find that

$$\frac{dw}{d\Omega} = \frac{2\pi}{\hbar} \rho(E_e) |H_{fi}|^2 = \frac{64}{\pi} \frac{m a_0^2}{\hbar^2} \frac{(e_0 a_0^2)}{\hbar} \frac{\cos^2\theta}{(k_e a_0)^9},$$

and the integrating through tells us that the transition rate

$$w = \frac{256}{3} \frac{m}{\hbar^3} \frac{e^2 E_0^2}{k_e^9 a_0^5}.$$

We'll now solve a related problem:

Example 154

Suppose we're in the ground state of the hydrogen atom Hamiltonian, and we're subjected to an external potential of $V(\vec{x}, t) = V_0 \cos(kz - \omega t)$.

We want to know the transition rate for the electron to be emitted with the momentum $\vec{p}$, and we want to compare this answer to the photoelectric effect calculation we did above. First, we will expand our potential as

$$V(\vec{x}, t) = \frac{V_0}{2}\left[e^{i(kz-\omega t)} + e^{-i(kz-\omega t)}\right],$$

where the two terms correspond to absorption and emission (though there is no longer any light to absorb or emit, we can still think about our system as gaining or losing energy). We'll focus on the first term of absorption, and then the transition rate will be given (again by Fermi's golden rule) by

$$w_{f\leftarrow i} = \frac{2\pi}{\hbar}\rho(E_f)|V_{fi}|^2.$$

We need to calculate the matrix element here, and much like before, we have to integrate the wavefunctions across space:

$$V_{fi} = \frac{V_0}{2}\frac{1}{\sqrt{\pi a_0^3}}\int d^3\vec{x}' e^{-i\vec{p}\cdot\vec{x}'/\hbar} e^{-r'/a_0} e^{ikz'},$$

where $e^{ikz'}$ is the term from the potential. If we make a change of variables here so that $\vec{q} = \frac{\vec{p}}{\hbar} - k\hat{z}$, then our integral (without the leading constants) looks like

$$\int d^3\vec{x}' e^{i\vec{q}\cdot\vec{x}'} e^{-r'/a_0} = \int \sin\theta d\theta d\phi (r')^2 dr' e^{iqr'\cos\theta} e^{-r'/a_0}$$

by switching to spherical coordinates, and we can evaluate this to get $\frac{4\pi a_0^3}{1+(a_0 q)^2}$. If we plug this back in with our density of states $\rho(E_f) = \frac{L^3}{8\pi^3}\frac{m}{\hbar^2}k_f d\Omega$, where $\vec{k}_f = \frac{\vec{p}}{\hbar}$, we find that

$$\boxed{\frac{dw}{d\Omega} = \frac{mV_0^2 a_0^3}{\pi\hbar^3}\frac{k_f}{(1+a_0^2q^2)^4}}.$$

We can notice **three main differences** in this answer compared to the one above:

- There is no $\cos^2\theta$ factor, because there is no polarized electromagnetic wave.
- We do not make the approximation that $a_0 q \ll 1$, so we can't get rid of the denominator here. This is because there is no "free electron assumption" that we can make this time. So in this problem, we can consider ejected electrons with small momenta, when we could not do so for the photoelectric effect.
- In this case, we use $\vec{q} = \vec{k}_f - k\hat{z}$, where $\vec{k}_f = \frac{\vec{p}}{\hbar}$. But in the photoelectric effect above, we essentially ignored the second term $k\hat{z}$ because we had the corresponding assumption $k_\gamma \cdot a_0 \ll 1$.

Example 155

We'll now move to discussion of spin contribution, thinking about coupling between spin and magnetic field and explaining **why we can neglect it** in the photoelectric effect calculation.

Our perturbation due to spin looks like

$$\delta H \to \delta H = \frac{e}{mc}\vec{S}\cdot\vec{B} = \delta H + \frac{e\hbar}{2mc}\vec{\sigma}\cdot(\nabla\times\vec{A}),$$

and now we can use the identity that $\nabla \times (f\vec{c}) = \nabla f \times \vec{c}$ (when $\vec{c}$ is a constant vector and f is a function) and plug in our previous vector potential $\vec{A}$ with $\vec{c} = \vec{E}_0$ to get that

$$\vec{B} = \nabla \times \vec{A} = \frac{c}{\omega} 2\sin(\vec{k}_\gamma \cdot \vec{r} - \omega t)\vec{k}_\gamma \times \vec{E}_0.$$

Here, we'll assume that $\vec{E}_0 = E_0\hat{z}$ is pointed in the z-direction, and $\vec{k}_\gamma = k_\gamma \vec{y}$ is pointed in the y-direction. Then we have

$$\vec{B} = \frac{c}{\omega} 2E_0 k_\gamma \sin(\vec{k}_\gamma \cdot \vec{r} - \omega t)\hat{x},$$

so that our Hamiltonian changes by a term

$$\delta H \to \delta H + \frac{e\hbar}{m\omega} E_0 k_\gamma \sin(\vec{k}_\gamma \cdot \vec{r} - \omega t)\sigma_x,$$

where $\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$ is the Pauli matrix. If we assume for example that our initial spin of the electron is in the z-direction (so that it's perpendicular to $\vec{B}$), then we can calculate $\delta H_{f\uparrow,i\downarrow}$, because that will let us know **whether the effect of coupling is strong enough to change the spin**. (The original δH term does not contribute to this matrix element because the overlap of ↑ with ↓ is zero.) To do this, we expand the sine in terms of exponentials again as

$$\sin(\vec{k}_\gamma \cdot \vec{r} - \omega t) = \frac{1}{2i}\left(e^{i(\vec{k}-\gamma\cdot\vec{r}-\omega t)} - e^{-i(\vec{k}-\gamma\cdot\vec{r}-\omega t)}\right)$$

with two terms corresponding to absorption and emission, then finding the matrix element requires us to compute the same integral, and we find that

$$|\delta H_{f\uparrow,i\downarrow}|^2 = \frac{1}{4}\frac{e^2\hbar^2}{m^2\omega^2} k_\gamma^2 E_0^2 \left(\frac{64\pi}{k_e^8 a_0^5 L^3}\right),$$

where we use the approximation $k_e \cdot a_0 \gg 1$. We then get the transition rate, and it turns out that the ratio between transition rates for a flipped spin versus no flipped spin is

$$\frac{w_{f\uparrow,i\downarrow}}{w_{f\downarrow,i\downarrow}} = \frac{3}{4}\frac{k_\gamma^2}{k_e^2} \ll 1,$$

where the last inequality comes from $k_\gamma \cdot a_0 \ll 1 \ll k_e \cdot a_0$. So the spin contribution can indeed be neglected!

34 April 22, 2021

We've been discussing the interaction between light and atoms, and we'll continue that discussion today. In particular, we'll study an argument of Einstein's about how light and atoms can be at equilibrium at some temperature.

Example 156

Consider a cavity at some temperature T. There is electromagnetic radiation inside the cavity, which we will model as blackbody radiation. This cavity also contains atoms in equilibrium with it, and each of those atoms has two levels $|a\rangle$ and $|b\rangle$ with energies E_a and E_b (we'll say there are N_a of them in $|a\rangle$ and N_b of them in $|b\rangle$).

We'll work with the following three facts:

- At equilibrium, N_a and N_b do not change in time, meaning that $\dot{N}_a = \dot{N}_b = 0$.
- At equilibrium, we have $\frac{N_b}{N_a} = \frac{e^{-\beta E_b}}{e^{-\beta E_a}} = e^{-\beta\hbar\omega_{ba}}$ – that is, we obey the **Boltzmann distribution**. Here, $\beta = \frac{1}{k_B T}$, where k_B is Boltzmann's constant, and $\omega_{ba} = \frac{E_b - E_a}{\hbar}$.

- At temperature T, we see blackbody radiation satisfying Planck's blackbody law:

$$\text{Radiation energy per unit volume of frequency } \in [\omega, \omega + d\omega] = U(\omega)d\omega = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega} - 1}d\omega.$$

We need to understand how this thermal equilibrium is maintained, and to do so, we need to understand what processes go on inside the cavity. We've already mentioned two of them: we have **absorption**, in which an atom starts at level $|a\rangle$, a photon comes in and is absorbed, and the atom ends at level $|b\rangle$. We also have **stimulated emission**, in which an atom starts at $|b\rangle$, a photon stimulates a downward transition to $|a\rangle$, and two photons come out.

We want to know the rate at which each of these processes occurs: for absorption, the rate should be proportional to the number of photons, which is proportional to $U(\omega_{ba})$, and also proportional to the number of atoms N_a as well as some temperature-independent quantity B_{ab} (which is inherent to the atom and tells us how likely the stimulation is to occur). In other words, the rate of absorption looks like $B_{ab}U(\omega_{ba})N_a$. And similarly, for stimulated emission, we expect that the rate for the process is proportional to $U(\omega_{ba})$ (number of photons of the correct frequency), B_{ba} (intrinsic to the atom), and N_b (number of atoms), so we'll write it as $B_{ba}U(\omega_{ba})N_b$.

But these two processes are not enough to maintain equilibrium, and let's see that now. At equilibrium, we need the rate of change of N_a and N_b to be zero, meaning that the total rate satisfies

$$0 = \dot{N}_b = B_{ab}U(\omega_{ba})N_a - B_{ba}U(\omega_{ba})N_b,$$

which simplifies to

$$N_a U(\omega_{ba})\left(B_{ab} - B_{ba}\frac{N_b}{N_a}\right) = 0,$$

so that (using our Boltzmann statistics assumption)

$$B_{ab} - B_{ba}e^{-\beta\hbar\omega_{ba}} = 0.$$

But this doesn't make sense, because B_{ab} and B_{ba} are temperature-independent, and the exponential does depend on temperature! So this cannot be true for all temperatures T, meaning that we cannot maintain the system at equilibrium.

What solves this issue is adding a new process called **spontaneous emission**: an atom starts at $|b\rangle$ and drops to $|a\rangle$, emitting a photon, **without external stimulation**. This rate is then not dependent on the radiation in the cavity, so the rate will be AN_b (proportional to some intrinsic property of the atom and the number of atoms). Here, A does depend on which levels $|a\rangle$ and $|b\rangle$ we're in, but we're just considering two states in the atom for now.

So now we can write down an equation for the total rate of change:

$$0 = \dot{N}_b = -AN_b + B_{ab}U(\omega_{ba})N_a - B_{ba}U(\omega_{ba})N_b.$$

Rearranging this, we find that

$$A = B_{ab}U(\omega_{ba})\frac{N_a}{N_b} - B_{ba}U(\omega_{ba}) \implies U(\omega_{ba}) = \frac{A}{B_{ab}}\frac{1}{\frac{N_a}{N_b} - \frac{B_{ba}}{B_{ab}}} = \frac{A}{B_{ab}}\frac{1}{e^{\beta\hbar\omega_{ba}} - \frac{B_{ba}}{B_{ab}}}.$$

But we also know the formula for $U(\omega)$ from our starting assumptions, and we can now compare the expression we got with

$$U(\omega) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega} - 1}.$$

We then learn that $\boxed{B_{ba} = B_{ab}}$ and also that $\boxed{\frac{A}{B_{ab}} = \frac{\hbar}{\pi^2 c^3}\omega_{ba}^3}$. In particular, notice that at high temperatures, there are many photons around, and thus stimulated emission will dominate. Specifically, if $k_B T$ is larger than the relevant energy scale $\hbar\omega_{ba}$, then stimulated emission is the primary process, but otherwise if $k_B T \ll \hbar\omega_{ba}$, then spontaneous emission will dominate instead.

Fact 157

Historically, Einstein knew about the existence of spontaneous emission and absorption when he made the original argument, and he used this calculation to show that stimulated emission must also occur!

Example 158

We'll now compute B_{ba} explicitly and use it to find the rate A of spontaneous emission.

Remark 159. *Computing A explicitly on its own requires us to quantize the electromagnetic field, but we've been treating electromagnetism classically in this class. (We should think of spontaneous emission as being driven by quantum fluctuations of the electromagnetic field, which are present even in vacuum.)*

So now let's work on our problem: we have atoms interacting with thermal radiation at temperature T, and we want to calculate the stimulated emission rate per atom B_{ba}. We know that the electric field is the primary contribution to the interaction of light and atoms (because the interaction with the magnetic field is suppressed by a factor of $\frac{v}{c} \propto \alpha$ compared to the electric field). We'll also assume that we're working with **optical transitions** $\lambda \in [400 \text{ nm}, 800 \text{ nm}]$, in which the wavelength of light is much larger than a_0 (so it is much wider than the atomic cloud). That means we can write the effect of the electromagnetic wave for a **particular mode** as

$$\vec{E}(\vec{r}, t) = E(t) \cdot \vec{n} = 2E_0 \cos(\omega t)\vec{n},$$

where $\vec{n}$ is the (unit-length) vector of polarization. This corresponds to a vector and scalar potential of

$$\Phi(\vec{r}, t) = -\vec{r} \cdot \vec{E}(t), \quad \vec{A} = 0,$$

so that $\nabla\Phi = \vec{E}$ and our perturbation is

$$\delta H = q\Phi(\vec{r}, t) = -q\vec{r} \cdot \vec{E}(t) = -q\vec{r} \cdot \vec{n}E(t),$$

where $q = -e$ is the charge of the electron. We can then define the **dipole operator**

$$\vec{d} = q \cdot \vec{r},$$

which points from the negative charge (the electron) to the positive charge (the nucleus of the atom). And thus we can rewrite

$$\delta H = -\vec{d} \cdot \vec{E}(t) = 2(-\vec{d} \cdot \vec{n}E_0)\cos(\omega t).$$

(this is indeed the energy of a dipole in an electric field). This is a harmonic perturbation, which we write as $2H' \cos(\omega t)$ for a time-independent Hamiltonian $\boxed{H' = -\vec{d} \cdot \vec{n}E_0}$.

So now we calculate the rate of stimulated emission due to a particular mode of light by calculating the **probability** $P_{a\leftarrow b}(t)$ associated to it: by Fermi's golden rule, the transition occurs with probability

$$P^{\omega}_{a\leftarrow b}(t) = \frac{4|H'_{ab}|^2}{\hbar^2} \frac{\sin^2\left(\frac{\omega_{ba}-\omega}{2}t\right)}{(\omega_{ba}-\omega)^2}.$$

The matrix element in this expression is

$$H'_{ab} = -E_0 \left\langle a \middle| \vec{d} \cdot \vec{n} \middle| b \right\rangle = -E_0 \vec{n} \cdot \left\langle a \middle| \vec{d} \middle| b \right\rangle = -E_0 \vec{n} \cdot \vec{d}_{ab},$$

where

$$\vec{d}_{ab} = (\langle a|d^x|b\rangle, \langle a|d^y|b\rangle, \langle d^z|b|\rangle) = q(\langle a|x|b\rangle, \langle a|y|b\rangle, \langle a|z|b\rangle).$$

So if we plug things back in, the probability of making a downward transition due to this particular mode after time t is

$$P^{\omega}_{a\leftarrow b}(t) = \frac{4E_0^2}{\hbar^2} |\vec{d}_{ab} \cdot \vec{n}|^2 \frac{\sin^2\left(\frac{\omega_{ba}-\omega}{2} t\right)}{(\omega_{ba} - \omega)^2}.$$

It's convenient to rewrite this formula in terms of the energy carried by the electric field per unit volume, which is

$$u_E = \frac{|\vec{E}|^2}{8\pi} = \frac{4E_0^2 \cos^2(\omega t)}{8\pi} = \frac{1}{2\pi} E_0^2 \cos^2(\omega t).$$

We have a rapidly oscillating cosine term, so on average (over time) this energy per unit volume is $\overline{u_E} = \frac{E_0^2}{4\pi}$. But electromagnetic waves also have a magnetic field, and recall that the energy in the electric and magnetic field are the same! So $\overline{u_B} = \overline{u_E}$, and thus the total energy is $u = \frac{1}{2\pi} E_0^2$. (Even though the atom mostly interacts with the electric fields, the energy is still equally distributed between the two fields.) Therefore, our probability of transition is

$$P^{\omega}_{a\leftarrow b}(t) = \frac{4}{\hbar^2} (2\pi u(\omega)) |\vec{d}_{ab} \cdot \vec{n}|^2 \frac{\sin^2\left(\frac{\omega_{ba}-\omega}{2} t\right)}{(\omega_{ba} - \omega)^2}$$

for a single mode of frequency ω and polarization $\vec{n}$. And because our atom interacts with an ensemble of modes of electromagnetic radiation – we'll basically see a continuum of light modes inside the cavity if it is very large – each mode ω_i and corresponding polarization $\vec{n}_i$ will have an amplitude $E_0(\omega_i)$, and the different modes are uncorrelated. So we need

$$P^{\text{total}}_{a\leftarrow b}(t) = \sum_i \frac{4}{\hbar^2} (2\pi u(\omega_i)) |\vec{d}_{ab} \cdot \vec{n}_i|^2 \frac{\sin^2\left(\frac{\omega_{ba}-\omega_i}{2} t\right)}{(\omega_{ba} - \omega_i)^2},$$

and we now need to perform the sum over all modes, where we're **summing over frequencies and averaging over polarizations** (to fit with the normalization of $u(\omega)$ above). For each frequency ω, we therefore need to find the average $\left\langle \left| \vec{d}_{ab} \cdot \vec{n} \right|^2 \right\rangle$ by doing so over the unit vector $\vec{n}_i$, and we can write this out by components as

$$= \left\langle \left| \sum_{j=x,y,z} \vec{d}^j_{ab} \cdot n^j \right|^2 \right\rangle = \left\langle \sum_j (\vec{d}^j_{ab} \cdot n^j)^* \sum_k (\vec{d}^k_{ab} \cdot n^k) \right\rangle = \sum_{j,k} (d^j_{ab})^* d^k_{ab} \langle n^j n^k \rangle.$$

But when $j \neq k$, by reflection symmetry the average is 0, and for the others we know that

$$\langle n_x^2 \rangle = \langle n_y^2 \rangle = \langle n_z^2 \rangle = \frac{1}{3}$$

(they must all be the same and they add to 1 because $\vec{n}$ is a unit vector). Thus,

$$\left\langle \left| \vec{d}_{ab} \cdot \vec{n} \right|^2 \right\rangle = \sum_{j,k} (d^j_{ab})^* d^k_{ab} \cdot \frac{1}{3} \delta^{jk} = \frac{1}{3} |\vec{d}_{ab}|^2,$$

so that if we plug this back into the total probability of transition, we have

$$P^{\text{total}}_{a\leftarrow b}(t) = \sum_i \frac{4}{3} \frac{1}{\hbar^2} (2\pi u(\omega_i)) |\vec{d}_{ab}|^2 \frac{\sin^2\left(\frac{\omega_{ba}-\omega_i}{2} t\right)}{(\omega_{ba} - \omega_i)^2}.$$

The sum over i is now a sum over frequencies:

$$= \frac{8\pi|\vec{d}_{ab}|^2}{3\hbar^2}\sum_i u(\omega_i)\frac{\sin^2\left(\frac{\omega_{ba}-\omega_i}{2}t\right)}{(\omega_{ba}-\omega_i)^2},$$

and now we can approximate this as an integral $\sum_i u(\omega_i) \to \int d\omega U(\omega)$ (since $U(\omega)$ is the radiation energy density) to get

$$= \frac{8\pi|\vec{d}_{ab}|^2}{3\hbar^2}\int d\omega U(\omega)\frac{\sin^2\left(\frac{\omega_{ba}-\omega}{2}t\right)}{(\omega_{ba}-\omega)^2}.$$

We'll use the usual strategy here: because the function in the fraction is sharply peaked around $\omega = \omega_{ba}$, we can approximate this integral for large enough t as

$$= \frac{8\pi|\vec{d}_{ab}|^2}{3\hbar^2}U(\omega_{ba})\int d\omega\frac{\sin^2\left(\frac{\omega_{ba}-\omega}{2}t\right)}{(\omega_{ba}-\omega)^2} = \boxed{\frac{4\pi^2|\vec{d}_{ab}|^2}{3\hbar^2}U(\omega_{ba})t}$$

(we've done the integral before and it evaluates to $\frac{\pi t}{2}$). So even though each individual mode contributes to our probability in an oscillatory way, again the sum over modes gives us a positive transition rate, much like Fermi's golden rule (even thuogh we're dealing with two discrete states here)! So this gives us a stimulated emission rate

$$w_{a\leftarrow b} = \frac{4\pi^2|\vec{d}_{ab}|^2}{3\hbar^2}U(\omega_{ba}) = B_{ba}U(\omega_{ba}),$$

and now we have the expression we're looking for:

$$\boxed{B_{ba} = \frac{4\pi^2}{3\hbar^2}|\vec{d}_{ab}|^2}.$$

(Indeed, we notice that $B_{ba} = B_{ab}$.) And Einstein's relation gives us the final answer we're looking for for **spontaneous emission**:

$$\boxed{A = \frac{\hbar\omega_{ba^3}}{\pi^2 c^3}B_{ab} = \frac{4}{3}\frac{\omega_{ba}^3}{\hbar c^2}|\vec{d}_{ab}|^2}.$$

At the end of the day, we've found that these transition rates only depend on the matrix element $\vec{d}_{ab}$.

35 April 26, 2021 (Recitation)

We've been talking about Einstein's A and B coefficients and making dipole transitions in the atom (absorption or spontaneous/stimulated emission). Today, we'll do some review of this, and then we'll derive some **selection rules** to understand which transitions are actually allowed by the dipole Hamiltonian.

Recall that those three processes above can be described in terms of light and atoms: there are two states $|a\rangle$ and $|b\rangle$ separated by an energy $\hbar\omega_{ba}$.

- **Absorption** occurs when an incoming photon with frequency approximately ω_{ba} causes the atom to move from $|a\rangle$ to $|b\rangle$, and the transition rate here is $N_a B_{ab} U(\omega_{ba})$, where N_a is the number of atoms at a, $U(\omega_{ba})$ is the density of photons at this frequency, and B_{ab} is some atom-dependent quantity.
- **Stimulated emission** occurs when an incoming photon causes an atom to move from $|b\rangle$ to $|a\rangle$, and then (because of energy conservation) two photons are then emitted outward as radiation. This rate is very similarly $N_b B_{ba} U(\omega_{ba})$.
- **Spontaneous emission** occurs without a photon: an atom goes from $|b\rangle$ to $|a\rangle$ and emits one photon. This

rate is independent of the presence of photons, and it is $N_b A$.

In lecture, we then went through Einstein's argument using statistical equilibrium and balancing the combined rate of transitions. We need $\dot{N}_a = \dot{N}_b = 0$, and we know that N_a and N_b have some ratio at equilibrium, given by the Boltzmann distribution $e^{-\beta\hbar\omega_{ab}}$ (where $\beta = \frac{1}{k_B T}$). We also have the blackbody radiation formula

$$U(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^2}{e^{\beta\hbar\omega} - 1}.$$

Plugging everything in, we ended up with the result

$$B_{ab} = B_{ba}, \quad A = B_{ab} \frac{\hbar\omega_{ba}^3}{\pi^2 c^3},$$

and we can find more explicit solutions by looking at **dipole transitions**: if we think about an electric field $\vec{E}(t) = 2E_0 \hat{n} \cos(\omega t)$ for a **given field** being applied (where we use the usual approximation to drop the spatial dependence), we can use the usual Fermi's golden rule on $\delta H = -\vec{d} \cdot \hat{n}(2E_0)\cos(\omega t)$ for the **dipole moment operator** $\vec{d} = q\hat{r}$. We then have $H' = -\vec{d} \cdot \hat{n} E_0$, and we can write this in terms of the energy density $u = \frac{E_0^2}{2\pi}$ (which depends on ω because we generally have a spectrum of different frequencies in our electric field, with different magnitudes). Reading off coefficients then allowed us to find B_{ab}, B_{ba}, and A:

$$B_{ba} = B_{ab} = \frac{4\pi^2}{3\hbar^2} |\vec{d}_{ab}|^2, \quad A = \frac{4}{3} \frac{\omega_{ba}^3}{\hbar c^3} |\vec{d}_{ab}|^2,$$

where we have the dipole matrix element $\vec{d}_{ab} = \left\langle a \middle| \vec{d} \middle| b \right\rangle = q \langle a | \vec{r} | b \rangle$.

We'll now talk more about these matrix elements in detail: we'll work out a lot of them in our problem set, but there's a few general rules that will help us out. We want to think about the hydrogen atom, and we want to understand when we can go from $|n', \ell', m'\rangle$ to $|n, \ell, m\rangle$.

Problem 160

When are the matrix elements

$$\langle n, \ell, m | \vec{r} | n', \ell', m' \rangle = \int d^3 r \psi_{n,\ell,m}^*(\vec{r}) \vec{r} \psi_{n',\ell',m'}(r)$$

nonzero, meaning that the corresponding transition is allowed?

Our first consideration is **parity**: if we look at the change of variables on the right-hand side replacing $\vec{r}$ to $-\vec{r}$, then the $\vec{r}$ gets flipped under parity, while the $d^3 r$ stays the same. Since each $\psi_{n,\ell,m}$ state is a definite parity state in hydrogen, this means the product $\psi_{n,\ell,m}^*(\vec{r})\psi_{n',\ell',m'}(r)$ must be odd (or else the change of variables gives us the negative of the original integral, meaning it was zero), which is the same as saying that the states must have opposite parity.

And because parity is $(-1)^\ell$ (the orbital part is what matters here, since the radial part only depends on magnitude), what this means is that ℓ and ℓ' must be of opposite parity, or in other words that $\boxed{\ell + \ell' \text{ is odd}}$. This is an example of a **selection rule**: it for example forbids us from making a transition $\ell' = 0$ to $\ell = 0$.

But it turns out that we can be more specific: it is required that we instead have $\boxed{\Delta\ell = \ell - \ell' = \pm 1}$. To show this, we should recall our earlier work with vector operators: we showed

$$\frac{1}{(2i\hbar)^2}[\vec{J}^2, [\vec{J}^2, \vec{V}]] = (\vec{V} \cdot \vec{J})\vec{J} - \frac{1}{2}(\vec{J}^2 V + \vec{V}\vec{J}^2)$$

for a vector operator $\vec{V}$. We'll apply this for $\vec{J} = \vec{L}$ (the operator which causes rotations) and $\vec{V} = \vec{r}$, and we can notice that

$$\vec{V} \cdot \vec{J} = \vec{r} \cdot \vec{L} = \vec{r} \cdot (\vec{r} \times \vec{p}) = 0.$$

Our result then ends up being

$$[\vec{L}^2, [\vec{L}^2, \vec{r}]] = 2\hbar^2(\vec{L}^2\vec{r} + \vec{r}\vec{L}^2),$$

and we basically want to take matrix elements of this formula to get useful results. We can write out the commutator on the left-hand side: we find that

$$(\vec{L}^2)^2\vec{r} - 2\vec{L}^2 r\vec{L}^2 + \vec{r}(\vec{L}^2)^2 = 2\hbar^2(\vec{L}^2 r + \vec{r}\vec{L}^2).$$

If we put a $\langle n, \ell, m|$ on the left of both sides and a $|n', \ell', m'\rangle$ on the right of both sides, the $\vec{L}^2$ operators can be applied against the bras and kets to get numbers (because we have eigenstates of $\vec{L}^2$, specifically with eigenvalues $\hbar^2\ell(\ell+1)$). So the left-hand side simplifies to (noticing that we have a perfect square)

$$\hbar^4\left(\ell(\ell+1) - \ell'(\ell'+1)\right)^2 \langle n, \ell, m|\vec{r}|n', \ell', m'\rangle,$$

and similarly, the right-hand side simplifies to

$$= 2\hbar^4[\ell(\ell+1) + \ell'(\ell'+1)] \langle n, \ell, m|\vec{r}|n', \ell', m'\rangle.$$

Simplifying, we find that the matrix element factors, powers of $\hbar$ cancel out, and what we have left is

$$\boxed{\langle n, \ell, m|\vec{r}|n', \ell', m'\rangle \left((\ell+\ell'+1)^2 - 1\right)\left((\ell-\ell')^2 - 1\right) = 0}.$$

So either the matrix element is zero, or $\ell = \ell' = 0$ from the second term, or $|\ell - \ell'| = 1$. But we already showed by the previous selection rule that $\ell = \ell' = 0$ doesn't work, so indeed we recover the result promised: transitions can only occur when $\boxed{\Delta\ell = \pm 1}$.

Remark 161. *The simplest way to think about this result physically is in terms of total angular momentum conservation: making the dipole approximation to the photon means the only angular momentum that's going on here is in the photon and the original state, and photons have spin 1.*

But we can also say more about the other quantum number m and try to understand $\Delta m = m - m'$. We'll do that one component at a time.

- For the z-component, notice that $[L_z, z] = L_z z - zL_z 0$, so if we take matrix elements of this expression (remembering that $|n, \ell, m\rangle$ is an eigenstate of L_z with eigenvalue $\hbar m$), we find that

$$(m - m')\hbar\langle n, \ell, m|z|n', \ell', m'\rangle = 0,$$

  so the only way to get a nonzero z-component of the matrix element is if $\Delta m = 0$.

- For the other components, we can notice that

$$[L_z, x] = i\hbar y, \quad [L_z, y] = -i\hbar x$$

  (essentially, a rotation in z turns x into y), and taking matrix elements on both sides will give us

$$(m - m')\hbar\langle n, \ell, m|x|n', \ell', m'\rangle = i\hbar\langle n, \ell, m|y|n', \ell', m'\rangle,$$

$$(m - m')\hbar\langle n, \ell, m|y|n', \ell', m'\rangle = -i\hbar\langle n, \ell, m|x|n', \ell', m'\rangle.$$

We can then solve for the two unknowns (matrix element of x and y), and we find that

$$((m-m')^2-1)\langle n,\ell,m|y|n',\ell',m'\rangle = 0,$$

and also an identical formula for the x-matrix element. So that tells us that the only way to get nonzero x- and y-components are if $\Delta m = \pm 1$.

So putting everything together, the only nonzero matrix elements for $\vec{r}$ (and thus the only nonzero dipole matrix elements) is if $\Delta \ell = \pm 1$ and $\Delta m = 0, \pm 1$. But the levels in n can jump in arbitrary ways, since those transitions depend on energy differences and those are dependent on the energies of the incoming photons.

36 April 27, 2021

Last lecture, we discussed Einstein's argument for the interaction of light and atoms – we discovered that in addition to the absorption and stimulated emission occurring when we treat light like a classical wave, we have an additional process, spontaneous emission, that also occurs without any external stimulation from a light source. We deduced with Einstein's argument that the rate of these spontaneous emissions is

$$A = \frac{4}{3}\frac{\omega_{ba}^3}{\hbar c^3}|\vec{d}_{ab}|^2,$$

where $\vec{d}_{ab}$ is the matrix element $\langle b|q\vec{r}|a\rangle$ of the dipole moment $q\vec{r}$ between our initial and final states. Since this is a decay rate, if there is no external radiation (light) source, then the number of atoms $N_b(t)$ in state b satisfies the rate equation

$$\frac{dN_b}{dt} = -AN_b \implies N_b(t) = N_b(0)e^{-At},$$

meaning that $\tau = \frac{1}{A}$ is the lifetime of our excited state $|b\rangle$ if it can decay to $|a\rangle$. More generally, we may have a bunch of different decay rates A_i because $|b\rangle$ can decay to a variety of other (lower-energy) states, and thus we can write down a total rate $A_{\text{total}} = A_1 + \cdots + A_n$. The lifetime involved then satisfies

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \cdots + \frac{1}{\tau_n}.$$

(If there are multi-step decays from $|b\rangle$ to a lower-energy state, all that matters is the initial decay rate.)

We've mentioned that spontaneous emission is accompanied by a photon, and indeed we can look at the frequency of the outgoing photons in such a process.

Fact 162

Much like in Fermi's golden rule, the frequency of the emitted photons is strongly peaked around ω_{ba} with width A: specifically, the distribution function is the Lorentzian

$$P(\omega) = \frac{A}{2\pi}\frac{1}{(\omega-\omega_{ab})^2 + \frac{A^2}{4}}$$

In fact, calculating this width is the usual experimental method for extracting the decay rate.

(This is the reason we often call A the **line width**.) For an atom like hydrogen, the electric dipole transition rate (recalling that our formula for A above assumes that the electric field contributes much more to the rate than the magnetic field) goes as

$$\hbar A \sim \alpha^5 m_e c^2.$$

Comparing this to the main energy scale in atomic physics, which is the Rydberg $\frac{1}{2}\alpha^2 m_e c^2$, we see that $\hbar A \ll \text{Ry}$. In fact, the fine structure scale $E_{\text{fs}} \sim \alpha^4 m_e c^2$, so we even have $\hbar A \ll E_{\text{fs}}$. So this means that resolving the energy difference from fine structure effects is not inhibited by the line width!

We know that the decay rate is only nonzero **(to the order that we're considering)** if the matrix element $\langle b|\vec{r}|a\rangle$ is zero, and there are certain **selection rules** for when the matrix element between two states $|n, \ell, m\rangle$ and $|n', \ell', m'\rangle$ is nonzero. As derived in recitation, we have the following results:

Proposition 163

The matrix elements $\langle n', \ell', m'|\vec{r}|n, \ell, m\rangle$ are zero unless $\ell' - \ell = \pm 1$, and in addition $\langle n', \ell', m'|z|n, \ell, m\rangle = 0$ unless $m' = m$, and $\langle n', \ell', m'|x|n, \ell, m\rangle = \langle n', \ell', m'|y|n, \ell, m\rangle = 0$ unless $m' - m = \pm 1$.

This concludes our discussion of light-atom interactions and time-dependent perturbation theory, and our next topic will be the **adiabatic approximation**. Here, we continue to study quantum systems with a time-dependent Hamiltonian $H(t)$, but we will assume that it varies **slowly as a function of time**. (This is a setup that often makes sense for cold-atom systems, and it is also used for adiabatic quantum computation.)

Example 164

The variation of the Hamiltonian may come from an experimentalist changing a parameter in a lab. For example, we may have a pendulum in which the length is changing, so that the Hamiltonian looks like $H(t) = \frac{p^2}{2m} + \frac{1}{2}m\omega(t)^2 x^2$.

We wish to figure out how to quantify the "slowness" of the change of $H(t)$, which comes from the slowness of the change of $\omega(t)$. To do so, we compare to the fundamental time scale of the system $T = \frac{2\pi}{\omega}$, the period of the oscillations. It then makes sense that we have a slowly-varying function if over each period of length T, the relative change in ω is small: another way to write this is that

$$|T \cdot \dot{\omega}| \ll \omega.$$

Plugging in our expression for T, this can be rewritten as

$$\left|\frac{\dot{\omega}}{\omega^2}\right| \ll 1 \implies \left|\frac{d}{dt}\left(\frac{1}{\omega}\right)\right| \ll 1 \implies \boxed{\frac{dT}{dt} \ll 1}.$$

This is a nice result because it's unitless, and it's reminiscent of the condition we had in the WKB approximation, in which $\left|\frac{d\lambda}{dx}\right| \ll 1$. Notice that we're not making any assumption here that the change in the Hamiltonian is small, though – over a long time period, H is allowed to change dramatically. So this is different from perturbation theory in that $\delta H(t)$ is not assumed to be small!

We'll be talking about adiabatic evolution for **quantum** systems in this class, meaning that we want to understand how H's slow variance affects the Schrodinger equation $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H(t)|\psi(t)\rangle$. The following concept is particularly useful in this setup:

Definition 165

The **instantaneous eigenstates** and **instantaneous energies** of $H(t)$ are the wavefunctions $|\psi_n(t)\rangle$ and eigenvalues $E_n(t)$ satisfying

$$H(t)|\psi_n(t)\rangle = E_n(t)|\psi_n(t)\rangle.$$

We often draw "level spaghetti" diagrams, plotting each E_n as a function of time. We've mentioned previously that in general, these instaneous eigenstates don't help us with time-dependent Hamiltonians, but we'll see now that they are useful when our Hamiltonian varies slowly in time. But we do need to avoid degeneracies: we will assume that the levels do not cross, so that we have

$$E_0 < E_1 < E_2 < \cdots$$

and we can choose an orthonormal basis $|\psi_n\rangle$.

Theorem 166 (Adiabatic theorem)

If our system is in an instantaneous eigenstate $|\psi_n(0)\rangle$ at $t = 0$, then

$$|\psi(t)\rangle \approx c_n(t)\,|\psi_n(t)\rangle$$

for all t, as long as $H(t)$ changes slowly. In other words, the probability of transitioning to a different state goes to 0 for a varying-slowly-enough H.

Proof sketch. We'll denote the full wavefunction solution by Ψ in this proof to avoid confusion. We expand the solution $|\Psi(t)\rangle$ in terms of the instantaneous eigenstates (we have completeness of the orthonormal basis at any point in time, because $H(t)$ is a Hermitian operator)

$$|\psi(t)\rangle = \sum_n c_n(t)\,|\psi_n(t)\rangle\,.$$

Plugging this into the time-independent Schrodinger equation, we have

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = i\hbar\sum_n \dot{c}_n\,|\psi_n(t)\rangle + c_n|\dot{\psi_n}(t)\rangle$$

by the product rule, and we know that this is equal to

$$= H(t)\,|\Psi(t)\rangle = \sum_n E_n(t)c_n(t)\,|\psi_n(t)\rangle\,.$$

We can thus manipulate this equality to get an equation for each $\dot{c}_n(t)$ by applying a $\langle\psi_k(t)|$ for some fixed k on both sides. By orthonormality, we find that

$$i\hbar\dot{c}_k + i\hbar\sum_n c_n(t)\left\langle\psi_k\middle|\dot{\psi}_n\right\rangle = E_k(t)c_k.$$

We'll split this up as

$$i\hbar\dot{c}_k = \left(E_k(t) - i\hbar\left\langle\psi_k\middle|\dot{\psi}_k\right\rangle\right)c_k(t) - i\hbar\sum_{n\neq k}\left\langle\psi_k\middle|\dot{\psi}_n\right\rangle c_n(t).$$

We wish to show that the equations for various k decouple, because that means that our system will remain in the instantaneous eigenstate $|\psi_k(t)\rangle$ if it started off in $|\psi_k(0)\rangle$. So we want to the "transition-causing terms" to be negligible, and we'll **assume that we can neglect them** for now (and return to it at the end of the discussion). Then we find that

$$\dot{c}_k = \left(-\frac{i}{\hbar}E_k(t) - \left\langle\psi_k\middle|\dot{\psi}_k\right\rangle\right)c_k \implies c_k(t) = \exp\left(-\frac{i}{\hbar}\int_0^t dt' E_k(t')\right)\exp\left(-\int_0^t dt'\left\langle\psi_k\middle|\dot{\psi}_k\right\rangle\right)c_k(0).$$

Introducing the notation

$$\theta_k(t) = -\frac{1}{\hbar}\int_0^t dt' E_k(t'), \quad \nu_k(t) = i\left\langle\psi_k\middle|\dot{\psi}_k\right\rangle, \quad \gamma_k(t) = \int_0^t dt'\nu_k(t),$$

we find that

$$c_k(t) = \exp\left(i\theta_k(t)\right)\exp\left(i\gamma_k(t)\right)c_k(0).$$

In particular, if $c_k(0) = \delta_{mk}$ (meaning that our state started in one of the instantaneous eigenstates), then $c_k(t) = 0$ for all t unless $m = k$, and thus our wavefunction takes the form (under this approximation)

$$|\Psi(t)\rangle \approx e^{i\theta_m(t)} e^{i\gamma_m(t)} |\psi_m(t)\rangle .$$

Here, $\theta_m(t)$ is known as the **dynamical phase**, and $\gamma_m(t)$ is known as the **Berry phase** or **geometric phase**. (The reason this phase is important is that we may not start in an instantaneous eigenstate – more generally, we'll have

$$\boxed{|\Psi(t)\rangle \approx \sum_k e^{i\theta_k(t)} e^{i\gamma_k(t)} c_k(0) |\psi_k(t)\rangle}.$$

We can verify that $\gamma_k(t)$ is real (so that we do have a phase), because

$$\langle \psi_k | \psi_k \rangle = 1 \implies \frac{d}{dt} \langle \psi_k | \psi_k \rangle = \langle \dot{\psi}_k | \psi_k \rangle + \langle \psi_k | \dot{\psi}_k \rangle = 0.$$

Since the two terms here are complex conjugates of each other, they can only be negatives of each other if they are purely imaginary.

It now remains to examine whether we can indeed drop the transition-causing terms: the terms that are being coupled together involve expressions that look like $\langle \psi_k | \dot{\psi}_n \rangle$ for $k \neq n$. Because we have instantaneous eigenstates, we know that (taking a derivative)

$$H |\psi_n\rangle = E_n(t) |\psi_n\rangle \implies \dot{H} |\psi_n\rangle + H |\dot{\psi}_n\rangle = \dot{E}_n |\psi_n\rangle + E_n |\dot{\psi}_n\rangle .$$

Applying a bra $\langle \psi_k |$ to both sides gives us

$$\langle \psi_k | \dot{H} | \psi_n \rangle + \langle \psi_k | H | \dot{\psi}_n \rangle = \dot{E}_n |\psi_k\rangle \psi_n + E_n \langle \psi_k | \dot{\psi}_n \rangle ,$$

and now the first term on the right is zero by orthonormality, and the second terms the two sides combine if we apply the H on the left-hand side on the bra to make $E_k \langle \psi_k | \dot{\psi}_n \rangle$. Thus, we have

$$\langle \psi_k | \dot{H} \rangle \psi_n = -(E_k - E_n) \langle \psi_k | \dot{\psi}_n \rangle ,$$

and thus rearranging gives us the identity

$$\boxed{\langle \psi_k | \dot{\psi}_n \rangle = -\frac{\langle \psi_k | \dot{H} | \psi_n \rangle}{E_k(t) - E_n(t)}}.$$

So as long as the energies do not cross (so $E_k(t) - E_n(t)$ is not too small), and we have a slowly varying Hamiltonian (so that the matrix element is indeed small), the adiabatic theorem will generally hold. Indeed, if we plug in our boxed expression back into the Schrodinger equation, we have

$$\left(i\hbar \frac{\partial}{\partial t} - E_k(t) - i\hbar \langle \psi_k | \dot{\psi}_k \rangle \right) c_k(t) = i\hbar \sum_{n \neq k} \frac{\langle \psi_k | \dot{H} | \psi_n \rangle}{E_k(t) - E_n(t)}.$$

We may be concerned that the effects of $\dot{H}$ will accumulate over large time periods, so that the locally small effects on the right-hand side will accumulate. But this does not happen: if we write our coefficients in terms of the phases $c_k(t) = e^{i\theta_k(t)} e^{i\gamma_k(t)} \tilde{c}_k(t)$, we then find that the equation simplifies to

$$i\hbar e^{i\theta_k(t)} e^{i\gamma_k(t)} \dot{\tilde{c}}_k(t) = i\hbar \sum_{n \neq k} \frac{\langle \psi_k | \dot{H} | \psi_n \rangle}{E_k(t) - E_n(t)} e^{i\theta_n(t)} e^{i\gamma_n(t)}.$$

Dividing out the phase on both sides gives us

$$\dot{\tilde{c}}_k(t) = \sum_{n \neq k} \frac{\langle \psi_k | \dot{H} | \psi_n \rangle}{E_k(t) - E_n(t)} e^{i(\theta_n - \theta_k)t} e^{i(\gamma_n - \gamma_k)t} \tilde{c}_n(t).$$

Integrating this equation from time 0 to t, we find that

$$\tilde{c}_k(t) - \tilde{c}_k(0) = \sum_{n \neq k} \int_0^t dt' \frac{\langle \psi_k | \dot{H} | \psi_n \rangle}{E_k(t') - E_n(t')} e^{i(\theta_n - \theta_k)t'} e^{i(\gamma_n - \gamma_k)t'} \tilde{c}_n(t').$$

And even if the window of time t is very large, the first fraction is a slowly-varying function of time, and we're integrating against a **rapidly-oscillating phase**. So most of the integral contribution will be zero, and thus the effects of $\dot{H}$ do not accumulate. ☐

We'll talk about this in more detail next time!

37 April 28, 2021 (Recitation)

We'll start today by finishing our discussion of spontaneous emission, giving a derivation that is more direct for finding the rate $A = \frac{4}{3}\frac{\omega_{ba}^3}{\hbar c^3}|\vec{d}_{ab}|^2$. It'll be a bit beyond the course material, but most of it fits with what we know here.

Basically, the stimulation of this process comes not from an external field but rather from the **quantization of photons**. Here's how we'll set that up:

Example 167

Consider an initial state $|i\rangle = |2, 1, m\rangle \otimes |0\rangle$, corresponding to a particular eigenstate of the hydrogen atom and zero photons, and a final state $|f\rangle = |1, 0, 0\rangle \otimes |k\rangle$, corresponding to the ground state of hydrogen and a photon with momentum $\vec{p} = \hbar\vec{k}$ (and thus frequency $\omega = kc$).

We'll think about having a "raising operator" for the photon

$$|k\rangle = a_k^\dagger |0\rangle,$$

and also lowering operators which satisfy $a_k |0\rangle = 0$. The point is that we have not just classical electromagnetic fields but quantum vector potentials written in terms of operators: we will use the fact that

$$\vec{A}(\vec{r}) = \int d^3k \left(\frac{\hbar c^2}{4\pi^2\omega}\right)^{1/2} \left[a_k \vec{\varepsilon}_k e^{i\vec{k}\cdot\vec{r}} + a_k^\dagger \vec{\varepsilon}_k^* e^{-i\vec{k}\cdot\vec{r}}\right]$$

(it makes sense to need both raising and lowering operators so that we have Hermiticity). Here, $\vec{\varepsilon}_k$ tells us the direction of the photon's polarization and are thus called photon polarization vectors. It's also important during this quantization process to explain the commutation relations: we have

$$[a_k, a_{k'}^\dagger] = \delta^3(k - k'),$$

which is the analog of the Kronecker delta for the continuous situation. So we'll now do our perturbation theory using this $\vec{A}$: consider the harmonic perturbation

$$\vec{A}(\vec{r}, t) = e^{i\omega t} A(\vec{r}),$$

so that we get

$$\delta H = -q\vec{r}\cdot\vec{E} = \frac{q}{c}\vec{r}\cdot\frac{\partial\vec{A}}{\partial t},$$

and plugging in the expression for $\vec{A}$ and using the same long-wavelength approximation we've been making so frequently, things simplify to

$$\approx \frac{i\omega q}{c}e^{i\omega t}\vec{r}\cdot\vec{A}(\vec{r}=0).$$

We can thus use Fermi's golden rule on our $e^{i\omega t}H'$ Hamiltonian perturbation, and what we find is that the transition rate

$$w_{i\to f} = \frac{2\pi}{\hbar}|H'_{fi}|^2\int d^3k\ \delta(E_i - E_f - \hbar\omega)$$

where we sum over the final state photon and use the fact that the remaining part of the integral involving the density of states is sharply peaked. (Basically, we sum over the final momentum of the photon, but we're constrained by energy conservation to have $E_f = E_i - \hbar\omega$.) We then need to evaluate the matrix element

$$\langle f|H'|i\rangle = \frac{i\omega}{c}\langle 1,0,0|q\vec{r}|2,1,m\rangle\otimes\left\langle\vec{k}\middle|\vec{A}(0)\middle|0\right\rangle.$$

This second term is the one that is new: notice that we can write $|k\rangle$ in terms of a creation operator, so

$$\left\langle\vec{k}\middle|\vec{A}(0)\middle|0\right\rangle = \left\langle 0\middle|a_k\int d^3k'(\cdots)^{1/2}a_{k'}^\dagger\vec{\varepsilon}_{k'}^{\,*}\middle|0\right\rangle,$$

where we've dropped the a'_k term because the annihilation operators make things vanish. So now we use the fact that $a_k a_{k'}^\dagger = a_{k'}^\dagger a_k + \delta^3(k-k')$, and now the first term has matrix element 0 in the ground state, so we can move the a_k past the $a_k^\dagger$ and pull the d^3k integral out of the matrix element to find that what we're left with is

$$= (\text{integral over } k)\cdot\left(\frac{\hbar c^2}{4\pi^2\omega}\right)^{1/2}\vec{\varepsilon}^{\,*}.$$

From here, we still have to deal with the delta function

$$\int d^3k\delta(E_i - E_f - \hbar ck).$$

The angular part gives us a factor of 4π, and the radial part is fixed by the delta function so that we must have $k = k_{if} = \frac{\omega_{if}}{c} = \frac{E_i - E_f}{c\hbar}$:

$$= 4\pi\int dk k^2\delta(E_i - E_f - \hbar ck) = \frac{4\pi}{\hbar c}k_{if}^2 = \frac{4\pi}{\hbar c^3}\omega_{if}^2.$$

Specifically, all ωs in our formula get replaced by an ω_{if}, and now that completes our calculation: working out the rest of the integrals gives us the answer for the rate A:

$$w_{i\to f} = \left(\frac{2\pi}{\hbar}\right)\left(\frac{\omega_{if}^2}{c^2}\right)|\vec{d}_{fi}|^2\frac{1}{3}\frac{\hbar c^2}{4\pi^2\omega_{if}}\cdot\left(\frac{4\pi}{\hbar c^3}\omega_{if}^2\right)\cdot 2.$$

Here, the factor of $\frac{1}{3}$ comes from the averaging over polarizations like we had with the $\hat{n}\cdot\vec{d}$ term in lecture – that $\hat{n}$ plays the same role that $\vec{\varepsilon}$ is playing for us right now – and the final factor of 2 comes from the fact that there are two spin states for our photon $m = \pm 1$. Simplifying everything here indeed recovers our desired formula!

Fact 168

Basically, the only quantum mechanical considerations going on here come from the raising and lowering operators $a_k, a_k^\dagger$, which don't talk to each other for different k.

We'll now turn to the adiabatic approximation mentioned in lecture, in which we have a slowly-varying time variation $H(t)$ (meaning that H varies slowly relative to the system's intrinsic time scales). In other words, if there is some internal timescale T_i for substantial variation, as well as some external timescale T_e affecting time-variation, we must have $T_i \ll T_e$.

But we can phrase this situation in terms of energies as well – we need to assume that states are nondegenerate and that there are no energy crossings, so another phrasing is that the **smallest** energy gap for any pair of energy levels satisfies $\Delta_{mn} = \min_t |E_m(t) - E_n(t)| > 0$. We can then think of our internal timescale as being $T_i \sim \frac{\hbar}{\Delta}$, and we can think of our external timescale also in terms of H via $T_e \sim \frac{\Delta}{|\dot{H}|}$ (an approximation for the time that we spend in a narrow energy region Δ in which levels are closest). So again $T_i \ll T_e$ is the approximation, and that puts some constraint on the time-varying nature of H:

$$\frac{\Delta}{|\dot{H}|} \ll \frac{\hbar}{\Delta} \implies \frac{\hbar|\dot{H}|}{\Delta^2} \ll 1.$$

In lecture, we mentioned the concept of **instantaneous eigenstates** being useful: treating time t as a parameter, we can find the eigenstates and eigenvalues $|\psi_n(t)\rangle, E_n(t)$ of the matrix $H(t)$ at any fixed time. We can then use the adiabatic theorem, which tells us that if our initial state $|\Psi(0)\rangle = |\psi_n(0)\rangle$ is some instantaneous eigenstate, and H is slowly varying with nondegenerate energies, then $| |\Psi(t)\rangle \approx e^{i\theta_n(t)} e^{i\gamma_n(t)} |\psi_n(t)\rangle$ is a phase times the corresponding instantaneous eigenstate at some later time.

However, notice that the nth energy level can be very different at different times – drastic evolutions are allowed, but we (approximately) do not make transitions between different energy levels.

Example 169

Consider the Hamiltonian $H(t) = H_0 + f(t)H'$, so that the time-dependent part is parameterized by some function f which is turned on slowly from 0 to 1 during the time interval $[0, T]$.

Then we have some instantaneous eigenstate $|\psi_n(0)\rangle$ at time $t = 0$ for H_0, and we have some instantaneous eigenstate $|\psi_n(T)\rangle$ at time $t = T$ for $H_0 + H'$ (where H' can be as big as H_0, for example). Then the adiabatic theorem tells us that as long as we dragged $f(t)$ slowly enough over time, we do indeed evolve approximately from one instantaneous eigenstate to another, even if those eigenstates look completely different.

38 April 29, 2021

Last time, we started talking about the adiabatic approximation: the idea is that we have a Hamiltonian $H(t)$ that changes slowly in time (though the overall change between initial and final Hamiltonian can be large). If we define instantaneous eigenstates $|\psi_n(t)\rangle$ for the Hamiltonian $H(t)$ at each time t, and it turns out that the instantaneous energies $E_n(t)$ do not cross (and that there is no degeneracy), then starting in $|\psi_n(0)\rangle$ at some initial state means that we will approximately stay in $|\psi_n(t)\rangle$, up to a phase $e^{i\theta_n(t)} e^{i\gamma_n(t)}$. (And starting in some linear superposition means we have a linear superposition of the final $e^{i\theta_n(t)} e^{i\gamma_n(t)} |\psi_n(t)\rangle$ states.)

We started talking about the justification for this result last time, and we'll continue that here. Basically, we decompose the full wavefunction into the instantaneous eigenstates with some time-changing coefficients $\tilde{c}_n(t) e^{i\theta_n(t)} e^{i\gamma_n(t)}$. What we need to show is that $\tilde{c}_n(t)$ is approximately constant in time under the assumptions of the adiabatic theorem:

we calculated the difference $\tilde{c}_k(t) - \tilde{c}_k(0)$ to be the exact expression

$$\sum_{n \neq k} \int_0^t dt' \frac{\langle \psi_k | \dot{H} | \psi_n \rangle}{(E_k - E_n)(t')} e^{i(\gamma_n - \gamma_k)t'} e^{i(\theta_n - \theta_k)t'} \tilde{c}_n(t').$$

To work with this, we need to understand how the different "degrees of slowness" work in this expression. If the evolution initially takes place between times 0 and T, but then we slow down time (stretching out the time axis) so that T gets larger, we get a family of Hamiltonians

$$H(t, T) = \tilde{H}\left(s = \frac{t}{T}\right),$$

where we parameterize $s \in [0, 1]$. So the evolution becomes slower as $T \to \infty$ – indeed, the chain rule tells us that $\frac{dH}{dt} \sim \frac{1}{T}$. So that means the matrix element of $\dot{H}$ gets smaller, but the window of integration gets larger – this means we should find a way to show that the integral is nevertheless not of order 1.

The point is that the dynamical phase θ_n, which is basically an integral of the instantaneous energies, satisfies

$$\dot{\theta}_n - \dot{\theta}_k = -\frac{1}{\hbar}(E_n - E_k)(t'),$$

and because the energies change slowly over time, locally we have $\theta_n - \theta_k \approx -\frac{1}{\hbar}(E_n - E_k)t'$. So the phase factor oscillates locally with a frequency determined by the **instantaneous energy difference** (and notably, not dependent on T). Since the rest of the integral for $\tilde{c}_k(t) - \tilde{c}_k(0)$ (the Berry phase and the matrix element) is slowly-varying in time, the θ_n rapid oscillation will wash out most of the integral to 0. This means that we only get contributions from the incomplete periods at the beginning and end, in which the integrand is proportional to $\frac{\dot{H}}{\Delta E}$ (since $\tilde{c}_n$ is a coefficient whose square gives a probability, it must be at most 1). Since the duration of the incomplete period is roughly $\frac{\hbar}{\Delta E}$, that means that we get the estimate

$$\tilde{c}_k(T) - \tilde{c}_k(0) \approx \frac{\hbar \dot{H}}{(\Delta E)^2}.$$

This is of order $\frac{1}{T}$, so the difference does indeed go to 0, and we've shown the adiabatic theorem. (However, we do need to notice that this result depends on ΔE being strictly positive – things break down if the energy levels get too close to each other.) And as an additional result, the probability of a non-adiabatic transition is

$$P_{n \leftarrow k}(T) \sim \frac{1}{T^2}.$$

Remark 170. *Our argument is pretty handwavy here (especially with the "washing out of the integral"), but it can indeed be made into a more formal proof. And we can improve the error bound here as well: if our system evolves between an initial and final Hamiltonian between times* 0 *and* T, *and the "turning on" and "turning off" of our Hamiltonian at time* 0 *and* T *is very smooth, meaning that the first* p *derivatives of* H *vanish, then*

$$P_{n \leftarrow k}(T) \leq O\left(\frac{1}{T^{2(p+1)}}\right).$$

We'll now consider a toy setup that lets us explore the adiabatic regime and also the corrections to it:

Example 171 (Landau-Zener problem)

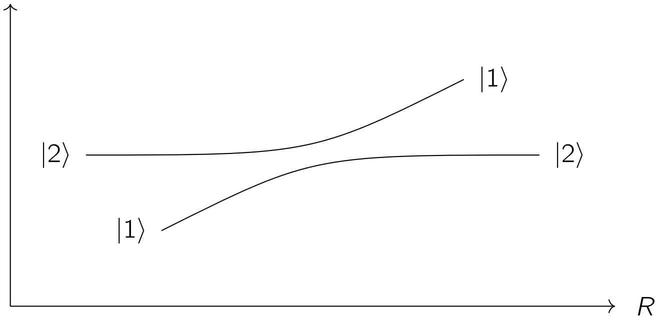
Suppose we have a system in which our Hamiltonian is a function of some parameter R, and suppose that two of the levels $E_+(R)$ and $E_-(R)$ come close to each other for a short period of time but don't quite cross. (Such "avoided crossings" are common.)

Before we discuss this particular problem, we'll first explain why we try to avoid level crossings in quantum mechanics.

If we have two energy levels, we can always write the Hamiltonian for those two levels in terms of the Pauli matrices: $H = a_0 I + \vec{a} \cdot \vec{\sigma}$, where $a_0, a_1, a_2, a_3 \in \mathbb{R}$. The energy levels are then $a_0 \pm |\vec{a}|$, where $\vec{a} = (a_1, a_2, a_3)$, and thus the energy difference $E_+ - E_- = 2|\vec{a}|$ goes to zero only when $\vec{a} = (0, 0, 0)$. In other words, we need to tune three different parameters to get a crossing, and thus crossings do not occur generically.

But there is an exception to this logic, which occurs when two levels have different quantum numbers. For example, if $[\vec{L}^2, H] = 0$ (the Hamiltonian commutes with angular momentum), and there are two energy levels with different ℓs $|\ell\rangle, |\ell'\rangle$, then we can guarantee the matrix element $\langle \ell | H | \ell' \rangle = 0$. This basically guarantees that a_1 and a_2 will be zero, and thus we only need to tune one parameter to get the energy levels to coincide.

So now we'll return to our problem: we tune our parameter R, and we want to ask about the probability of making a transition between instantaneous eigenstates over time. The system that Landau and Zener had in mind was to have two atoms (such as Na and Cl) which can form a polar molecule. Specifically, on their own, they are neutral atoms, but when they get close together, we should think of them as Na+ and a Cl- ions. Our parameter R will then be the separation between the two atoms – we'll then have the **ionic state** (Na+, Cl-) and the **atomic state** (Na, Cl), and we know that these levels will come close at some distance, because at a close enough distance it becomes more favorable to see an ionic state than an atomic state. Since we mentioned that energy levels should not cross, the energy diagram will look something like this:



What we'll imagine is that a sodium atom is scattered at a chlorine atom, and we want to calculate the probability that we make the non-adiabatic transition to the ionic state. In particular, if we move R very slowly, then we will follow the bottom branch of this energy diagram, so that as the sodium atom is scattered it will transition to the ionic state and then back to the atomic state. But there is some probability of an energy transition near the near-crossing, meaning that we jump to the top branch and exit in the ionic state.

For a process like this, it makes sense to have R vary as a function of time, and the highest probability occurs near the near-crossing point.

Example 172

But we'll instead do an even simpler problem: we ignore all energy levels except these two, and we start with a Hamiltonian

$$H(t) = \frac{\alpha t}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \alpha > 0.$$

(We'll soon add an additional parameter into this expression.)

The instantaneous eigenstates are always $|1\rangle = \begin{bmatrix} 1 & 0 \end{bmatrix}$ and $|2\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$, with energies $\pm \frac{\alpha t}{2}$, so that these energies intersect at time 0. We now have a true energy crossing, and we can solve the time-evolution exactly: the time-dependent Schrodinger equation gives us

$$|\psi_1(t)\rangle = \exp\left(-\frac{i}{\hbar}\int_0^t E_1(t')dt'\right)|1\rangle = \exp\left(-\frac{i\alpha t^2}{4\hbar^2}\right)|1\rangle\,,$$

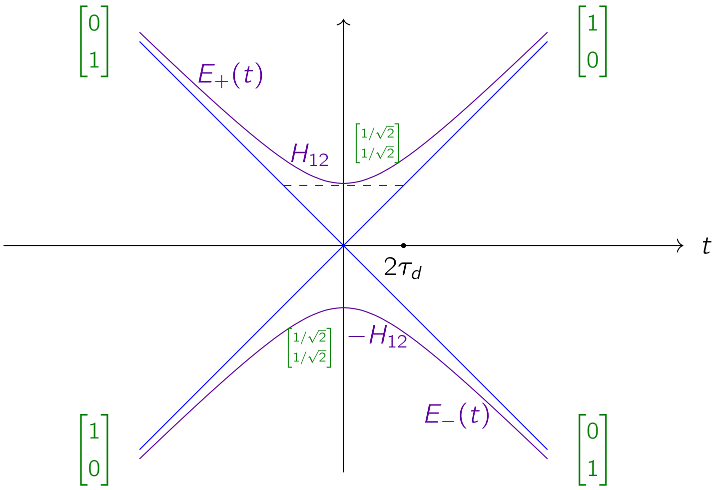
and similarly the time-evolution for the other state is

$$|\psi_2(t)\rangle = \exp\left(\frac{i\alpha t^2}{4\hbar^2}\right)|2\rangle\,.$$

But we can make the problem more interesting by adjusting our Hamiltonian so that we avoid the level crossing: suppose that we introduce a constant off-diagonal term

$$H(t) = \begin{bmatrix} \frac{\alpha t}{2} & H_{12} \\ H_{12}^* & -\frac{\alpha t}{2} \end{bmatrix},$$

where to be concrete we'll make $H_{12} > 0$ a real number. We then have $H(t) = \frac{\alpha t}{2}\sigma^z + H_{12}\sigma^x$, and the eigenvalues of this Hamiltonian are $\pm\sqrt{\frac{(\alpha t)^2}{4} + H_{12}^2}$. Our energy diagram now looks as below (blue is with H_{12} equal to zero, and purple is with H_{12} nonzero):



The interesting point here is that our system's instantaneous eigenstates change from those of σ^z to those of σ^x and back as t goes from $-\infty$ to 0 to ∞ – along the purple paths, the spin rotates from $+z$ to $-x$ to $-z$, or from $-z$ to $+x$ to $+z$. (We actually switch between the two levels on a given branch!) So we'll phrase our question as follows: if we start in the lower branch at time $t = -\infty$, what is the probability of a non-adiabatic transition – that is, **what is the probability that we end up in the higher branch** at time $t = \infty$?

The characteristic timescale τ_d over which the instantaneous eigenstates are changing considerably can be estimated by looking at the horizontal dashed line above and letting its length be $2\tau_d$. We then have

$$\frac{\alpha}{2}\cdot 2\tau_d = H_{12} \implies \tau_d = \frac{H_{12}}{\alpha}.$$

For the adiabatic theorem to apply, this time must be much larger than the intrinsic timescale of the quantum problem, which is determined by the energy difference between the states: this intrinsic timescale is largest when the levels are closest, so

$$T_{12} \approx \frac{\hbar}{\Delta E} \approx \frac{\hbar}{2H_{12}} \sim \frac{\hbar}{H_{12}}.$$

So the adiabatic theorem applies if $\tau_d \gg T_{12} \implies \frac{H_{12}^2}{\hbar\alpha} \gg 1$. (And this is in fact the only dimensionless parameter in the problem.) In this case, we don't actually need the adiabatic theorem to find the probability of a transition, which can be found analytically to be

$$P_{\text{non-adiabatic}} = \exp\left(-2\pi \frac{H_{12}^2}{\hbar \alpha}\right).$$

So this transition probability is exponentially small in α – basically, if α is small, we stay in a given branch, but if α is large, we will basically follow the blue lines and switch to the other branch with high probability. (This is confusing, though, because staying in a branch means we will transition from spin-up to spin-down! That's happening because the instantaneous eigenstates change drastically over the evolution.)

From here, we'll move on to a discussion of the **Berry phase** (named after Sir Michael Berry)

$$\gamma_n = i \int_0^t dt' \left\langle \psi_n \middle| \dot{\psi}_n \right\rangle.$$

The role of this phase is particularly important in various applications like condensed matter physics and quantum magnetism, and we'll understand it now. Suppose that our Hamiltonian is a function of some number of parameters $H(\vec{R}) = H(R_1, R_2, \cdots, R_N)$: for each value of the parameters, we have some eigenstates satisfying

$$H(\vec{R}) \left| \psi_n(\vec{R}) \right\rangle = E_n(\vec{R}) \left| \psi_n(\vec{R}) \right\rangle.$$

If $\vec{R}$ is a function of time, we then get a Hamiltonian $H(\vec{R}(t))$, and we then have instantaneous eigenstates

$$H(\vec{R}(t)) \left| \psi_n(\vec{R}(t)) \right\rangle = E_n(\vec{R}(t)) \left| \psi_n(\vec{R}(t)) \right\rangle.$$

Proposition 173

The Berry phase only depends on the geometry of the path $\vec{R}(t)$ in this parameter space (and that's why it's also called the **geometric phase**).

Proof. We know that

$$\gamma_n(t) = \int_0^t dt' \nu_n(t'),$$

where we write in the $\vec{R}$ dependence

$$\nu_n(t) = i \left\langle \psi_n(\vec{R}(t)) \middle| \frac{d}{dt} \middle| \psi_n(\vec{R}(t)) \right\rangle.$$

Taking the time-derivative by the chain rule, we find that

$$\frac{d}{dt} \left| \psi_n(\vec{R}(t)) \right\rangle = \frac{\partial}{\partial R_1} \left| \psi_n \right\rangle \frac{dR_1}{dt} + \cdots + \frac{\partial}{\partial R_N} \left| \psi_n \right\rangle \frac{dR_N}{dt} = \vec{\nabla}_R \left| \psi_n(\vec{R}(t)) \right\rangle \cdot \frac{d\vec{R}}{dt}.$$

Plugging in, we then have

$$\nu_n(t) = i \left\langle \psi_n(\vec{R}(t)) \middle| \vec{\nabla}_R \middle| \psi_n(\vec{R}(t)) \right\rangle \cdot \frac{d\vec{R}}{dt},$$

so that the Berry phase is

$$\gamma_n(t) = i \int_0^t dt' \left\langle \psi_n(\vec{R}(t')) \middle| \vec{\nabla}_R \middle| \psi_n(\vec{R}(t')) \right\rangle \cdot \frac{d\vec{R}}{dt}.$$

If we say that $\vec{R}(t)$ travels along a path Γ from $\vec{R}_i$ to $\vec{R}_f$, then we're doing a line integral

$$= i \int_\Gamma \left\langle \psi_n(\vec{R}) \middle| \vec{\nabla}_R \middle| \psi_n(\vec{R}) \right\rangle \cdot d\vec{R}.$$

This indeed doesn't depend on the parameterization of the path, so the Berry phase is indeed only dependent on the geometry, as desired. ☐

The integrand in our proof above,

$$\vec{A}_n(\vec{R}) = i \left\langle \psi_n(\vec{R}) \middle| \vec{\nabla}_R \middle| \psi_n(\vec{R}) \right\rangle ,$$

is known as the **Berry connection**, and the Berry phase is then the integral of the Berry connection over the path Γ. We'll discuss more about the properties of this Berry phase, including its gauge dependence for the instantaneous eigenstates, next time!

39 May 3, 2021 (Recitation)

We'll discuss the adiabatic approximation today, doing a few examples. Recall that we can make this approximation when we have a separation of timescales $T_i \ll T_e$ (meaning that the time for a significant change in the external Hamiltonian is much longer than the timescales internal to the system). In this situation, we can write our wavefunction in terms of the instantaneous eigenstates

$$|\Psi(t)\rangle = e^{i\theta_n(t)} e^{i\gamma_n(t)} |\psi_n(t)\rangle ,$$

where $|\psi_n(t)\rangle$ is the eigenstate of $H(t)$ at time t (so we treat time essentially as a parameter) with corresponding energy $E_n(t)$. We then have the **dynamic phase** $\theta_n(t) = -\frac{1}{\hbar}\int_0^t dt' E_n(t')$ and the **geometric phase** $\gamma_n(t) = \int_0^t dt' \nu_n(t')$, where $\nu_n = i \langle \psi_n | \dot{\psi}_n \rangle$ (which is real by properties of the inner product).

Example 174

Consider an infinite square well with walls at $x = 0, a$, and suppose that a changes in time as $w(t) = a + vt$ (so our right wall is moving to the right, making our well grow wider).

We know the energies and eigenstates of an infinite square well – at all times t, we must have $\psi(x = 0, t) = \psi(x = w(t), t) = 0$ (that is, the wavefunction vanishes at the two walls).

We can turn this into an adiabatic problem, asking when the approximation is valid and seeing what solution we end up with. For simplicity, assume that we start in one of the instantaneous eigenstates at $t = 0$, namely

$$\psi_n(x, 0) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \quad E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}.$$

More generally, the instantaneous nth level eigenstate is

$$\psi_n^{\text{inst}}(x, t) = \sqrt{\frac{2}{w}} \sin\left(\frac{n\pi x}{w}\right), \quad E_n = \frac{n^2\pi^2\hbar^2}{2mw^2}$$

(since all that's changed is the width of the well). To figure out the relevant internal timescales, notice that the difference between energy levels can be bounded as

$$E_n - E_m \geq E_1 = \frac{\pi^2\hbar^2}{2ma^2}$$

(treating w as order a), which gives us an energy scale of

$$T_i \sim \frac{\hbar}{\Delta E} \sim \frac{\hbar}{E_1} \sim \frac{ma^2}{\hbar}.$$

Then the external time is the amount of time it takes to make a significant change in the width, which is $T_e \sim \frac{a}{v}$. So for our approximation to be valid, we will want to have

$$T_e \gg T_i \implies \frac{a}{v} \gg \frac{ma^2}{\hbar} \implies \boxed{v \ll \frac{\hbar}{ma}}.$$

But once we make this assumption, we can notice that the energy levels all change in the same manner and thus there are no energy crossings. This nondegeneracy then allows us to make our adiabatic approximation, and our answer now depends on finding the phase factors. We have

$$\theta_n(t) = -\frac{1}{\hbar}\int_0^t dt' E_n(t') = -\frac{\pi^2\hbar n^2}{2m}\int_0^t \frac{dt'}{(a+vt')^2} = -\frac{\pi^2\hbar n^2}{2m}\cdot -\frac{1}{v}\cdot \frac{1}{a+vt'}\bigg|_0^t,$$

which we can further simplify to

$$-\frac{\pi^2\hbar n^2}{2m}\frac{1}{v}\left(\frac{1}{a}-\frac{1}{w}\right) = -\frac{\pi^2\hbar n^2}{2mv}\frac{vt}{aw(t)} = \boxed{-\frac{\pi^2\hbar^2 n^2}{2ma^2}\cdot\frac{t}{\hbar}\frac{a}{w(t)}}.$$

So now notice that $\frac{\pi^2\hbar^2n^2}{2ma^2}$ is the energy $E_n(0)$ of the original eigenstate, so multiplying by $-\frac{t}{\hbar}$ gives us the usual time-evolution phase! The adiabatic approximation thus gives us an extra $\frac{a}{w(t)}$ term for that phase. We can also calculate that the $\gamma_n(t)$ phase turns out to be $\boxed{0}$, because the **instantaneous eigenstates are all real**, and thus the time-derivatives are also real. That means $\langle \psi_n | \dot{\psi}_n \rangle$ is real, but we also showed it is in general purely imaginary, so it must be zero. So plugging everything back in, we get the wavefunction

$$\boxed{\Psi(x,t) = \psi_n^{\text{inst}}(x,t)\exp\left[-\frac{iE_n(0)t}{\hbar}\frac{a}{w(t)}\right]}$$

for a slowly-moving wall.

Example 175

We can actually compare this answer to the exact answer to figure out the accuracy of our adiabatic approximation.

Basically, if we solve Schrodinger's equation $i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t)$, we get the relatively simple solution

$$\Psi_n(x,t) = \sqrt{\frac{2}{w(t)}}\sin\left(\frac{n\pi x}{w(t)}\right)\exp\left(-\frac{iE_n(0)t}{\hbar}\frac{a}{w(t)}\right)\exp\left(\frac{imvx^2}{2\hbar w(t)}\right)$$

(so we just gain an extra exponential factor at the end). We can then think about superpositions of these solutions, and we want to ask whether it makes sense to write

$$\Psi(x,t) = \sum_n c_n \Psi_n(x,t).$$

It turns out the answer is yes, because the Ψ_ns are orthogonal – for example, at time $t = 0$, we can notice that

$$\langle \Psi_m(0)|\Psi_n(0)\rangle = \int dx \Psi_m^*(x,0)\Psi_n(x,0) = \delta_{mn},$$

because the extra phase term cancels between the bra and the ket. If we now think about starting in the ground state of the original well

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

then we are not in the ground state of the general Hamiltonian, and instead we can compute the coefficients in our

Ψ_m basis to find

$$c_m = \int_0^a dx \Psi(x,0)\Psi_m^*(x,0) = \frac{2}{a}\int_0^a dx \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right)\exp\left(-\frac{imvx^2}{2\hbar a}\right).$$

Making a change of variables $z = \frac{\pi}{a}x$ and letting $\alpha = \frac{mva}{2\pi^2\hbar}$ gives us

$$c_m = \frac{2}{\pi}\int_0^\pi dz \sin(z)\sin(mz)\exp\left(-i\alpha z^2\right).$$

Noticing that α is the term that we assumed was small in the adiabatic approximation $v \ll \frac{\hbar}{ma}$, we can Taylor expand it to 1 to find

$$c_m \approx \frac{2}{\pi}\int_0^\pi dz \sin(z)\sin(mz),$$

so that $c_m = \delta_{m1}$. In other words, in this limit, we do indeed follow the $m = 1$ level: there are no transitions because the extra factor is negligible, and thus we just have $\Psi(x,t) = \psi_1^{\text{inst}}(x,t)e^{i\theta_1(t)}$ like before.

We'll finish with another example:

Example 176

Suppose we have a magnetic field which is oscillatory (instead of linear) so that

$$\vec{B}(t) = B_0(\sin\alpha\cos(\omega t), \sin\alpha\sin(\omega t), \cos\alpha).$$

In other words, we have a magnetic field that rotates around the z-axis, and we want to understand what happens if we have a Hamiltonian

$$H(t) = \frac{e}{m}\vec{B}\cdot\vec{s}$$

on a two-state system with spin $\vec{s}$. We can write this Hamiltonian as a matrix

$$H(t) = \frac{\hbar\omega_1}{2}\begin{bmatrix} \cos\alpha & e^{-i\omega t}\sin\alpha \\ e^{[}i\omega t]\sin\alpha & -\cos\alpha \end{bmatrix},$$

where $\omega_1 = \frac{eB_0}{m}$ is a characteristic frequency of precession. The eigenvalues of such a matrix are then $E_\pm = \frac{\hbar\omega_1}{2}$, and then ω, ω_1 can be thought of as the external and internal frequencies, respectively. So in the adiabatic limit, we want

$$T_e \gg T_i \implies \boxed{\omega \ll \omega_1}$$

(since the characteristic timescale is the reciprocal of the characteristic frequency). Our instantaneous eigenstates are then

$$\chi_+(t) = \begin{bmatrix} \cos\frac{\alpha}{2} \\ e^{i\omega t}\sin\frac{\alpha}{2} \end{bmatrix}, \quad \chi_-(t) = \begin{bmatrix} \sin\frac{\alpha}{2} \\ -e^{-i\omega t}\cos\frac{\alpha}{2} \end{bmatrix},$$

with (time-independent in this case) energies E_+, E_-, respectively. So we will apply the adiabatic approximation: suppose at time $t = 0$, we're in the χ_+ state, which is corresponding to spin up along the direction of $\vec{B}$. Since $E_+ > E_-$ (there are no energy crossings), the adiabatic theorem tells us that

$$|\Psi(t)\rangle = e^{i\theta_+(t)}e^{i\gamma_+(t)}|\chi_+(t)\rangle.$$

Because the interpretation of this χ_+ state is as the **spin-up state in the direction of the magnetic field**, what the adiabatic theorem tells us is that for a slowly-varying magnetic field, our spin will always align with it.

40 May 4, 2021

We've been discussing the adiabatic theorem recently, understanding for a slowly-varying Hamiltonian, our system stays in the instantaneous eigenstates up to a calculable phase (which is different for different energy levels, so this phase becomes important when we deal with superpositions). Last time, we started discussing Berry's phase $\gamma_n = i\int_0^t dt' \left\langle \psi_n \middle| \dot{\psi}_n \right\rangle$ – we found that the phase can be thought of as a line integral in parameter space $\vec{R} = (R_1, \cdots, R_N)$, in such a way that the Berry phase depends on the path taken but not the parameterization:

$$\gamma_n = \int_\Gamma d\vec{R} \cdot \vec{A}_n(\vec{R}),$$

where we have the **Berry connection**

$$\vec{A}_n(\vec{R}) = i \left\langle \psi_n(\vec{R}) \middle| \nabla_{\vec{R}} \middle| \psi_n(\vec{R}) \right\rangle.$$

In contrast, the dynamical phase $\theta_n(t)$ does depend on the details of how we evolve along the parameter path Γ: for example, if $E_n(t') = E_n$ is constant along the evolution, then $\theta_n(t)$ is proportional to t, so it does depend on how quickly we traverse our path.

We'll focus more on the Berry connection now: notice that the states $\psi_n(\vec{R})$ (the eigenstates for the Hamiltnoians $H_n(\vec{R})$) are only defined up to a phase, so we can define

$$\left|\psi_n'(\vec{R})\right\rangle = e^{-i\beta(\vec{R})} \left|\psi_n(\vec{R})\right\rangle,$$

where $\beta(\vec{R})$ is real. Then we notice that

$$\vec{A}_n'(\vec{R}) = i \left\langle \psi_n'(\vec{R}) \middle| \nabla_{\vec{R}} \middle| \psi_n'(\vec{R}) \right\rangle = i \left\langle \psi_n(\vec{R}) \middle| e^{i\beta(\vec{R})} \nabla_{\vec{R}} e^{-i\beta\vec{R}} \middle| \psi_n(\vec{R}) \right\rangle$$

(we can always take $\vec{R}$ out of the inner product because it's basically a constant parameter, not like the position operator). And now we can simplify this by applying the gradient on the two terms to the right:

$$= i \left\langle \psi_n(\vec{R}) \middle| \nabla_{\vec{R}} \middle| \psi_n(\vec{R}) \right\rangle + \nabla_{\vec{R}}\beta \left\langle \psi_n(\vec{R}) \middle| \psi_n(\vec{R}) \right\rangle,$$

Since $\left\langle \psi_n(\vec{R}) \middle| \psi_n(\vec{R}) \right\rangle = 1$, what this tells us is that

$$\vec{A}_n'(\vec{R}) = \vec{A}_n(\vec{R}) + \nabla_{\vec{R}}\beta.$$

This looks a little bit like a gauge transformation, and this changes our Berry phase to

$$\gamma_n' = \int_\Gamma d\vec{R} \cdot \vec{A}_n'(\vec{R}) = \int_\Gamma d\vec{R} \cdot (\vec{A}_n(\vec{R}) + \vec{\nabla}_{\vec{R}}\beta),$$

and now the first term is the ordinary Berry phase, and the second term is the line integral of a gradient, which simplifies to the difference at the endpoints $\beta(\vec{R}_f) - \beta(\vec{R}_i)$:

$$\boxed{\gamma_n' = \gamma_n + \beta(\vec{R}_f) - \beta(\vec{R}_i)}.$$

So this is not a gauge invariant quantity for an open path Γ, but that's not actually a problem – it turns out that combining the changes to the Berry phase and the wavefunction $\psi_n(\vec{R})$ will give us a **consistent answer** for the evolution of our system (the changes cancel out). And there's also a special case where Γ is closed, meaning that the difference $\beta(\vec{R}_f) - \beta(\vec{R}_i)$ vanishes, and thus γ_n is a gauge invariant quantity for closed paths (this makes sense because we can really only compare the initial and final phases meaningfully if they are relative to the same Hamiltonian $H(\vec{R})$).

Here's a few other points that are important for us to keep in mind:

- As mentioned in recitation, if $\psi_n(t)$ is a real wavefunction (in position space), then $\gamma_n = 0$, because

  $$\gamma_n(t) = i\langle\psi_n|\dot{\psi}_n\rangle = i\int d^3r\psi_n(\vec{r},t)\frac{d}{dt}\psi_n(\vec{r},t) = i\int d^3r\frac{1}{2}\frac{d}{dt}\left(\psi_n(\vec{r},t)^2\right) = i\frac{d}{dt}\int d^3r\psi_n^2(\vec{r},t) = i\frac{d}{dt}1 = 0.$$

  This is not surprising, because if ψ_n is real, $i\langle\psi_n|\dot{\psi}_n\rangle$ is also manifestly pure imaginary, but we've defined it to always be real.

- As a special case of the closed loop Γ that we considered above, if our loop is trivial in that it travels along some path Γ_1 and then retraces that path backwards, then the Berry phases will always cancel and $\gamma_n = 0$. In particular, this is always the case when our parameter space is one-dimensional and we have the same initial and final value of R.

- Finally, suppose we have a three-dimensional parameter space, and we want to calculate the Berry phase along a closed loop

  $$\gamma_n = \oint_\Gamma \vec{A}_n(\vec{R})\cdot d\vec{R}.$$

  By Stokes' Theorem, we can write this line integral as

  $$= \int_S(\vec{\nabla}\times\vec{A}_n(\vec{R}))\cdot d\vec{S} = \int_S \vec{D}_n\cdot d\vec{S}$$

  for any surface S with boundary $\partial S = \Gamma$, and we have the integrand $\vec{D}_n = \vec{\nabla}\times\vec{A}_n(\vec{R})$ is called the **Berry curvature**. Notably, this Berry curvature is gauge invariant under the transformations $\vec{A}_n \to \vec{A}_n + \nabla_{\vec{R}}\beta$ that we just discussed, and we can think of this $\vec{D}_n$ as serving a similar role as the **magnetic field** and how it relates to the vector potential!

Remark 177. *If we think about electromagnetism in spacetime, the vector and scalar potential are unified into a single four-vector* $A_\mu = (\phi, \vec{A})$*, with transformations* $A_\mu \to A_\mu + \partial_\mu\alpha$ *and field strength (including both electric and magnetic field)* $F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu$*. So if we generalize the previous discussion to more than three dimensions, we can construct a more general two-component antisymmetric tensor in the place of* $\vec{D}_n(\vec{R})$*.*

Example 178

Consider a spin 1/2 electron in a magnetic field $\vec{B} = B_0\vec{n}$ for some unit vector $\vec{n}$, so that the Hamiltonian is $H = -\vec{\mu}\cdot\vec{B}$ with electron magnetic moment $\vec{\mu} = -g\mu_B\cdot\frac{\vec{S}}{\hbar} \approx -\mu_B\vec{\sigma}$. In other words, we will use the Hamiltonian $H(\vec{n}) = (\mu_B B_0)\vec{n}\cdot\vec{\sigma}$ with parameter $\vec{n}$ living on the unit sphere.

We know that the eigenstates for each direction $\vec{n}$ are the two states $|\vec{n},\pm\rangle$ with eigenvalues $\pm\mu_B B_0$ (since $(\vec{n}\cdot\vec{\sigma})$ has eigenvalues ±1). If we want to let $\vec{n}$ change direction in time, slowly enough so that the adiabatic theorem will apply, we need the characteristic time of variance in $\vec{n}$ to be much larger than the quantum timescales $t_{\text{quant}} = \frac{\hbar}{\Delta E} \sim \frac{\hbar}{\mu_B B_0}$. But if we're in this regime, we have a slowly-rotating magnetic field, and we can calculate the Berry phase that is picked up **along a closed path**. If we follow the $|\vec{n},+\rangle$ state, we have

$$\gamma_+ = \int_\Gamma \vec{A}_+(\vec{R})\cdot d\vec{R},$$

and (parameterizing with polar coordinates, left as an exercise) we find that the total Berry phase will evaluate to $-\frac{1}{2}\Omega$, where Ω is the solid angle subtended by the path (specifically, the solid angle of the region that we traveled counterclockwise around). And for a more general spin $\vec{S}$ (instead of a spin 1/2 particle), we know that $(\vec{S} \cdot \vec{n})$ has eigenstates running from $-s$ to s in steps of 1. If we're in the top state with eigenvalue s, the Berry phase will then turn out to be $-s\Omega$.

Suppose now that we have a family of paths that run along the "parallels" or "latitudes" of the sphere, and consider the one at angle θ. The solid angle subtended is then

$$\Omega(\theta) = 2\pi(1 - \cos\theta)$$

(we can check that this works for $\theta = 0, \frac{\pi}{2}, \pi$). In particular, if we take a path exactly at the south pole, we pick up a Berry phase $-4\pi S$, but because such a path is actually staying at a fixed point, no phase should be picked up! Since our phase is only defined modulo 2π, this tells us that

$$-4\pi S \in 2\pi\mathbb{Z} \implies 2S \in \mathbb{Z},$$

and thus we've found an argument for why our spin needs to be a half-integer (which is indeed the case!).

Example 179

We'll finish the adiabatic approximation discussion by thinking about **molecules and the Born-Oppenheimer approximation**, and our central question here is to determine the spectrum of molecules.

We already know that atoms with atomic number $Z > 1$ are already difficult to deal with, because of factors like the Coulomb repulsion between electrons, and the analysis of molecules becomes even harder. For example, if we consider H_2, even fixing the two positions of the nuclei and only considering how the two electrons behave, we **lose rotational symmetry** except along the axis connecting the two nuclei, and that makes studying the system a lot harder.

Furthermore, it isn't clear why we can fix the positions of the two nuclei – the distance may change, so vibrational motion factors seem to play a role. But we can handle this part of the problem, because nuclei are much heavier than electrons (typically the ratio is about 10^{-4}). So the nuclei move much slower than the electrons do, and thus we can apply the adiabatic theorem, freezing the separation distance R between the nuclei. This then gives us some nuclear potential $V_N(R)$ for configuration of the nuclei, and this potential will generally have an **equilibrium separation** (because at large separations we have $-\frac{1}{R^6}$ behavior due to van der Waals, but for small separations we have very large V due to Coulomb repulsion). So we can then consider small vibrations along this equilibrium separation, and we can say that the electrons adiabatically adjust to the "instantaneous eigenstates" of the nuclear evolution.

More quantitatively, the typical energy scale for electronic excitations is $\text{Ry} \sim \frac{\hbar^2}{ma_0^2}$ (where m is the electron mass), and similarly the typical energy scale for nuclear vibrations in the potential $V_N(R)$ is also the Rydberg. Since the length scale for the nuclear vibrations is a_0, we can estimate the spring constant via

$$H_N = \frac{p^2}{2M} + \frac{1}{2}kx^2 \implies k \sim \frac{[E]}{L^2} \sim \frac{\hbar^2/ma_0^2}{a_0^2} = \frac{\hbar^2}{ma_0^4}.$$

This then tells us the frequency of vibrations

$$\omega_N = \sqrt{\frac{k}{M}} = \sqrt{\frac{\hbar^2}{Ma_0^4 m}} = \sqrt{\frac{m}{M}}\frac{\hbar}{ma_0^2}.$$

In other words, the energies associated with the vibration, $\hbar\omega_N$, are on the order of $\sqrt{\frac{m}{M}}\frac{\hbar^2}{ma_0^2}$, so the vibrational energy is smaller than the electronic energy scale by a factor of $\left(\frac{m}{M}\right)^{1/2} \approx 10^{-2}$. So the vibrational frequencies are indeed smaller than the electronic frequency scales, and the vibrational times are thus sufficiently large and the adibatic approximation works.

In addition to the effects due to changing the equilibrium separation between the nuclei, we also need to think about rotations of the two-nuclei system as a solid body: in other words, we want to estimate the timescales associated with **molecular rotation**. Since the rotational energy can be written as $E \sim \frac{\vec{L}^2}{I}$ for moment of inertia I, we can write this as $\frac{\hbar^2 \ell(\ell+1)}{Ma_0^2} \sim \frac{m}{M} \frac{\hbar^2}{ma_0^2}$. So the rotational energy is suppressed by a factor of $\frac{m}{M} \sim 10^{-4}$, and the main point of these calculations is that

$$\boxed{E_{\text{electronic}} : E_{\text{vibrational}} : E_{\text{rotational}} = 1 : \sqrt{\frac{m}{M}} : \frac{m}{M}}.$$

We can in fact compute the effective potentials and solve for the nuclear motion more explicitly, but these are the key points of the Born-Oppenheimer approximation (which we can read more about on our own).

We're now ready to move to our next topic of the class, **scattering**, which is relevant to a variety of fields of current physics research. One example of scattering comes from taking a beam of electrons or X-rays and shooting them at a target crystal, looking at the distribution of the outgoing directions and energies to study the crystal and electronic structure. And another one comes from taking two protons (or other particles) and smashing them together in the Large Hadron Collider, looking at what particles come out and at what angles and energies to understand what different particle processes are possible. Scattering processes determine properties of what's around us (oxygen molecules interacting in a gas, or electrons scattering in a material), and we'll start exploring this in the coming lectures!

41 May 5, 2021 (Recitation)

Today, we'll do a nice application of the adiabatic theorem, the **solar neutrino problem**. In the 1960s, it was found that there was a deficit of electron neutrinos produced by the sun compared to what was expected by models, and this problem was only resolved in 2002. So we'll describe the story here and understand how the adiabatic approximation plays into the solution.

Fact 180

During solar fusion, neutrinos are produced via a process taking an electron and a proton to a neutron and an electron neutrino (in symbols, $e^- p \to n\nu_e$), and this is a weak interaction.

In practice, the lowest energy neutrino comes from the process $4e^- + 4p \to {}^4\text{He} + 2\nu_e$ (where each helium atom has two protons, two neutrons, and two electrons), and another process comes from ${}^8\text{B} + e^- \to {}^8\text{Be} + \nu_e$. And what was found was that the energy of the neutrino (which depends on which process it's produced by) affected the extent to which the neutrino output deviated compared to what was expected.

In the SNO experiment, a big balloon of D_2O (replacing hydrogen with deuterium) was put far underground. Because neutrino oscillations between different kinds of neutrinos $(\nu_e, \nu_\mu, \nu_\tau)$ can happen – for example, electron neutrinos can scatter off deuterons and cause the process $\nu_e + d \to pp + e^-$ – the power of this experiment was that it could keep track of the total flux of neutrinos. It turns out that the total flux, $5.1 \times 10^6 \text{cm}^{-2} s^{-1}$, was pretty consistent with what was expected, and $\frac{2}{3}$ of the electron neutrinos ν_e born in the sun changed into the ν_μ or ν_τ types.

So to account for the measured deficit from the sun, there were two explanations given. The first one, "just so," is that the electron neutrinos oscillate into the other types as they travel between the sun and the earth. What this would predict is that the oscillation depends on the distance traveled and the energy of the neutrino, and the idea was that the ratio of those quantities was just right to line up with the mass difference of the neutrinos. But this one was ruled out by another experiment, and instead the explanation turned out to be that the electron neutrinos oscillate into other types of neutrinos inside the sun.

Example 181

To study the "just so" explanation, we'll consider a two-state system $\{|\nu_e\rangle, |\nu_\mu\rangle\}$, which we can also describe with basis $\{|\nu_H\rangle, |\nu_L\rangle\}$ ("heavy" and "light"), the energy eigenstates.

We can thus relate the two sets of bases via

$$|\nu_L\rangle = (\cos\theta)|\nu_e\rangle - (\sin\theta)|\nu_\mu\rangle, \quad |\nu_H\rangle = (\sin\theta)|\nu_e\rangle + (\cos\theta)|\nu_\mu\rangle,$$

where θ is the **mixing angle** – we can alternatively write this in terms of the change-of-basis matrix $U = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$. Mathematically, just-so oscillations (our first explanation) would take place in vacuum, and they can be explained as follows: we know that our energy eigenstates satisfy

$$i\hbar\frac{d}{dt}|\nu_H\rangle = E_H|\nu_H\rangle, \quad i\hbar\frac{d}{dt}|\nu_L\rangle = E_L|\nu_L\rangle,$$

and because the masses of neutrinos here are much smaller than the other energies in the problem, we actually have an **ultrarelativistic** problem: the energy $E = \sqrt{p^2c^2 + m^2c^4}$ can be expanded as

$$E_H|\nu_H\rangle = \left(pc + \frac{m_H^2c^2}{2pc} + \cdots\right)|\nu_H\rangle, \quad E_L|\nu_H\rangle = \left(pc + \frac{m_L^2c^2}{2pc} + \cdots\right)|\nu_L\rangle.$$

We'll define these two energies to be $E_H = E_0 + \Delta_0$ and $E_L = E_0 - \Delta_0$, and we can explicitly calculate that

$$E_0 \approx pc, \quad \Delta_0 = \frac{\Delta m^2c^4}{4pc} \approx \frac{\Delta m^2c^4}{4E_0}.$$

So in two-component notation, we can describe the light and heavy components of our state as

$$i\hbar\frac{d}{dt}\begin{bmatrix} a_L \\ a_H \end{bmatrix} = \begin{bmatrix} E_0 - \Delta_0 & 0 \\ 0 & E_0 + \Delta_0 \end{bmatrix}\begin{bmatrix} a_L \\ a_H \end{bmatrix},$$

but because we're interested in the two different types of neutrinos, we need to change to the $\begin{bmatrix} a_e \\ a_\mu \end{bmatrix} = U\begin{bmatrix} a_L \\ a_H \end{bmatrix}$ basis. We therefore get

$$i\hbar\frac{d}{dt}\begin{bmatrix} a_e \\ a_\mu \end{bmatrix} = U\begin{bmatrix} E_0 - \Delta_0 & 0 \\ 0 & E_0 + \Delta_0 \end{bmatrix}U^{-1}\begin{bmatrix} a_e \\ a_\mu \end{bmatrix},$$

and doing out the matrix multiplication gives us

$$= \begin{bmatrix} E_0 - \Delta_0\cos(2\theta) & -\Delta_0\sin(2\theta) \\ -\Delta_0\sin(2\theta) & E_0 + \Delta_0\cos(2\theta) \end{bmatrix}\begin{bmatrix} a_e \\ a_\mu \end{bmatrix}.$$

This blue term is our Hamiltonian, and we have shown earlier in this class that if we're in the $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$ state at time $t = 0$ (that is, we have an electron neutrino), then we can calculate the probability of being an electron neutrino at some later distance from the sun to be (assuming that $x = ct$, traveling near the speed of light)

$$\mathbb{P}(\nu_e, x) = \left|\left\langle \nu_e \middle| \psi\left(t = \frac{x}{c}\right)\right\rangle\right|^2 = 1 - \sin^2(2\theta)\sin^2\left(\frac{\Delta_0 x}{\hbar c}\right).$$

So the dependence indeed depends on the value of $\frac{x}{E_0}$, since there is a $\frac{1}{E_0}$ dependence in Δ_0. In other words, if vacuum oscillations were the reason we saw less electron neutrinos than expected, then we'd need to have exactly the right value of $\frac{x}{E_0}$ so that the sine term was at the right phase.

Example 182

We can now turn to the other explanation, which is oscillation of neutrinos inside the sun. The main difference is that the sun is full of electrons and has some density $\rho(x)$ of electrons per unit volume, so electron neutrinos can scatter off electrons and change the Hamiltonian:

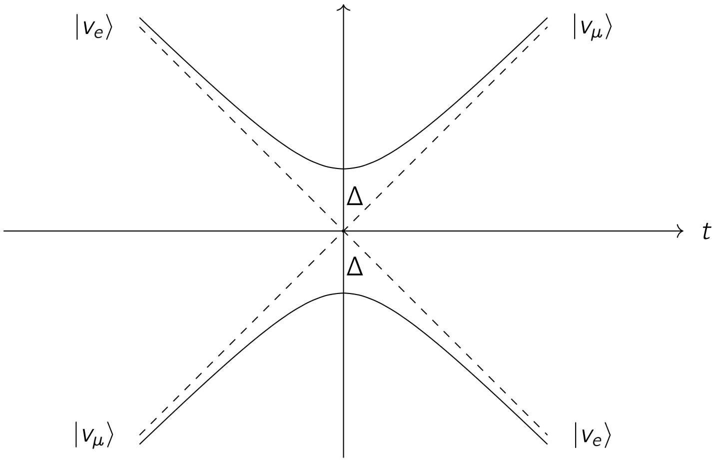
$$H_{\text{sun}} = H_{\text{vac}} + \begin{bmatrix} \sqrt{2}G_F \rho(x)(\hbar c)^3 & 0 \\ 0 & 0 \end{bmatrix},$$

where $\sqrt{2}G_F \approx \frac{1}{(246 \text{ GeV})^2}$ is the Fermi constant.

This extra term means that the Hamiltonian now looks like

$$H_{\text{sun}} = (\text{constant})I + \begin{bmatrix} \frac{G_F}{\sqrt{2}}\rho(x)(\hbar c)^3 - \Delta_0\cos(2\theta) & -\Delta_0\sin(2\theta) \\ -\Delta_0\sin(2\theta) & -\frac{G_F}{\sqrt{2}}\rho(x)(\hbar c)^3 + \Delta_0\cos(2\theta) \end{bmatrix},$$

and we can see some connections to the Hamiltonian $H = \begin{bmatrix} \gamma t & \Delta \\ \Delta & \gamma t \end{bmatrix}$ from lecture: recall that in that problem, the adiabatic approximation allowed the spin-up state to slowly rotate into the spin-down state. That's similar to what's going on here:



Basically, x (the distance from the center of the sun) plays the role of t, the $-\Delta_0\sin(2\theta)$ takes the role of the off-diagonal term Δ, and the diagonal term in our Hamiltonian H_{sun} takes the role of γt (though it's not a perfect analogy, since $\rho(x)$ is not linear in x). So then the "time-evolution" of our system is that the center of the sun is on the left side of the picture (very negative x) and the surface of the sun is on the right (very positive x), so the y-axis in our diagram above corersponds to the "balancing point" $x = x_c$ where

$$\frac{G_F}{\sqrt{2}}(\hbar c)^3\rho(x_c) = \Delta_0\cos(2\theta),$$

meaning that the diagonal terms of the Hamiltonian vanish. If we want to use the adiabatic approximation, we need the off-diagonal term to be much larger than the diagonal term when the energies get close to each other, meaning that (instead of a time-derivative we have a spatial-derivative, since x is playing the role of t) the adiabatic approximation is valid when (constraint (1))

$$\Delta_0^2 \sin^2(2\theta) \gg \hbar(\hbar c)^3 \frac{G_F}{\sqrt{2}} c \frac{d}{dx}\rho(x_c).$$

(This formula is the analog of $\Delta^2 \gg \hbar\dot{H}$.) And furthermore, we also need (constraint (2))

$$\frac{G_F}{\sqrt{2}}(\hbar c)^3 \rho(x=0) > \Delta_0 \cos(2\theta),$$

so that the $x = x_c$ coordinate is actually passed through by the neutrinos (and thus we can actually follow the paths in the diagram above to switch $|\nu_e\rangle$ into $|\nu_\mu\rangle$). And it turns out that the parameters in nature work out so that we are in a regime where (1) and (2) are basically satisfied (the actual value of Δ_0 is large enough that the adiabatic approximation is valid, and it is small enough to basically be on the boundary of constraint (2)! So in summary, the density of electrons allow electron neutrinos to change into muon neutrinos because of this adiabatic evolution.

42 May 6, 2021

Last time, we briefly started talking about scattering in the context of collisions of particles. More than two particles can be created when two particles collide, and those products don't need to be the same type as the incoming particles, but when the initial and final products are the same, we call the process a **scattering** process.

Furthermore, we have **elastic scattering** when the internal state of the particles does not change. (In contrast, an example of an **inelastic** scattering process is where an electron is shot at a hydrogen atom, causing the other electron inside the hydrogen atom to jump to an excited state.) We'll focus on elastic scattering here, and we'll make a few additional assumptions as well: we'll assume our particles are nonrelativistic, we'll ignore spin, and we'll assume that in a two-particle scattering with particles at positions $\vec{r}_1, \vec{r}_2$, the interaction between them is via a potential $V(\vec{r}_1 - \vec{r}_2)$ only depend on the distance between them.

We can then switch to a center-of-mass reference frame, where we have a **single** particle scattering off of a potential

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

where μ is the reduced mass. It turns out that even with these simplifications, we'll have a lot of calculations to do!

Since this problem is (strictly speaking) time-dependent, we can reduce it to the time-independent Schrodinger equation with appropriate boundary conditions.

Example 183

We'll first recall how we make this kind of reduction from the time-dependent to time-independent Schrodinger equation in one dimension.

The setup is that we have some potential V (imagine a mountain, as we would see in scattering), and we have an initial state (at $t \to -\infty$) given by a wave packet moving to the right. Our final state then has a **transmitted** wave packet (moving to the right) and a reflected wave packet (moving to the left) at $t \to \infty$. And to figure out the behavior of this system, we can solve the time-**independent** Schrodinger equation

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\psi = E\psi, \quad E = \frac{\hbar^2 k^2}{2m},$$

where E depends on the initial wavepacket, with the **scattering boundary conditions**

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \text{ as } x \to -\infty, \psi(x) = Fe^{ikx} \text{ as } x \to \infty.$$

Then we claim that $T = |\frac{F}{A}|^2$ is the transmission probability (this is the probability that our particle is found on the right of the mountain potential), and $R = |\frac{B}{A}|^2$ is the reflection probability (this is the probability that our particle has been reflected back to the left of our mountain potential).

Example 184

We now generalize to three dimensions, supposing that we have a potential $V(\vec{r})$ localized near the origin going to 0 as $r \to \infty$ sufficiently quickly. Suppose that at $t \to -\infty$, we have an incoming wavepacket incoming, moving in the $+z$ direction.

We can then describe the final state as $t \to \infty$ as a scattered wavepacket, which will basically be a **spherical outgoing wave**, plus an unscattered wavepacket moving in the $+z$ direction (corresponding to the particle missing the potential). We now want to turn this into a time-independent problem, and we can do so by solving the three-dimensional time-independent Schrodinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\psi(\vec{r}) = E\psi(\vec{r}).$$

We'll assume that $V(\vec{r}) \to 0$ vanishes **faster than** $\frac{1}{r}$ as $r \to \infty$ – in fact, often we will assume for simplicity that $V(\vec{r}) = 0$ for $r > a$. Since our energy can be written as $E = \frac{\hbar^2 k^2}{2m}$, our Schrodinger equation becomes

$$\left(-\frac{\hbar^2}{2m}(\nabla^2 + k^2) + V(\vec{r})\right)\psi(\vec{r}) = 0,$$

and for a fixed energy (in other words, a fixed k) this equation has infinitely many solutions. (For example, when $V(\vec{r}) = 0$, our solutions are the plane waves $\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}$, where $|\vec{k}|$ is fixed but the direction can be arbitrary.) So we need to impose some boundary conditions, and motivated by the one-dimensional discussion, our incoming wave should be $\psi(\vec{r}) = e^{ikz}$. But our scattered wave cannot be $\psi_s(\vec{r}) = e^{ikr}$, because that isn't a solution to the free-particle Schrodinger equation (remember that our scattered waves are supposed to be the asymptotic forms, so far away from the potential they should behave like free particles). Instead, we make a small tweak: it turns out that $\frac{e^{ikr}}{r}$ does solve the Schrodinger equation for $r \neq 0$. (Here, r and k are just the magnitudes of $\vec{r}$ and $\vec{k}$, so they are scalars.)

Noticing that this solution has no angular dependence, which is bad because we know that the scattering process should have some dependence on the angle, we make the general ansatz

$$\psi_s(\vec{r})f_k(\theta,\phi) = \frac{e^{ikr}}{r},$$

So putting this all together, we'll thus look for a solution to the Schrodinger equation satisfying

$$\boxed{\psi(\vec{r}) = e^{ikz} + f_k(\theta,\phi)\frac{e^{ikr}}{r} \text{ as } r \to \infty}.$$

Here, $f_k(\theta,\phi)$ is known as the **scattering amplitude** (it plays a similar role to F in the one-dimensional case), having dimensions of length, and it will be determined by the details of the potential.

Remark 185. *Notice that in one dimension, the space away from the potential is disconnected, but in three dimensions, the space is connected (we basically have $\mathbb{R}^3$ minus a ball). So we can't have different expressions to the left and to the right and use different coefficients A and B like we did in one dimension!*

Remark 186. *We're really guessing the form of the solution here – if we want to see the work of how the reduction, we can consult Messiah chapter 10 or Merzbacher chapter 13.*

In physical experiments, what is actually measured in a scattering experiment is the **differential cross-section**. Basically, we set up a beam of particles moving towards the target (of potential $V(\vec{r})$), and then there is a detector far away from the target (where the potential is basically 0), which counts the number of particles which hit it. If the detector subtends an angle $d\Omega$, then a steady beam of incoming particles corresponds to a steady beam hitting the detector. So we can compute $\frac{dN^{\text{out}}}{dt}$, which is the number of particles hitting $d\Omega$ per unit time. But to get a more normalized quantity, we divide this by $\frac{dN^{\text{in}}}{dt\,dA}$, which is the flux of incoming particles. This gives us the **differential cross-section**

$$d\sigma = \frac{dN^{\text{out}}/dt}{dN^{\text{in}}/(dt\,dA)}.$$

This has dimensions of area, and it will be proportional to $d\Omega$.

Remark 187. *Classically, the reason for the name of "differential cross-section" is that if we have a bunch of classical particles moving (deterministically) from the beam through the potential, then a given solid angle $d\Omega$ can be traced back to a* **particular** *region in the original beam, which will generally come from some area element $d\sigma$.*

But we want to relate this differential cross-section back to our Schrodinger equation, and we do so by noting that the numerator and denominator only depend on behavior far away from the potential, so we can use our boundary conditions. First, we calculate the denominator: since the incident beam is the plane wave $\psi = e^{ikz}$, and we can calculate the flux by looking at the **probability current**

$$\vec{j}_{\text{in}} = \frac{\hbar}{m}\text{Im}(\psi^* \nabla\psi) = \frac{\hbar k}{m}\hat{z}.$$

This is indeed along the z-direction, and therefore

$$\frac{dN}{dt\,dA} = \vec{j}_{\text{in}} \cdot \hat{z} = \frac{\hbar k}{m}.$$

Now for the numerator, we want to calculate the flux of outgoing particles by looking at the scattered part $\psi_s = f_k(\theta, \phi)\frac{e^{ikr}}{r}$, and this time we have the probability current

$$\vec{j}_{\text{out}} = \frac{\hbar}{m}\text{Im}(\psi_s^* \nabla\psi_s).$$

Using the fact that $\vec{\nabla} = \frac{\partial}{\partial r}\hat{r} + \frac{1}{r}\frac{\partial}{\partial\theta}\hat{\theta} + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\hat{\phi}$ in spherical coordinates, we get

$$\nabla\psi_s(\vec{r}) = f_k(\theta, \phi)\left(\frac{ike^{ikr}}{r} - \frac{e^{ikr}}{r^2}\right)\hat{r} + \frac{1}{r}\frac{\partial f_k}{\partial\theta}\frac{e^{ikr}}{r}\hat{\theta} + \frac{1}{r\sin\theta}\frac{\partial f_k}{\partial\phi}\frac{e^{ikr}}{r}\hat{\phi}.$$

Since we are interested in this behavior far away from the scattering, the order $\frac{1}{r^2}$ terms all be dropped, and only the first term remains. Thus this is approximately $f_k(\theta, \phi)\frac{ike^{ikr}}{r}\hat{r}$, and plugging back in gives us

$$\vec{j}_{\text{out}} \approx \frac{\hbar k}{m}\frac{|f_k(\theta, \phi)|^2}{r^2}\hat{r}.$$

This means that

$$\frac{dN^{\text{out}}}{dt} = \vec{j}_{\text{out}} \cdot d\vec{A} = \vec{j}_{\text{out}} \cdot r^2 d\Omega\hat{r} = \frac{\hbar k}{m}|f_k(\theta, \phi)|^2 d\Omega,$$

and thus the numerator is $\frac{\hbar k}{m}|f_k(\theta, \phi)|^2$. Putting everything together yields

$$\boxed{d\sigma = |f_k(\theta, \phi)|^2 d\Omega}.$$

As expected, this number is proportional to the solid angle, and thus we commonly use the notation

$$\frac{d\sigma}{d\Omega} = |f_k(\theta, \phi)|^2$$

even though this is a ratio of differentials rather than a derivative. So the quantity that is measure by experimentalists is the scattering amplitude that we can find by solving the time-independent Schrodinger equation! And if we want to find the total number of particles scattered in any direction, normalized by the flux of the incoming particles, we get

$$\sigma = \int d\sigma = \int |f_k(\theta, \phi)|^2 d\Omega.$$

So everything goes back to solving the Schrodinger equation. First, we assume that our potential $V(\vec{r}) = V(r)$ has spherical symmetry (this does not mean that the differential cross-section is uniform, because our incoming particle beam breaks the symmetry).

Example 188

We will first review how to solve the three-dimensional free particle Schrodinger equation in spherical coordinates (meaning that $V = 0$).

In general, our solutions will have an energy $E = \frac{\hbar^2 k^2}{2m}$, and they will be of the form

$$\psi(\vec{r}) = \frac{U_{E,\ell}(r)}{r} Y_{\ell,m}(\theta, \phi),$$

where $U_{E,\ell}$ solves the one-dimensional Schrodinger equation

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V_{\text{eff}(\vec{r})}\right) U_{E,\ell} = \frac{\hbar^2 k^2}{2m} U_{E,\ell}(r)$$

for the effective potential

$$V_{\text{eff}}(\vec{r}) = V(\vec{r}) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2]}.$$

Since $V = 0$ in this case, our equation simplifies to (dividing through by a constant)

$$\left(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2}\right) U_{E,\ell}(r) = k^2 U_{E,\ell}(r).$$

If we introduce the dimensionless $\rho = k \cdot r$, then our equation becomes

$$\left(-\frac{d^2}{d\rho^2} + \frac{\ell(\ell+1)}{\rho^2}\right) U_{E,\ell}(\rho) = U_{E,\ell}(\rho).$$

Notice that the energy is not quantized for the free particle, which is why it has dropped out of this equation! And the solutions to this last equation are known and given by

$$U_{E,\ell}(\rho) = A_\ell \rho j_\ell(\rho) + B_\ell \rho n_\ell(\rho).$$

Here, $j_\ell(\rho)$ is the **spherical Bessel function**

$$j_\ell(\rho) = (-1)^\ell \rho^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\ell \frac{\sin\rho}{\rho},$$

and $n_\ell(\rho)$ is the **spherical Neumann function**

$$n_\ell(\rho) = (-1)^{\ell+1}\rho^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\ell \frac{\cos\rho}{\rho}.$$

It turns out that $j_\ell(\rho)$ is not singular as $\rho \to 0$, but $n_\ell(\rho)$ is singular. And we also have the asymptotics $\rho j_\ell(\rho) \to \sin\left(\rho - \frac{\ell\pi}{2}\right)$ and $\rho n_\ell(\rho) \to -\cos\left(\rho - \frac{\ell\pi}{2}\right)$ as $\rho \to \infty$.

Since we also know that plane waves are solutions to the free particle, that must mean a solution like e^{ikz} can be written as a linear superposition of the spherical solutions:

$$e^{ikz} = e^{ikr\cos\theta} = \sum_{\ell,m} c_{\ell,m}\frac{U_{E,\ell}(r)}{r}Y_{\ell,m}(\theta,\phi).$$

Combining the coefficients in our solution for $U_{E,\ell}$ with the $c_{\ell,m}$, we can write this as

$$= \sum_{\ell,m}(A_{\ell,m}j_\ell(kr) + B_{\ell,m}n_\ell(kr))Y_{\ell,m}(\theta,\phi).$$

But because the left-hand side has no ϕ-dependence, we must have $A_{\ell,m} = B_{\ell,m} = 0$ for $m \neq 0$ (because $Y_{\ell,m}(\theta,\phi) \propto e^{im\phi}$). In addition, because the left-hand side is finite at the origin, but the Neumann functions blow up at the origin, we must only have nonzero A coefficients. From here, we can in fact find the coefficients and get the **Rayleigh formula**

$$\boxed{e^{ikz} = \sqrt{4\pi}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}i^\ell Y_{\ell,0}(\theta)j_\ell(kr)}.$$

In particular, all angular momentum values ℓ enter in the superposition! And because we know that as $r \to \infty$,

$$j_\ell(kr) = \frac{1}{kr}\sin\left(kr - \frac{\ell\pi}{2}\right) = \frac{1}{kr}\left(\frac{e^{i(kr-\frac{\ell\pi}{2})} - e^{-i(kr-\frac{\ell\pi}{2})}}{2i}\right),$$

we can plug everything back in to find that

$$e^{ikz} \approx \frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}i^\ell Y_{\ell,0}(\theta)\frac{1}{2i}\left(\frac{e^{i(kr-\frac{\ell\pi}{2})}}{r} - \frac{e^{-i(kr-\frac{\ell\pi}{2})}}{r}\right).$$

So we have a sum over angular harmonics, and within each angular harmonic ℓ, we have a spherical wave going outward and a spherical wave going inward! And next time, we'll learn how to extend this analysis to the case where we have a finite potential $V(\vec{r})$.

43 May 10, 2021 (Recitation)

We'll discuss scattering today, thinking about how we can transition from wave packets into the time-independent Schrodinger equation and also looking a bit at one-dimensional scattering. (In lecture tomorrow, we'll get a bit more into the main techniques that we have for solving scattering problems.)

Recall that the setup of three-dimensional scattering is that we have a potential $V(\vec{x})$ (which is usually localized so that it is only nonzero in a bounded region) which we scatter a beam of particles off, and in particular we often measure the number of particles scattered to a given solid angle

$$\frac{d^2N^{\text{scattered}}}{dtd\Omega} = \frac{d^2N^{\text{incident}}}{dtdA}\frac{d\sigma}{d\Omega}.$$

In an experiment, the left-hand side is something we count with a detector by looking at some $d\Omega = \sin\theta d\theta d\phi$, and the first fraction on the right-hand side is the flux that we're sending into the system. So $\frac{d\sigma}{d\Omega}$, the **differential cross-section**, is the relevant quantity to predict using quantum mechanics.

By convention, we send in our beam of particles traveling in the $+z$ direction which we can think of as a wave packet, and we can imagine that it produces an outgoing wavepacket in the $+z$ direction, plus a spherically outgoing wave. But we can connect this to the energy eigenstate description as follows: suppose that the size of our incoming packet is Δz, and suppose the spatial range of our potential is R (this was a in lecture). The limit that we're solving this problem in is actually

$$\Delta z \gg R,$$

and we'll think about this in terms of wavenumbers: for our wavepacket, $\Delta k \sim \frac{1}{\Delta z} \ll \frac{1}{R}$, so we're saying that Δk (the spread of the wavenumbers) is small, and thus our setup is close to having a **well-defined momentum** (which is what would be the case if $\Delta k = 0$). And as $\Delta k \to 0$, we can indeed reduce our setup to an energy eigenstate problem: the incoming plane wave has some definite energy E, so that

$$\psi_{\text{in}} = e^{ikz - iEt/\hbar},$$

and the outgoing wave can then be parameterized as

$$\psi_{\text{out}} = e^{-iEt/\hbar}\left(e^{ikz} + f_K(\theta,\phi)\frac{e^{ikr}}{r}\right)$$

for $r \gg R$, because we want to consider the outgoing wave far away from the potential so that we essentially have a free particle. So we have $\psi_{\text{out}} = \psi_{\text{in}} + \psi_{\text{scattering}}$, and we also know that the energy (for a free particle) must have $E = \frac{\hbar^2 k^2}{2m}$.

Example 189

Let's now think about what's actually happening as we take $\Delta k \to 0$ and understand why we can use the time-independent Schrodinger equation.

Note that we're losing some causality if we write down the incoming and outgoing waves as above, since **both waves exist at all times**. To understand why this is okay, consider a wave packet solution where the distribution of wavenumbers k is given by some $g(k)$ centered at some k^0 and with some width Δk. Our new ψ for the wave packet is now a superposition

$$\psi_{\text{packet}}(k^0, \Delta k) = \int dk g(k) \psi_{\text{plane}}(k),$$

and our outgoing wave is now similarly

$$\psi_{\text{out}} = \int_0^\infty dk g(k)\left(e^{ikz} + \frac{e^{ikr}}{r} f_K\right) e^{-iE_k t/\hbar}.$$

We're taking the limit where this wavepacket has small Δk: recall that the **group velocity** of our wave packet is $v_g = \frac{\hbar k^0}{m}$, so the wavepacket crosses the region where the potential V is nonzero in time

$$\Delta t \sim \frac{\Delta z}{v_g}$$

(remember that $\Delta z \gg R$, so the width of the wave packet is the relevant length that needs to be passed through the potential). As $\Delta k \to 0$, we have $\Delta t \to \infty$, so we've basically stretched out solution out into an infinite plane wave which never finishes crossing the origin!

Similarly, we can think about timescale for the outgoing wave: suppose that the wavepacket is at the origin of the potential $\vec{x} = 0$ at time $t = 0$. Then we want to know when the scattering wave starts – if the wavefront takes ΔT time to pass the potential, then the scattering starts at time $t = -\frac{\Delta T}{2}$ because it's halfway through at time $t = 0$. Since $\Delta T \to \infty$, we see that this time $-\frac{\Delta T}{2} \to -\infty$ as $\Delta k \to 0$, and that's why we also see the scattering wave existing at all times. (So the time-dependence is simple – we have energy eigenstates because $g(k) = \delta(k - k^0)$, and now it makes sense for us to say that nothing else besides the $e^{-iEt/\hbar}$ term is being affected by time.)

We'll now set up a problem in one-dimensional scattering that helps us say some things about three-dimensional scattering as well:

Example 190

Suppose we have a one-dimensional problem with an infinite barrier for all $x \le 0$ and some localized potential $V(x)$ for $x > 0$ so that $V(x) = 0$ for all $x > R$.

If there was no additional potential, meaning $V(x) = 0$ for any positive x, we'd be scattering particles off of a wall, so our solutions would need to vanish at the origin and we'd have solutions of the form

$$\psi_0(x) = \sin(kx) = \frac{e^{ikx} - e^{-ikx}}{2i},$$

where we can think of e^{-ikx} as the incident wave and e^{ikx} as the reflected wave (together forming a standing wave). So for all $x \ge R$, our wavefunction now takes the form

$$\psi_V = \frac{e^{ikx+2i\delta_K} - e^{-ikx}}{2i} = e^{i\delta_K}\sin(kx + \delta_k)$$

for some real phase shift δ_K depending on $V(x)$, since we need $|\psi_{\text{in}}|^2 = |\psi_{\text{out}}|^2$ by probability conservation. So we want to understand how V has affected the scattering, which we can see by calculating the **scattering wavefunction**

$$\psi_S = \psi_V - \psi_0 = e^{ikx}\left(e^{2i\delta_K} - 1\right),$$

which we define as $e^{ikx} f_k$ for the **scattering amplitude** f_k (noticing that the e^{ikx} term means that everything is outgoing here). The probability of scattering due to the potential is then

$$|\psi_S|^2 = |f_k|^2 = \sin^2\delta_K.$$

And it turns out that we'll see an analog of this in three dimensions as well, remembering that we also have $\frac{d\sigma}{d\Omega} = |f_k(\theta, \phi)|^2$ from lecture. It turns out that (as we'll see soon) the total cross-section

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega}$$

can be written as a sum over partial waves

$$= \sum_\ell \frac{4\pi}{k^2}(2\ell + 1)\sin^2\delta_\ell,$$

where we have a different phase shift for each partial wave. For now, though, we'll look at a particular example where the analogy is clear without needing to sum over partial waves: basically, choosing a particular ℓ to dominate gives us a one-dimensional problem. Specifically, if we have low-energy scattering so that $k \to 0$, the s wave (that is, the $\ell = 0$ wave) dominates. If we then imagine a central position $V = V(r)$ bound in some region $r \le R$, then recall that we can write the Schrodinger equation in the form

$$\psi(\vec{x}) = \frac{U_{E,\ell}(r)}{r} Y_{\ell,0}(\theta),$$

where there's no ϕ-dependence because we take $m = 0$. We then get a differential equation

$$\left(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2}\right) U_{E,\ell}(r) = k^2 U_{E,\ell}(r).$$

But taking $\ell = 0$ and $k \to 0$, we just have $-\frac{d^2}{dr^2} U_{E,0}(r) = 0$, meaning that U is a linear function of r which we can write as $c(r - a)$. And we can be more precise by solving the Schrodinger equation with a finite k, so that we have a simple harmonic oscillator

$$U_0(r) = \frac{A}{k} \sin(kr + \delta_0(k))$$

for the **S-wave phase shift** $\delta_0(k)$ (which is much like the δ_k phase shift we observed above). As $k \to 0$, we have

$$\lim_{k\to 0} U_0(r) = \lim_{k\to 0} \frac{A}{k} \sin\left(k\left(r + \frac{\delta_0(k)}{k}\right)\right) = A\left(r + \lim_{k\to 0} \frac{\delta_0(k)}{k}\right).$$

And now we can match up coefficients with the $c(r - a)$ solution we had above – the most important feature is that we have the **scattering length**

$$a = -\lim_{k\to 0} \frac{\delta_0(k)}{k},$$

which tells us about how scattering behaves at low energies. In particular, $\sin\delta_0$ behaves like $-ka$, so the cross-section will be

$$\sigma = \frac{4\pi}{k^2} \sin^2\delta_0 \approx 4\pi a^2.$$

In other words, the unit-length quantity determines our cross-section, and it has a lot of physical significance for our wavefunction as well.

44 May 11, 2021

Last lecture, we started discussing scattering: we scatter particles off of a potential $V(r)$, and we calculate how many particles hit each patch $d\Omega$ of the solid angle. We then discussed that we would like to calculate the **differential cross-section** $\frac{d\sigma}{d\Omega}$, which we do by solving the time-independent Schrodinger equation with energy $E = \frac{\hbar^2 k^2}{2m}$ (depending on the incoming beam), subject to the boundary condition

$$\psi(\vec{r}) \to e^{ikz} + f_k(\theta, \phi) \frac{e^{ik\cdot r}}{r}$$

as $r \to \infty$, where we need to solve for f_k in the process. This then gives us the differential cross-section $\frac{d\sigma}{d\Omega} = |f_k(\theta, \phi)|^2$, and we can then get the total cross-section by integrating $\sigma = \int d\Omega \frac{d\sigma}{d\Omega}$.

From there, the next step is to solve the three-dimensional Schrodinger equation, and we're doing so in the special case where $V(\vec{r})$ is spherically symmetric. Then we can look for solutions that are products of a radial and a spherical wavefunction, and we then reduce to the one-dimensional problem with an additional centrifugal barrier term.

Last time, we noticed that in the spatial region where $V = 0$ (and we have a free particle), we have solutions given by the spherical Bessel and Neumann functions. Since we also know plane waves solve the Schrodinger equation in

$V = 0$, plane waves must be a linear superposition of those functions, and in fact it turns out

$$e^{ikz} = \sqrt{4\pi}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}i^{\ell}Y_{\ell,0}(\theta)j_{\ell}(kr),$$

and only the $m = 0$ terms contribute. If we then take the limit $r \to \infty$, we indeed see the incoming and outgoing spherical wave in the **partial wave** expansion

$$\to \frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}i^{\ell}Y_{\ell,0}(\theta)\frac{1}{2i}\left[\frac{e^{i(kr-\ell\pi/2)}}{r} - \frac{e^{-i(kr-\ell\pi/2)}}{r}\right].$$

In particular, in each angular momentum channel ℓ, the incoming and outgoing components have the same amplitude.

So now we want to attack the problem in the region where $V(r) \neq 0$. We again look for solutions of the form

$$\psi(\vec{r}) = \frac{U_{E,\ell}(r)}{r}Y_{\ell,m}(\theta,\phi),$$

where

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr2} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} + V(r)\right)U_{E,\ell}(r) = \frac{\hbar^2k^2}{2m}U_{E,\ell}(r).$$

(So we have an effective potential going as $\frac{c}{r^2}$ from the centrifugal barrier, plus the localized $V(r)$.) We also require that $U(r=0) = 0$ (because the wavefunction should be finite at the origin, and it contains a $\frac{U(r)}{r}$ term), and we still have a one-dimensional free particle as $r \to \infty$ because both terms of the effective potential go to 0. So our solutions will look like

$$U(r) = F_\ell e^{ikr} + G_\ell e^{-ikr}$$

as $r \to \infty$, in certain very particular linear combinations so that they also satisfy $U(r=0) = 0$. Though we can't find the exact values of F_ℓ, G_ℓ without solving the Schrodinger equation, we can still say that $|F_\ell|^2 = |G_\ell|^2$. This is because we can imagine sending in particles with an amplitude G_ℓ into the potential, , and then we get back particles with an amplitude of F_ℓ, and there is no transition probability (because we can't have r negative, so the origin can be thought of as a hard wall). So the probability of reflection is 1, and that indeed gives us $|G_\ell| = |F_\ell|$.

Therefore, F_ℓ and G_ℓ must differ by only a phase, and we'll parameterize this by setting

$$U_\ell(r) \propto e^{i(kr-\ell\pi/2+2\delta_\ell)} - e^{-i(kr-\ell\pi/2)}$$

as $r \to \infty$, so that the phase is characterize by $2\delta_\ell$ and $e^{2i\delta_\ell} = (-1)^{\ell+1}\frac{F_\ell}{G_\ell}$. (Here, δ_ℓ is a **phase shift** defined modulo π, and it's different for different spherical harmonics ℓ. Note that we choose it in this particular manner so that $\delta_\ell = 0$ when $V = 0$, as discussed earlier.) It will turn out that knowing all of these phase shifts δ_ℓ is enough to determine $f_k(\theta,\phi)$ and thus obtain our scattering cross-section.

Returning to the Schrodinger equation, our general solution takes the form

$$\psi(\vec{r}) = \sum_{\ell,m}c_{\ell,m}\frac{U_{E,\ell}(r)}{r}Y_{\ell,m}(\theta,\phi),$$

and we're interested in those solutions that satisfy a particular boundary condition. So we'll match to that boundary condition above: because we've just parameterized our solutions in terms of the phase shifts δ_L, we find that

$$\psi(\vec{r}) \xrightarrow{r\to\infty} \sum_{\ell,m}c_{\ell,m}\left(\frac{e^{i(kr-\ell\pi/2+2\delta_L)} - e^{-i(kr-\ell\pi/2)}}{r}\right)Y_{\ell,m}(\theta,\phi),$$

and we want to match this to our boundary conditions

$$\psi(\vec{r}) \xrightarrow{r} e^{ikz} + f_k(\theta, \phi)\frac{e^{ikr}}{r}.$$

Everything here is a spherical wave except the plane wave term e^{ikz}, and we use the Rayleigh formula now (writing it in terms of spherical harmonics) to get

$$= \frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}i^\ell Y_{\ell,0}\frac{1}{2i}\left(\frac{e^{i(kr-\ell\pi/2)}}{r} - \frac{e^{-i(kr-\ell\pi/2)}}{r}\right) + f_k(\theta,\phi)\frac{e^{ikr}}{r}.$$

So the first has an outgoing and an incoming term, and the second term has just an outgoing term. We now match our two desired solution forms for $\psi(\vec{r})$ to find our unknown coefficients $c_{\ell,m}$ – since the incoming wave only comes from the plane wave e^{ikz} term and we know that expansion already, we have $c_{\ell,m} = 0$ for all $m \neq 0$, and

$$c_{\ell,0} = \frac{\sqrt{4\pi}}{k}\sqrt{2\ell+1}i^\ell\frac{1}{2i}.$$

Therefore, we find

$$\psi(\vec{r}) = \frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}i^\ell\frac{1}{2i}\left(\frac{e^{i(kr-\ell\pi/2+2\delta_\ell)}}{r} - \frac{e^{-i(kr-\ell\pi/2)}}{r}\right)Y_{\ell,0}(\theta).$$

Now that the incoming part of the solution and the boundary conditions are satisfied, we can now match the outgoing parts to determine an expression for $f_k(\theta,\phi)$. We find that (because outgoing wave has two pieces, from the scattered wave and the plane wave)

$$\left(\frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}i^\ell\frac{1}{2i}e^{i(-\ell\pi/2+2\delta_\ell)}Y_{\ell,0}(\theta)\right)\frac{e^{ikr}}{r} = \left(\frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}i^\ell\frac{1}{2i}e^{-i\ell\pi/2}Y_\ell,0(\theta) + f_k(\theta,\phi)\right)\frac{e^{ikr}}{r}.$$

Canceling the $\frac{e^{ikr}}{r}$ factors and moving both sums to one side, we get

$$f_k(\theta,\phi) = \frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}i^\ell\frac{1}{2i}e^{-i\ell\pi/2}\left(e^{2i\delta_\ell}-1\right)Y_{\ell,0}(\theta).$$

And now because $e^{-\ell\pi/2} = (-i)^\ell$, this cancels with the i^ℓ. And we can also manipulate the exponential terms to get a sine out of the difference of exponentials:

$$\boxed{f_k(\theta,\phi) = \frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}e^{i\delta_\ell}\sin(\delta_\ell)Y_{\ell,0}(\theta)}.$$

So we've expressed our scattering amplitude solely in terms of the phase shift – in fact, each phase shift tells us the coefficient of the corresponding spherical harmonic $Y_{\ell,0}$. (And in particular, the scattering is ϕ-independent, which makes sense because our system is symmetric around the z-axis. So the differential cross-section will also be ϕ-independent.) This leads us to the total cross-section

$$\sigma = \int \frac{d\sigma}{d\Omega}d\Omega = \int d\Omega f_k^*(\theta)f_k(\theta),$$

and inserting our form of f_k into this equation gives us

$$= \frac{4\pi}{k^2}\int d\Omega\sum_{\ell,\ell'}\sqrt{2\ell+1}\sqrt{2\ell'+1}e^{-i\delta_\ell}e^{i\delta_{\ell'}}\sin(\delta_\ell)\sin(\delta_{\ell'})Y^*_{\ell,0}(\theta)Y_{\ell',0}(\theta).$$

But we know that our spherical harmonics are orthonormal, so $\int d\Omega Y^*_{\ell,0}(\theta)Y_{\ell',0}(\theta) = \delta_{\ell,\ell'}$ and our double sum collapses into a single sum:

$$\boxed{\sigma = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell}.$$

So the total cross-section is the sum of the **partial cross-sections**

$$\sigma_\ell = \frac{4\pi}{k^2}(2\ell+1)\sin^2(\delta_\ell)$$

over all ℓ. And because δ_ℓ is a real phase, we can make the **partial wave unitarity** bound

$$\sigma_\ell \le \frac{4\pi}{k^2}(2\ell+1).$$

So conservation of probability (which was what gave us the reality of δ_ℓ) basically tells us that there's only so much scattering that can happen, which is a useful consistency check in particle physics.

We may notice that our expression for σ and for f_k look very similar, and it turns out that we always have

$$\sigma = \frac{4\pi}{k}\text{Im}(f_k(\theta=0)).$$

In other words, the scattering amplitude that is basically not deflected from the z-axis tells us about the integral of scattering over all angles! This is known as the **optical theorem**, because the scattered part of the outgoing spherical wave and the outgoing plane wave give us an interference pattern. Indeed, it turns out that

$$Y_{\ell,0}(\theta=0) = \sqrt{\frac{2\ell+1}{4\pi}} \implies \text{Im}(f_k(\theta=0)) = \frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)\text{Im}(e^{i\delta_\ell})\sin\delta_\ell,$$

and the imaginary part of $e^{i\delta_\ell}$ is $\sin\delta_\ell$, so we indeed get our $\sin^2\delta_\ell$ showing up like in σ_ℓ.

What's left for us to do is to calculate the phase shifts δ_ℓ, and those come from solving the effective one-dimensional Schrodinger equation for each angular momentum channel ℓ.

Example 191 (Hard sphere potential)

Suppose we have the potential

$$V(r) = \begin{cases} \infty & r \le a \\ 0 & \text{otherwise.} \end{cases}$$

We can think of the scattering process as bouncing particles off a completely inpenetrable wall. Our effective potential is then

$$V_{\text{eff}}(r) = \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} + V(r) = \begin{cases} \infty & r \le a \\ \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} & \text{otherwise.} \end{cases}$$

We then need to solve the one-dimensional Schrodinger equation to get $U_\ell(r)$, and our boundary condition is now that $U_\ell(a) = 0$. But we have a free particle with centrifugal barrier for all $r \ge a$, and we've already found that the solutions are the spherical Bessel and Neumann functions:

$$U_\ell(r) = r\left(A_\ell j_\ell(kr) + B_\ell n_\ell(kr)\right).$$

To impose the boundary condition $U_\ell(a) = 0$, we must have

$$\frac{B_\ell}{A_\ell} = -\frac{j_\ell(ka)}{n_\ell(ka)},$$

and since we care about δ_ℓ, what matters to us is the asymptotic form of the solution as $r \to \infty$. This requires using the asymptotic behavior of the spherical Bessel and Neumann functions, and we find that

$$U_\ell(r) \xrightarrow{r\to\infty} \frac{1}{k}\left(A_\ell \sin\left(kr - \frac{\ell\pi}{2}\right) - B_\ell \cos\left(kr - \frac{\ell\pi}{2}\right)\right),$$

which we need to match against

$$U_\ell(r) \xrightarrow{r\to\infty} e^{i(kr-\ell\pi/2+2\delta_\ell)} - e^{-i(kr-\ell\pi/2)}.$$

Pulling out an $e^{i\delta_\ell}$ in the latter expression shows us that it is proportional to a sine term:

$$U_\ell(r) \propto \sin\left(kr - \frac{\ell\pi}{2} + \delta_\ell\right) = \sin\left(kr - \frac{\ell\pi}{2}\right)\cos(\delta_\ell) + \cos\left(kr - \frac{\ell\pi}{2}\right)\sin(\delta_\ell).$$

So we must have a ratio of coefficients given by

$$\frac{A_\ell}{\cos\delta_\ell} = -\frac{B_\ell}{\sin\delta_\ell} \implies \boxed{\tan\delta_\ell = \frac{j_\ell(ka)}{n_\ell(ka)}}.$$

So for each k, we can compute the phase shifts δ_ℓ, and that gives us the total cross-section

$$\sigma = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell.$$

In particular, because $\sin^2 x = \frac{\tan^2 x}{1+\tan^2 x}$, we have

$$\boxed{\sigma = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\frac{j_\ell(ka)^2}{j_\ell(ka)^2 + n_\ell(ka)^2}}.$$

This example turns out to be very illustrative – if we look at scattering in the low-energy limit $k \to 0$, we'll get behavior that is generic for short-range potentials. In this case, as $ka \to 0$, the spherical Bessel and Neumann functions have known asymptotics:

$$j_\ell(x) \to \frac{x^\ell}{(2\ell+1)!!}, \quad n_\ell(x) \to \frac{-(2\ell-1)!!}{x^{\ell+1}},$$

where the double factorial misses every other term as it counts down (so $5!! = 5\cdot 3\cdot 1$). So plugging in these forms into our phase shift yields

$$\tan\delta_\ell = -\frac{1}{(2\ell+1)!!(2\ell-1)!!}(ka)^{2\ell+1} \ll 1.$$

So then we can approximate $\tan x \approx x$ and find that

$$\delta_\ell \approx -\frac{(ka)^{2\ell+1}}{(2\ell+1)!!(2\ell-1)!!}.$$

So phase shifts become progressively smaller for large ℓs, and the largest phase shift comes from the $\ell = 0$ channel. The scattering amplitude is then

$$f_k(\theta,\phi) = \frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}e^{i\delta_\ell}\sin(\delta_\ell)Y_{\ell,0}(\theta),$$

and the dominant term comes from $\ell = 0$ because we have a $\sin\delta_\ell \approx \delta_\ell$ term – that evaluates to $-ka$. This yields

$$f_k(\theta,\phi) \approx \frac{\sqrt{4\pi}}{k}(-ka)Y_{00}(\theta) = \frac{\sqrt{4\pi}}{k}(-ka)\frac{1}{\sqrt{4\pi}} = \boxed{-a}.$$

So in the low-energy limit, the scattering amplitude becomes angle-independent (uniform in any direction), so the differential cross-section is just a^2, and the total cross-section $\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = 4\pi a^2$ is the surface area of the hard sphere! (Classically, the cross-section of the hard sphere is πa^2, so the quantum case gives us a factor of 4.) We'll talk more about this angle independence next time.

45 May 12, 2021 (Recitation)

Last recitation, we made an analogy of three-dimensional scattering with one-dimensional scattering by thinking about having one partial wave dominate our sum over ℓ (and indeed, this is the case when we have low energies and thus low k, as we saw in lecture). One point is that as long as V is zero outside of a localized range, we can always define a scattering length a.

Today, we'll continue that discussion – first, we'll go to higher orders instead of just keeping the leading-order contribution. We often get combinations that look like $e^{i\delta_0} \sin \delta_0$ (where the 0 subscript indicates that we're looking at the $\ell = 0$ partial wave), and to motivate how we do our Taylor expansion, we'll rewrite this as

$$= \frac{\sin \delta_0}{e^{-i\delta_0}} = \frac{\sin \delta_0}{\cos \delta_0 - i \sin \delta_0} = \frac{1}{\cot \delta_0 - i}.$$

So it turns out that we should expand in this parameter $\cot \delta_0$ for small k: we have, as $k \to 0$,

$$k \cot \delta_0 \approx -\frac{1}{a} + \frac{1}{2} r_0 k^2 + O(k^4)$$

(recall that a is defined as the limit $\lim_{k \to 0} \frac{\delta_0(k)}{k}$). This is called the **effective range expansion**, and if we do this for higher partial waves δ_ℓ as well, we'll get similar-looking expansions.

Example 192

We'll now connect this discussion to that of the hard sphere, where our radial potential is ∞ for all $r < b$ and 0 otherwise.

We must have $\psi(r = b) = 0$, which gives us a condition on our wavefunction

$$U_0 \sim \sin(kr + \delta_0).$$

This gives us a condition on our phase $\delta_0 = -kb$, and we'll notice that the scattering length a is just the radius of the ball b. If we draw the wavefunction $U_0(r)$, we have a horizontally shifted sine function which vanishes at $r = b$. (In words, we can say that a **repulsion** from the potential V gives us a **negative** phase shift δ_0, which pushes the wavefunction outward from the origin.)

If we focus in on low-energy scattering and take $k \to 0$, our sine function also becomes more linear. And to illustrate what's going on with the scattering length, if we replace our infinite well with a **finite but positive** well, the scattering length a will satisfy $0 < a < b$ (it won't push the wavefunction outward as much, but it will still have some effect). Remember that because our sine function will look linear near the x-axis ($U_0 \approx c(r - a)$), the interpretation of a in this case is the **intercept of the linear part** of the wavefunction where $V = 0$, and that will now be before $r = b$. (And similarly, an attractive finite square well will pull the wavefunction inward, making the phase shift positive and thus making a negative.)

If we keep making this square well $V = -V_0$ deeper and deeper, our scattering length a will get more and more negative, and it turns out that $a \to -\infty$ at a **finite** value of V_0, where the wavefunction in the outside region becomes flat. A (normalizable) bound state will enter the problem with $k = 0$ at this infinite scattering length – if we then further decrease V_0, our bound state's energy also decreases, and our wavefunction in the outside region has phase shifted so much that the value of a becomes positive again (since the slope of the outside region is now negative, rather than positive).

Continuing to make V_0 small, at a certain point, we get an intercept of $a = 0$: remembering that the cross-section should be $4\pi a^2$ for low-energy scattering, this tells us that there is a suppression of low-energy scattering for certain potentials V_0. And then finally, when we reach a phase where $a = -\infty$ again, we will get another bound state appearing at the threshold $k = 0$. We can understand the bound states by citing the solutions to the finite square well, which satisfy

$$k' \cot(k'b) = -\frac{1}{\hbar}\sqrt{-2mE}, \quad k' = \frac{1}{\hbar}\sqrt{2m(E+V_0)}.$$

So if we want to understand the special case where the states show up at $k = 0 \implies E = 0$, we have the condition that $\cot(k'b) = 0$, and thus we must have $b = \frac{(n+\frac{1}{2})\hbar\pi}{\sqrt{2mV_0}}$ for some integer n.

We'll now turn to a discussion of **partial waves**: recall that we can approximate our solution for r away from the potential V as

$$\psi(\vec{r}) = e^{ikz} + f_k(\theta)\frac{e^{ikr}}{r},$$

where

$$f_k(\theta) = \frac{1}{k}\sum_{\ell=0}^{\infty} e^{i\delta_\ell}\sin(\delta_\ell)(\sqrt{4\pi}\sqrt{2\ell+1}Y_{\ell,0}(\theta))$$

and the differential cross-section is just $\frac{d\sigma}{d\Omega} = |f_k(\theta)|^2$; integrating over solid angles and using orthogonality gives us

$$\sigma = \frac{4\pi}{k^2}\sum_\ell (2\ell+1)\sin^2(\delta_\ell).$$

So the main task we have is to calculate the phase shifts δ_ℓ – we'll talk more about this in lecture, but the idea is to write our wavefunction as a product of radial and angular dependence

$$\psi = \sum_\ell R_\ell(r) Y_{\ell,0}(\theta),$$

and we'll solve this for each ℓ separately. If V is zero at some $r > R$, then we know that our solution is

$$R_\ell(r) = A_\ell j_\ell(kr) + B_\ell n_\ell(kr) = A_\ell(j_\ell(kr) - \tan\delta_\ell n_\ell(kr)),$$

and we calculate δ_ℓ by solving the Schrodinger equation in the region where V is **nonzero**, in particular decomposing into radial and angular parts again. We can then match both the radial wavefunction $R_\ell(r)$ and its derivative $R'_\ell(r)$ at $r = R$, and that will give us a formula for δ_ℓ.

Example 193

Suppose that we have a potential of the form

$$V(r) = \begin{cases} \infty & r < b \\ -V_0 & b < r < c \\ 0 & r > c. \end{cases}$$

For simplicity, we'll just try to compute the $\ell = 0$ phase shift $\delta_0(k)$.

In the region $b < r < c$, we know that we must have sine-type solutions with wavenumber given by $k_1^2 = \frac{2m}{\hbar^2}(E+V_0)$, but we need to pick the sine function so that it vanishes at $r = b$ because of the infinite well on the left. Therefore, for $b < r < c$, we must have a solution of the form

$$U_0(r) = \frac{A}{k_1}\sin(k_1(r-b)).$$

We then compare that solution to the solution in the $r > c$ region; if we plug in the spherical Bessel and Neumann functions for $\ell = 0$, we find that for $r > c$,

$$U_0(r) = \frac{c}{k}\sin(kr + \delta_0).$$

We must match up these wavefunctions and their derivatives (or we can equivalently match up $R_0 = \frac{U_0(r)}{r}$), and one trick to get simple calculations is to ask for $\frac{U'(r)}{U(r)}$ to be continuous (since this will get rid of the coefficients in the front) at $r = c$. We find that

$$\frac{k_1\cos(k_1(c-b))}{\sin(k_1(c-b))} = \frac{k\cos(kc+\delta_0)}{\sin(kc+\delta_0)}$$

meaning that

$$k_1\cot(k_1(c-b)) = k\cot(kc+\delta_0).$$

The only thing that is unknown here is δ_0, so we can solve for it here, and we find that (reciprocating the above formula to use tans instead of cots)

$$\boxed{\delta_0(k) = -kc + \tan^{-1}\left(\frac{k}{k_1}\tan(k_1(c-b))\right)}.$$

We can check that various limits of this expression work: if we set $V_0 = 0$, then we get the hard sphere solution, and expanding in δ_0 will make $k \approx k_1$ and thus the $\tan^{-1}$ and tan cancel out. And if we think about the scattering length as $k \to 0$, setting $b = 0$ so that we just have a single finite well for simplicity, we find that

$$k_1 = \frac{\sqrt{2mV_0}}{\hbar} = \gamma \implies \delta_0(k) = -kc + \frac{k}{\gamma}\tan(\gamma c).$$

This gives us the scattering length

$$a = c - \frac{1}{\gamma}\tan(\gamma c),$$

and thus a is not quite c for the finite well. Instead, it can take on various real-number values, and this connects back to the argument that we made with the slopes of the intercepts earlier in the recitation and justifies the values for bound states!

Remark 194. *It can be shown that for $\ell = 0$, we get*

$$f_{\ell=0} = \frac{1}{k}e^{i\delta_0}\sin(\delta_0) = \frac{1}{k(\cot\delta_0 - i)} = \frac{1}{-\frac{1}{a} - ik}$$

by taking the small-k approximation. So for small k we have $|f|^2 \sim a^2$, but if we send $a \to \infty$ first, then we get a scale-invariant problem and σ is proportional to $\frac{1}{k^2}$ instead. So as $k \to 0$, we do get a large cross-section, and we need to consider higher-order terms to understand what's really going on in the system.

46 May 13, 2021

We've been analyzing scattering for a central potential V that only depends on the distance to the origin – the idea is to decompose into different angular momentum channels, solve the one-dimensional radial equation with effective potential, and study the asymptotic behavior of the wavefunction for $r \to \infty$. We then defined the phase shift δ_ℓ so that $U_\ell(r) \propto \sin\left(kr - \frac{\ell\pi}{2} + \delta_\ell\right)$ as $r \to \infty$, so that we can find the scattering amplitude $f_k(\theta)$ and the differential and total cross-section in terms of that phase shift.

We then applied this formalism to a special case of a hard-sphere potential, finding that in the low-energy limit $ka \ll 1$, we have $\delta_\ell \propto -(ka)^{2\ell+1}$, so that the $\ell = 0$ channel will dominate the scattering. We then find that $f_k \approx -a$ becomes angle-independent, and the cross-section becomes $4\pi a^2$. A natural question to ask is whether this behavior is a general phenomenon, and it turns out that this is **common to all short-range potentials**: we will generically have

$$\delta_\ell \propto k^{2\ell+1} \text{ as } k \to 0.$$

This motivates defining the **scattering length**

$$a_s = -\lim_{k\to 0} \frac{\delta_0(k)}{k},$$

which can be positive or negative depending on the problem, and this leads us to the familiar

$$f_k \approx -a_s, \quad \frac{d\sigma}{d\Omega} = a_s^2, \quad \sigma = 4\pi a_s^2.$$

But there's an exception where something different happens, and that's when we have **bound states** in the potential. If this bound state's energy $-E_b$ approaches the continuum threshold, meaning that $E_b \to 0$, then our scaling behavior will break down, our scattering length will go to ∞, and the phase shift will go to $\frac{\pi}{2}$ (so that $\sin \delta_\ell$ becomes maximal in magnitude). (This has applications to cold-atom physics and **Feshbach resonance**, where the tuning of our potential comes from an external magnitude field.)

Example 195

We'll now explore the reason that we expect $\delta_0 \propto k$ generically, leading us to f_k being angle-independent.

Recall that the only breaking of spherical asymmetry in the problem comes from the direction that the incoming particles are coming from, but as $k \to 0$, the length of the wavevector goes to zero, so we lose the sense of directionality. Another way to say this is that as $k \to 0$, we have a very large wavelength for our incoming wave, which will be approximately constant over the size of the short-range potential. This means that the plane wave will appear less biased in one particular direction.

From here, we'll take a step back and try to develop methods that work when we don't just have central potentials. (But we'll still assume that $V \to 0$ as $r \to \infty$.) We're going to need to do perturbation theory in the potential V – this is called the **Born approximation** – after all, even in the spherically symmetric case, there's still quite a bit of work in solving the one-dimensional Schrodinger equation.

Let's start by being exact. We now need to solve the equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\psi(\vec{r}) = E\psi(\vec{r}), \quad E = \frac{\hbar^2 k^2}{2m}.$$

We'll rescale our potential as $V(\vec{r}) = \frac{\hbar^2}{2m}U(\vec{r})$, so that we need to solve the equation

$$(-\nabla^2 + U(\vec{r}))\psi(\vec{r}) = k^2\psi(\vec{r}) \implies \boxed{(\nabla^2 + k^2)\psi(\vec{r}) = U(\vec{r})\psi(\vec{r})}.$$

We'll now turn this differential equation into an integral equation as follows: suppose we have a **Green's function** for the operator $(\nabla^2 + k^2)$, meaning that we have a function $G(\vec{r})$ satisfying

$$(\nabla^2 + k^2)G(\vec{r}) = \delta^3(\vec{r}),$$

or equivalently $(\nabla_{\vec{r}}^2+k^2)G(\vec{r}-\vec{r}') = \delta^3(\vec{r}-\vec{r}')$. Then this Green's function can be used to turn our differential equation into

$$\boxed{\psi(\vec{r}) = \psi_0(\vec{r}) + \int d^3\vec{r}' G(\vec{r}-\vec{r}')U(\vec{r}')\psi(\vec{r}')},$$

where $\psi_0(\vec{r})$ satisfies the homogeneous equation

$$(\nabla^2 + k^2)\psi_0(\vec{r}) = 0.$$

Proposition 196

The two boxed equations above (differential and integral) are equivalent.

Proof. Suppose that $\psi(\vec{r})$ satisfies the integral equation. Then applying the operator $(\nabla^2 + k^2)$ on both sides, we get

$$(\nabla_{\vec{r}^2} + k^2)\psi(\vec{r}) = 0 + \int d^3\vec{r}'(\nabla_{\vec{r}}^2 + k^2)G(\vec{r}-\vec{r}')U(\vec{r}')\psi(\vec{r}'),$$

where we've moved the operator inside the integral (convergence issues are not a problem as long as our short-term potential is well-behaved and decaying). Now by the definition of the Green's function, we get that this is

$$= \int d^3\vec{r}'\delta(\vec{r}-\vec{r}')U(\vec{r}')\psi(\vec{r}') = U(\vec{r})\psi(\vec{r}),$$

which is the differential equation that we want. On the other hand, if we start with the differential equation, we can just define

$$\psi_0(\vec{r}) = \psi(\vec{r}) - \int d^3\vec{r}' G(\vec{r}-\vec{r}')U(\vec{r}')\psi(\vec{r}'),$$

and we can verify that $(\nabla^2 + k^2)\psi_0(\vec{r}) = 0$ by doing the exact same manipulations. Then the integral equation is clearly satisfied by our choice of ψ_0. $\square$

It turns out that there are two different Green's functions that work for us in this case: we claim that they are the incoming and outgoing waves

$$G_\pm(\vec{r}) = -\frac{1}{4\pi}\frac{e^{\pm ikr}}{r},$$

where $r = |\vec{r}|$. We can verify that this works: first, we check that for all $\vec{r} \neq 0$, we have $(\nabla^2 + k^2)G_\pm(\vec{r}) = 0$. By the Laplacian formula in polar coordinates $\nabla^2 = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})$, where we're only using the radial part, we have (just doing the $+$ case for concreteness)

$$\nabla^2 G_+(\vec{r}) = -\frac{1}{4\pi}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\left(-\frac{1}{r^2}e^{-ikr} + \frac{ike^{ikr}}{r}\right)\right),$$

which simplifies to

$$= -\frac{1}{4\pi}\frac{1}{r^2}\frac{\partial}{\partial r}\left(-e^{ikr} + ikre^{ikr}\right) = -\frac{1}{4\pi}\frac{1}{r^2}\left(-ike^{ikr} + ike^{ikr} - k^2re^{ikr}\right) = \frac{k^2}{4\pi}\frac{1}{r}e^{ikr},$$

which is indeed $-k^2G_+(\vec{r})$. (Taking a complex conjugate on both sides gives us what we want for G_-, as well.) And then for $\vec{r} = 0$, we notice that $G_\pm(\vec{r}) \to -\frac{1}{4\pi r}$ because the phase factor goes to 1, and indeed $\nabla^2\left(-\frac{1}{4\pi r}\right)\delta^3(\vec{r})$ (we may remember this from electrostatics).

So now that we've verified our Green's function works, we can plug this into our integral equation. And knowing which Green's function to use, as well as which $\psi_0(\vec{r})$, can be found by looking at the boundary conditions we're imposing as $r \to \infty$, which are

$$\psi(\vec{r}) = e^{ikz} + f_k(\theta, \phi)\frac{e^{ikr}}{r}.$$

So it makes sense to make $\psi_0(\vec{r})$ the plane wave e^{ikz}, and it makes sense to use $G_+(\vec{r})$, because our integral equation then takes the form

$$\psi(\vec{r}) = e^{ikz} + \int d^3\vec{r}' G_+(\vec{r} - \vec{r}')U(\vec{r}')\psi(\vec{r}').$$

We need to check that the second term here is indeed a spherically outgoing wave so that our boundary conditions are satisfied – indeed, because $G_+(\vec{r} - \vec{r}') = -\frac{1}{4\pi}\frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}$, and the potential U goes to 0 rapidly as $r \to \infty$, we can effectively think of our integral as getting significant contributions from a finite region for $\vec{r}'$ near the origin. And as $\vec{r}$ gets very far away from the origin, we can expand the denominator as

$$|\vec{r} - \vec{r}'| = \sqrt{(\vec{r} - \vec{r}')^2} = \sqrt{r^2 - 2\vec{r}\cdot\vec{r}' + \vec{r}'^2} = r\sqrt{1 - 2\frac{\vec{r}}{r^2}\cdot\vec{r}' + \frac{\vec{r}'^2}{r^2}}.$$

Since $r \gg r'$ here, we'll approximate this square root with the binomial expansion as

$$\approx r\left(1 - \frac{\vec{r}}{r^2}\cdot\vec{r}'\right) = r - \hat{r}\cdot\vec{r}'.$$

And we can actually simplify our Green's function form now: the denominator can be approximated as r, and the numerator we have to be a bit more careful with because things are coming in as a phase. Basically, as $r \to \infty$, we have

$$G_+(\vec{r} - \vec{r}') \approx -\frac{1}{4\pi r}e^{ikr}e^{-ik\hat{r}\cdot\hat{r}'},$$

so that the integral equation as $r \to \infty$ becomes

$$\psi(\vec{r}) = e^{ikz} + \left(-\frac{1}{4\pi}\int d^3\vec{r}' e^{-ik\hat{r}\cdot\vec{r}'}U(\vec{r}')\psi(\vec{r}')\right)\frac{e^{ikr}}{r}.$$

In other words, all of the $\vec{r}$-dependence has been taken out of the integral, except through $\hat{r}$, which tells us about the angle (θ, ϕ) of our vector. So this fits our desired boundary condition $e^{ikz} + f_k(\theta, \phi)\frac{e^{ikr}}{r}$ as desired!

We now have an expression for the scattering amplitude, but it's misleading, because it still depends on the wavefunction $\psi(\vec{r}')$ over the range of the potential. This means we can't get away from solving for ψ, and here's where we'll do our perturbative expansion. We'll introduce some notation first: let $\vec{k}_i = k\cdot\hat{z}$ be the wavevector of the incident beam, so that we can rewrite our integral equation as

$$\psi(\vec{r}) = e^{i\vec{k}_i\cdot\vec{r}} + \int d^3\vec{r}' G_+(\vec{r} - \vec{r}')U(\vec{r}')\psi(\vec{r}').$$

We'll iterate this equation by plugging in $\psi(\vec{r}')$ back in for itself:

$$\psi(\vec{r}) = e^{i\vec{k}_i\cdot\vec{r}} + \int d^3\vec{r}' G_+(\vec{r} - \vec{r}')U(\vec{r}')\left(e^{i\vec{k}_i\cdot\vec{r}'} + \int d^3\vec{r}'' G_+(\vec{r}' - \vec{r}'')U(\vec{r}'')\psi(\vec{r}'')\right),$$

so that we can split the contributions into a term with one integral and another with two integrals:

$$\psi(\vec{r}) = +e^{i\vec{k}_i\cdot\vec{r}} + \int d^3\vec{r}' G_+(\vec{r} - \vec{r}')U(\vec{r}')e^{i\vec{k}_i\cdot\vec{r}'} + \int d^3\vec{r}' G_+(\vec{r} - \vec{r}')U(\vec{r}')\int d^3\vec{r}'' G_+(\vec{r}' - \vec{r}'')U(\vec{r}'')\psi(\vec{r}'').$$

This iteration procedure can be repeated by substituting in an expression for $\psi(\vec{r}'')$, so we have a term with a double integral and another with a triple integral: if we keep iterating this, we'll end up with an expression like

$$\psi(\vec{r}) = e^{i\vec{k}_i\cdot\vec{r}} + \int d^3\vec{r}' G_+(\vec{r}-\vec{r}')U(\vec{r}')e^{i\vec{k}_i\cdot\vec{r}'} + \int d^3\vec{r}' G_+(\vec{r}-\vec{r}')U(\vec{r}') \int d^3\vec{r}'' G_+(\vec{r}'-\vec{r}'')U(\vec{r}'')e^{i\vec{k}_i\cdot\vec{r}''}$$
$$+ \int d^3\vec{r}' G_+(\vec{r}-\vec{r}')U(\vec{r}') \int d^3\vec{r}'' G_+(\vec{r}'-\vec{r}'')U(\vec{r}'') \int d^3\vec{r}''' G_+(\vec{r}''-\vec{r}''')U(\vec{r}'')e^{i\vec{k}_i\cdot\vec{r}'''} + \cdots .$$

In other words, every successive term has an extra integral factor, and each one has a phase term for its corresponding variable. What we're really doing here is doing a perturbative expansion in U (or equivalently V), but let's first do the **first Born approximation**, where we just keep the first integral term. Then we have

$$\psi(\vec{r}) \approx e^{i\vec{k}_i\cdot\vec{r}} + \int d^3\vec{r}' G_+(\vec{r}-\vec{r}')U(\vec{r}')e^{i\vec{k}_i\cdot\vec{r}'}.$$

Then as $r \to \infty$, we use our expansion of the Green's function from earlier, and we find that

$$\psi(\vec{r}) \xrightarrow{r\to\infty} e^{i\vec{k}_i\cdot\vec{r}} + \left(-\frac{1}{4\pi}\int d^3\vec{r}' e^{-ik\hat{r}\cdot\vec{r}'} U(\vec{r}')e^{i\vec{k}_i\cdot\vec{r}'}\right)\frac{e^{ikr}}{r}.$$

We can then read off the scattering amplitude

$$f_k(\theta,\phi) = -\frac{1}{4\pi}\int d^3\vec{r}' U(\vec{r}')e^{i(\vec{k}_i - k\hat{r})\cdot\vec{r}'}.$$

If we then let $\vec{k}_s = k\cdot\hat{r}$ be the momentum of the scattered particle, we can define $\vec{K} = \vec{k}_s - \vec{k}_i$ to be the **momentum transfer** between the incident and scattered particle, and our scattering amplitude then becomes

$$\boxed{f_k(\theta,\phi) = -\frac{1}{4\pi}\int d^3\vec{r}' e^{-i\vec{K}\cdot\vec{r}'}U(\vec{r}')},$$

to first-order in U. (In words, this is very simple: to get the scattering amplitude, we just need to take the Fourier transform of U, with wavevector given by the momentum transfer!)

Looking more at the geometry of this scattering process, we should remember that the scattered momentum is the same length as the incident momentum, but it points an angle θ away from the z-axis. The length of $\vec{k}$ can then be obtained with the law of cosines:

$$\vec{K}^2 = \vec{k}_s^2 + \vec{k}_i^2 - 2\vec{k}_s\cdot\vec{k}_i = 2k^2 - 2k^2\cos\theta = 4k^2\sin^2\frac{\theta}{2}.$$

In other words, the length of $\vec{K}$ will be $2k\sin\frac{\theta}{2}$. And if we now think about the special case where we have a central potential, $U(\vec{r}')$ only depends on the length of $\vec{r}'$, and we integrate over all $\vec{r}'$ so the integral for $f_k(\theta,\phi)$ **only depends on the length of** $|\vec{K}|$. Since $|\vec{K}|$ only depends on θ and not ϕ, this is consistent with what we've previously found. In such a case, the calculation simplifies dramatically: if we choose our new z-axis along the $\vec{k}$-direction, we find that

$$\vec{r}' = r'(\sin\Theta\cos\Phi, \sin\Theta\sin\Phi, \cos\Theta),$$

and then we have

$$f_k = -\frac{1}{4\pi}\int r'^2 dr' \int_0^{\pi}\sin\Theta d\Theta \int_0^{2\pi} d\Phi e^{-iKr'\cos\Theta}U(r').$$

The Φ integral gives us a factor of 2π, and if we let $\mu = \cos\theta$, we can evaluate the integral to be

$$= -\frac{1}{2}\int r'^2 dr' \int_{-1}^{1} d\mu e^{-iKr'\mu}U(r') = -\frac{1}{2}\int r'^2 dr' U(r')\left.\frac{e^{-iKr'\mu}}{-iKr'}\right|_{-1}^{1},$$

simplifying to

$$f_k = -\frac{1}{K}\int_0^\infty dr' r' U(r')\sin(Kr').$$

And because $U(r) = \frac{2m}{\hbar^2}V(r)$, we get our final expression for the scattering amplitude in the spherically symmetric case:

$$f_k(\theta) = -\frac{2m}{\hbar^2 k}\int_0^\infty dr' r' V(r')\sin(Kr'),$$

where $K = k\sin\frac{\theta}{2}$. We'll talk more about the higher-order terms and validity of the Born approximation next time!

47 May 17, 2021 (Recitation)

We'll discuss the Born approximation for scattering today, doing a review and then applying it to some examples.

Recall that we're trying to solve the scattering problem, which is the Schrodinger equation with wavefunctions suitable for scattering:

$$(\nabla^2 + \hbar^2)\psi(\vec{r}) = U(\vec{r})\psi(\vec{r}),$$

where $U(\vec{r})$ is the rescaled potential $U = \frac{2m}{\hbar^2}V$ and $E = \frac{\hbar^2 k^2}{2m}$. To do this, we introduced the **Green's functions**, which allow us to rewrite this differential equation as an integral equation

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int d^3\vec{r}' G(\vec{r} - \vec{r}')U(\vec{r}')\psi(\vec{r}'),$$

where $(\nabla^2 + k^2)\psi_0(\vec{r}) = 0$ and $(\nabla^2 + k^2)G(\vec{r} - \vec{r}') = \delta^3(\vec{r} - \vec{r}')$. To make this specific to our scattering setup, we used the $\psi_0 = e^{ikz}$ to set up the incoming wave, and we used $G(\vec{r}) = -\frac{1}{4\pi r}e^{ikr}$ as an outgoing spherical wave. And the Born approximation comes in when we try to solve the equation: since ψ appears on both sides of the equation, we can substitute it back in for itself above in an iterative way. If we assume that $\psi \approx \psi_0$, we then get the first-order approximation

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int d^3\vec{r}' G(\vec{r} - \vec{r}')U(\vec{r}')\psi_0(\vec{r}'),$$

Since we're interested in the scattering at large r, and we know the potential is localized, we can write that there is some b such that $U(\vec{r}' > b) = 0$. Then for $r \gg r' \sim b$ when the integrand is nonzero, we can expand the Green's function to get

$$\psi(\vec{r}) = \psi_0 + \frac{e^{ikr}}{r}f_k^{(1)}(\theta, \phi) + \cdots,$$

where

$$f_k^{(1)}(\theta, \phi) = -\frac{1}{4\pi}\int d^3\vec{r}' e^{-i\vec{q}\cdot\vec{r}'}U(\vec{r}').$$

In other words, to find the (first-order approximation) of the scattering amplitude, we're doing a Fourier transform of our rescaled potential! Here, recall that $\vec{q}$ is the **momentum transfer** (denoted $\vec{K}$ in lecture)

$$\vec{q} = k\hat{r} - k\hat{z},$$

where we can think of a particle coming in with momentum $k\hat{z}$ and scattering out with momentum $k\hat{r}$. (So the direction of $\hat{r}$ is the reason that this expression for $f_k^{(1)}$ depends on the angles θ, ϕ.) And doing some algebra, we found that the magnitude of the momentum transfer $q = |\vec{q}| = 2k\sin\frac{\theta}{2}$.

One thing we haven't discussed yet, though, is when this Born approximation is good. Essentially, we want to make sure that ψ is close to ψ_0, and we can do that by making the first-order integral term small. One way to do this is to ensure that

$$|V| \ll \frac{\hbar^2}{mb^2},$$

so that the potential is small, and another way is to look at the case where the momentum k is very large (since this makes the "free energy" term ψ_0 larger and larger):

$$|V| \ll \frac{\hbar^2}{mb^2}(kb).$$

Basically, when k gets large enough, the integral oscillates quickly and thus doesn't give a large contribution relative to ψ_0. So because the Born approximation looks at large k instead of small k (like for partial waves), the two methods of solving scattering problems are complementary!

If we now look at the special case where V is a central potential (as in lecture), we can reduce the form of the solution to

$$\boxed{f_k^{(1)}(\theta) = -\frac{1}{q}\int_0^\infty dr'r'\left(\frac{2m}{\hbar^2}V(r')\right)\sin(qr')}.$$

We can notice that the whole function here is now just dependent on $q = 2k\sin\frac{\theta}{2}$ (not on k and θ independently), which is different from the approach with partial waves where k and θ appeared separately. And if we now turn to the differential cross-section

$$\frac{d\sigma}{d\omega} = |f^{(1)}(\theta)|^2,$$

we'll notice that the sign of the potential drops out, because replacing V with $-V$ just adds an overall sign to $f^{(1)}$.

Remark 197. *Note that $f_k^{(1)}(\theta)$ is always real, but by the optical theorem, the imaginary part of $f_k^{(1)}(0)$ (which is zero) should be related to the total scattering cross-section, which seems odd. And the resolution here is that*

$$\sigma = \int d\Omega |f^{(1)}(\theta)|^2$$

is already second-order in V, so we need the second-order Born approximation to get that this is $\frac{4\pi}{k}\text{Im}f^{(2)}(0)$.

Finally, we'll probe a few particular limits. If we now look at the regime where $kb \ll 1$, and we have a small potential $|V|$, this means that we're looking at the limit $q \to 0$. Then we find that $\sin(qr')$ and the $\frac{1}{q}$ in our integral for $f_k^{(1)}$ cancel out, and the phase goes away. So indeed, $f_k^{(1)}$ is an integral over the potential without any q-dependence:

$$f^{(1)}(\theta, \phi) = -\frac{1}{4\pi}\frac{2m}{\hbar^2}\int d^3r'V(\vec{r}'),$$

so the angular dependence drops out as expected. And if we look at the regime where we have large k, we'll make q large and make $\sin(qr')$ oscillate more quickly. So the bulk of the contribution to the integral comes from the parts where $q \lesssim \frac{1}{b}$, and that gives us a formula for k and θ:

$$\sin\frac{\theta}{2} \lesssim \frac{1}{2kb}.$$

In other words, we get a contribution from the range of angles where θ is close to 0 (of order $\frac{1}{kb}$), meaning that little deflection happens.

Example 198

Let's now look at some particular central potentials V and see how they affect the boxed expression for $f_k^{(1)}(\theta)$ above: first, we'll analyze the Gaussian $V(r) = V_0 e^{-\frac{r^2}{2b^2}}$.

In this case, we find that

$$f(\theta) = -\frac{2m}{\hbar^2 q}\int_0^\infty dr\ r\sin(qr)e^{-\frac{r^2}{2b^2}}V_0,$$

and since we know that the Fourier transform of a Gaussian is a Gaussian, we can find that the answer for the amplitude becomes

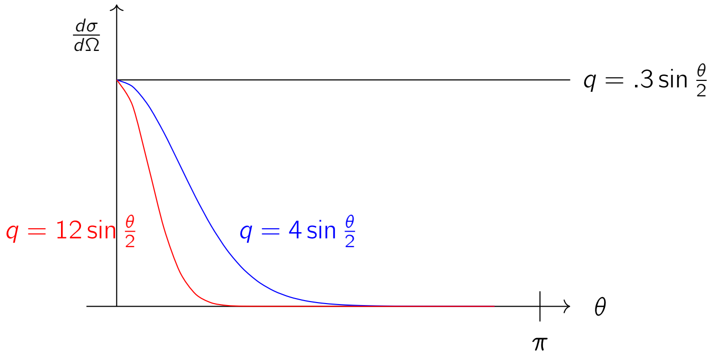
$$= -b\pi^{1/2}\frac{mV_0 b^2}{2\hbar^2}e^{-q^2b^2/2}.$$

(Notice that we're assuming b is small enough so that the $\frac{mV_0b^2}{2\hbar^2}$ term is small, which is where the Born approximation comes into the picture.) We then have

$$\frac{d\sigma}{d\Omega} = \frac{\pi b^2}{4}\left(\frac{mV_0 b^2}{\hbar^2}\right)^2 e^{-q^2b^2}.$$

Then the differential cross-section for a fixed θ as a function of k will be (the right half of a) Gaussian: by the time k is of order $\frac{1}{b}$, it will die off. In other words, once we get past the size of the potential, we don't see any cross-section, so we can get some fundamental information about the potential by scattering particles off of it.

On the other hand, if we fix k and look at the differential cross-section as a function of θ, the answer will depend on how large k is: if k is very small, then q will be small regardless of θ and thus the cross-section is almost uniform in θ. But as k gets larger, we start seeing the Gaussian shape, and the differential cross-section is largest for small θ, as shown below:



Example 199

Finally, we'll consider a finite spherical square well, where $V(r) = \pm V_0$ for $r \le b$ and 0 otherwise.

Plugging things in and doing the integral, since $V(r')$ is constant on the nonzero part, we're basically integrating $r\sin(qr)$ across a finite range, and it turns out that

$$f(\theta) = -\frac{2mV_0}{\hbar^2 q^3}(\sin(qb) - qb\cos(qb)),$$

and we can rewrite this in a similar form as above to get a dimensionless function of q:

$$\frac{d\sigma}{d\Omega} = 4b^2\left(\frac{mV_0b^2}{\hbar^2}\right)^2\frac{(\sin(qb)-qb\cos(qb))^2}{(qb)^6}.$$

We now get oscillatory behavior in the differential cross-section, and there are points where $\frac{d\sigma}{d\Omega} = 0$. So if we vary our energy and look at a fixed angle, we'll see that there will be total transmission at certain values of k and thus no scattering into this particular angle! And that's something that is indeed experimentally observed as well (the Ramsauer-Townsend effect).

48 May 18, 2021

Last time, we discussed the Born approximation, which is a way to do perturbation theory (in the strength of the potential) for scattering. Basically, after defining the rescaled potential U and Green's function G_+, we found that we can write a solution for the wavefunction with appropriate boundary conditions as an infinite series

$$\psi(\vec{r}) = e^{i\vec{k}_i \cdot \vec{r}} + \int d^3\vec{r}_1 G_+(\vec{r} - \vec{r}_1) U(\vec{r}_1) e^{i\vec{k}_i \cdot \vec{r}_1} + \cdots ,$$

where the kth order term has k integrals, k copies of the Green's function, and k copies of the rescaled potentials. Truncating at this first order approximation gives us an amplitude asymptotically as $r \to \infty$ that looks like

$$f_k(\theta, \phi) = -\frac{1}{4\pi} \int d^3\vec{r}_1 e^{-i\vec{k}\cdot\vec{r}_1} U(\vec{r}_1),$$

where $\vec{k}$ is the vector difference between the initial and final momentum. (So we have a Fourier transform of the potential at a particular wavevector $\vec{k}$.)

If we think about what's going on pictorally here, first note that the zeroth order term $e^{i\vec{k}_i\cdot\vec{r}}$ is the incident plane wave (evaluated at some position $\vec{r}$), and the first order term is an integral over the range of the potential. Over this range, we can imagine the plane wave $e^{i\vec{k}_i\cdot\vec{r}_1}$ hitting a point $\vec{r}_1$, and from there we multiply it with the value of the potential $U(\vec{r}_1)$ and also the value of the Green's function (also known as a **propagator**) $G_+(\vec{r} - \vec{r}_1)$. In other words, we can think of a particular point $\vec{r}_1$ as corresponding to **a particle scattering off the particular location $\vec{r}_1$ into $\vec{r}$.**

And with this type of analysis in mind, notice that we can think of the second order term (with two integrals) as hitting the potential at a point $\vec{r}_2$, gaining a factor of $U(\vec{r}_2)$, and then **rescattering to another point in the potential** through the propagator $G_+(\vec{r}_1 - \vec{r}_2)$. We then gain another factor of $U(\vec{r}_1)$ and then rescatter to our final destination with the help of $G_+(\vec{r} - \vec{r}_1)$. So the point is that the kth order term can be geometrically thought of as scattering off of k different points in the potential before reaching the final destination! And this is actually getting us into the beginnings of Feynman diagrams, though we won't keep going in that direction.

Example 200

We can now aim to be more quantitative with our study, understanding when the Born approximation is valid.

First of all, we expect that the first order term should be much smaller than the zeroth order term, so we will compare their magnitudes. Denoting $\psi_0 = e^{i\vec{k}_i\cdot\vec{r}}$ and $\psi_1 = \int d^3\vec{r}_1 G_+(\vec{r} - \vec{r}_1)U(\vec{r}_1)e^{i\vec{k}_i\cdot\vec{r}_1}$, we want $|\psi_1| \ll |\psi_0| = 1$. Since $\psi_1 \approx f_k(\theta, \phi)\frac{e^{ikr}}{r}$ as $r \to \infty$, the term in the denominator shows that $|\psi_1| \ll 1$ in that regime, and the dangerous regime is the one where $\vec{r}$ is inside the potential.

Suppose that the characteristic length scale of the potential is a, and suppose that the typical magnitude of the potential over this range is $|V|$. Then (writing out the Green's function)

$$|\psi_1| = -\frac{1}{4\pi} \int d^3\vec{r}_1 \frac{e^{ik|\vec{r} - \vec{r}_1|}}{|\vec{r} - \vec{r}_1|} U(\vec{r}_1) e^{i\vec{k}_i\cdot\vec{r}_1}.$$

Since this integral is over the range of the potential, we can estimate this as

$$\sim a^3 \cdot \frac{1}{a}|U|.$$

(we might worry that there might be divergence as $\vec{r}_1$ approaches $\vec{r}$, but the volume element cancels that out). So our condition is that

$$|U|a^2 = \frac{2m|V|a^2}{\hbar^2} \ll 1 \implies \boxed{|V| \ll \frac{\hbar^2}{ma^2}}.$$

This is the weak-potential condition, and we may remember it from the study of attractive potentials: if we have an attractive potential with depth $|V|$ and width a, then this condition is the condition (in three dimensions) that guarantees that we have no bound states.

But we know that the Born approximation is supposed to tell us about scattering states, so we need to look more carefully to understand why bound states are relevant. Basically, at $V = 0$, we only see scattering states, but once we get to a deep enough well, we suddenly see a bound state appearing! So this is non-analytic behavior, and in particular it will not be picked up by perturbation theory. So we need to make sure bound states do not appear for the Born approximation to make sense. (And to get this to apply for repulsive potentials, the argument is that the radius of convergence is the same whether we have negative or positive coefficients.)

But there's another situation where we can make more flexible approximations – when the particle has high energy, it is not affected very much by the potential, so the effect is also weak. If we consider the limit where $ka \gg 1$, then we can instead have

$$\boxed{|V| \ll \frac{\hbar^2}{ma^2}(ka)}$$

(so the factor of ka allows for our potential to be larger). The reason for this is that the phase term $e^{ik|\vec{r}-\vec{r}_1|}$ **oscillates quickly** when k is sufficiently large, and that washes out most of the contributions of the integral.

This concludes our discussion of scattering, and we'll now move to the final topic of the course, which is **identical particles**. This is a particularly important topic in lots of fields of modern physics, and it comes up whenever our system has more than one particle.

Definition 201

Two particles are identical if there are no experiments that can be done to distinguish their intrinsic properties, like spin, charge, and magnetic moment.

Example 202

As far as we know, all electrons are identical, and so are protons and neutrons (even though the latter two are not elementary particles). Similarly, hydrogen atoms are identical (even though they can be in different states at a particular time, those states can be realized by both atoms). But a proton and neutron are not identical.

In classical mechanics, if we have multiple electrons, we will often label them and call one "electron 1" and another "electron 2," and we can then write down a classical Hamiltonian which satisfies $H(\vec{r}_1, \vec{p}_1, \vec{r}_2, \vec{p}_2) = H(\vec{r}_2, \vec{p}_2, \vec{r}_1, \vec{p}_1)$. And if we shoot two electrons at each other and they scatter off of each other, their trajectories will be defined at every point in time, so we can track which electron is which.

But in quantum mechanics, if we imagine scattering two indistinguishable particles at each other and detecting particles at two outgoing detectors, we cannot answer the question of "which particle hit which detector," because there is no well-defined notion of a trajectory (we can't measure their positions during the scattering because that would collapse the wavefunction). So we need to be more explicit about how to define quantum states of several particles.

We know that if our particles are **distinguishable**, we can describe them using tensor product spaces: letting V_1 be the Hilbert space of particle 1 and V_2 be the Hilbert space of particle 2, the total Hilbert space will be the tensor product $V = V_1 \otimes V_2$. In particular, if V_1 is spanned by $\{|u_i\rangle\}$ and V_2 is spanned by $\{|v_j\rangle\}$, then V will be spanned by the vectors $\{|u_i\rangle \otimes |v_j\rangle\}$. (We sometimes put subscripts 1 and 2 on $|u_i\rangle$ and $|v_j\rangle$, respectively, to indicate that they correspond to the first and second particles.)

But suppose we have two **indistinguishable** particles – for simplicity, suppose we have two electrons, and we'll just focus on the spin states here for simplicity. Then each particle can be in the $|+, z\rangle$ or $|-, z\rangle$ state, and together the two electrons can either be in the $|+\rangle_1 \otimes |+\rangle_2$ state (both up), $|-\rangle_1 \otimes |-\rangle_2$ state both down), or in a state where one is up and one is down.

For this last state, it seems that we can either use $|+\rangle_1 \otimes |-\rangle_2$ or $|-\rangle_1 \otimes |+\rangle_2$, but the two particles are identical (so making a choice of one or the other is odd). It makes sense to try to identify the two states, but we run into trouble if we try to do that – instead, the answer is that we must use **symmetric and antisymmetric states**

$$|S\rangle = \frac{1}{\sqrt{2}}(|+\rangle_1 \otimes |-\rangle_2 + |-\rangle_1 \otimes |+\rangle_2), \quad |A\rangle = \frac{1}{\sqrt{2}}(|+\rangle_1 \otimes |-\rangle_2 - |-\rangle_1 \otimes |+\rangle_2).$$

It turns out that if we have **bosons**, then $|S\rangle$ is the correct combination to use, and if we have **fermions**, then $|A\rangle$ is the correct one.

More generally, let's say that we have two identical particles, and for each particle, we have the Hilbert space V spanned by an orthonormal basis $\{|i\rangle\}$. The two-particle Hilbert space then lives in $V \otimes V$, but we have to put further constraints when we have identical particles.

Definition 203

The **permutation operator** P_{12} is defined by its action on basis states of $V \otimes V$:

$$P_{12} |i\rangle_1 \otimes |j\rangle_2 = |j\rangle_1 \otimes |i\rangle_2 .$$

Proposition 204

For bosons, our wavefunction $|\psi\rangle$ for the two identical particles must satisfy $P_{12} |\psi\rangle = |\psi\rangle$, and for fermions, our wavefunction must satisfy $P_{12} |\psi\rangle = - |\psi\rangle$.

If we denote the spaces satisfying those conditions as the **symmetric subspace** V_S and the **antisymmetric subspace** V_A, it turns out that $V \otimes V = V_S \oplus V_A$ for two particles, but this will not hold more generally for more than two particles. The space V_S (for bosons) is spanned by the states $|i\rangle_1 \otimes |j\rangle_2 + |j\rangle_1 \otimes |i\rangle_2$, and normalizing for different values of i, j gives us

$$|i\rangle_1 \otimes |i\rangle_2 , \quad \frac{1}{\sqrt{2}}(|i\rangle_1 \otimes |j\rangle_2 + |j\rangle_1 \otimes |i\rangle_2), \quad i \neq j.$$

On the other hand, the space V_A (for fermions) is spanned by

$$\frac{1}{\sqrt{2}}(|i\rangle_1 \otimes |j\rangle_2 - |j\rangle_1 \otimes |i\rangle_2), \quad i \neq j,$$

this time noting that we can't set $i = j$ because that gives us a state of zero. So this leads us to the **Pauli exclusion principle**: two fermions cannot be in the same state because of this permutation operator.

If we now return to the case of two spin 1/2 particles, we have a basis (dropping tensor product symbols)

$$\left\{|+\rangle_1 |+\rangle_2 , \frac{1}{\sqrt{2}}(|+\rangle_1 |-\rangle_2 + |-\rangle_1 |+\rangle_2), |-\rangle_1 |-\rangle_2\right\}$$

for bosons, and a basis of just one element

$$\left\{\frac{1}{\sqrt{2}}(|+\rangle_1 |-\rangle_2 - |-\rangle_1 |+\rangle_2)\right\}$$

for fermions. (So if we have two electrons with the same spatial wavefunction, they can't both be spin up.)

Fact 205

In nonrelativistic physics, there is no indication of which particles should be bosons or fermions. But quantum field theory gives us the **spin statistics theorem** in three spatial dimensions, which tells us that particles with integer spin (like pions and the W and Z bosons) are bosons, and particles with half-integer spins (like electrons, protons, and neutrons) are fermions.

In particular, notice that a hydrogen atom is a boson because it has a proton and an electron (so integer total spin), and some isotopes of helium are bosons while others are fermions because of the number of neutrons.

Suppose now that we have N particles, so that our wavefunctions live in the tensor product space $V \otimes V \otimes \cdots \otimes V$. We can then label our states as

$$|i_1\rangle_1 |i_2\rangle_2 \cdots |i_N\rangle_N ,$$

and again we have an additional constraint on our states:

Definition 206

The transposition operator $P_{(\ell m)}$ is defined by its action on basis states:

$$P_{(\ell m)} |i_1\rangle_1 |i_2\rangle_2 \cdots |i_\ell\rangle_\ell \cdots |i_m\rangle_m \cdots |i_N\rangle_N = |i_1\rangle_1 |i_2\rangle_2 \cdots |i_m\rangle_\ell \cdots |i_\ell\rangle_m \cdots |i_N\rangle_N .$$

Much like before, we now require

$$P_{(\ell m)} |\psi\rangle = \pm |\psi\rangle \qquad \text{for all } m \neq \ell,$$

where we require the positive sign for bosons and the negative sign for fermions, and we similarly define the symmetric and antisymmetric subspaces here. And this time, we build a basis for these subspaces by thinking about the structure of permutations.

Definition 207

A **permutation** $\alpha \in S_n$ is a bijection $\alpha : \{1, 2, \cdots, n\} \to \{1, 2, \cdots, n\}$, meaning that $\alpha(i) \neq \alpha(j)$ for $i \neq j$.

For example, there are 6 different permutations for $n = 3$, which we can represent as 123 (identity), 213 (swapping 1 and 2), 132 (swapping 2 and 3), 321 (swapping 1 and 3), and 231 and 312 (cyclic shifts). More generally, there are $n!$ permutations for permutations on n elements. The idea is that we can build a bosonic state by symmetrizing one of our initial unconstrained states: if we have N particles, then

$$|\psi\rangle_B = \sum_{\alpha \in S_N} \left|i_{\alpha(1)}\right\rangle_1 \left|i_{\alpha(2)}\right\rangle_2 \cdots \left|i_{\alpha(N)}\right\rangle_N .$$

We'll discuss this more next time!

49 May 19, 2021 (Recitation)

We'll discuss identical particles today: the idea is that indistinguishable particles (such as two electrons) behave in a way so that swapping them keeps probabilities the same: letting α_1, α_2 be quantum numbers of the "first" and "second" particle,

$$dV_1 dV_2 |\psi(\alpha_1, \alpha_2)|^2 = dV_1 dV_2 |\psi(\alpha_2, \alpha_1)|^2,$$

which means that $\psi(\alpha_1, \alpha_2)$ and $\psi(\alpha_2, \alpha_1)$ can only differ by a phase $e^{i\delta}$. But we can swap twice and get back to where we started, so that

$$\psi(\alpha_1, \alpha_2) = e^{i\delta}\psi(\alpha_2, \alpha_1) = e^{2i\delta}\psi(\alpha_1, \alpha_2),$$

which can only happen if our original phase $e^{i\delta}$ is either 1 or -1. We can formalize this by using the (Hermitian) exchange operator P_{12}, taking $\psi(\alpha_1, \alpha_2)$ to $\psi(\alpha_2, \alpha_1)$: then we have $P_{12}^2 = I$, and $[P_{12}, H] = 0$ (because the Hamiltonian doesn't know which particle is which, meaning it is unchanged by exchange).

So we can think about the simultaneous eigenstates of P_{12} and H, and things are a little deeper in that eigenstates of P_{12} with eigenvalue 1 are **bosons** (giving us a wavefunction symmetric under interchange), and eigenstates with eigenvalue -1 are **fermions** (giving us a wavefunction antisymmetric under interchange). And it turns out that bosons have integer spin, and fermions have half-integer spin – this is something we can prove using relativistic quantum field theory.

If we use the notation $|\alpha, \beta\rangle = |\alpha\rangle_1 \otimes |\beta\rangle_2$, where we have two identical particles indexed by 1 and 2, then we can form the symmetric and antisymmetric wavefunctions

$$\frac{1}{\sqrt{2}}(|\alpha, \beta\rangle + |\beta, \alpha\rangle), \quad \frac{1}{\sqrt{2}}(|\alpha, \beta\rangle - |\beta, \alpha\rangle)$$

for all $\alpha \neq \beta$. And when $\alpha = \beta$, we have the symmetric wavefunction $|\alpha, \alpha\rangle$, but there is no corresponding antisymmetric wavefunction: as we mentioned in lecture, we can't have two identical fermions in the same state, and this is the Pauli exclusion principle.

Example 208

Suppose we have a one-dimensional harmonic oscillator potential, and we have five electrons inside this potential (but with no Coulomb interactions between them).

We know that electrons are spin 1/2 fermions, and so it makes sense to ask about questions like the energy and spin of the ground state and excited states and how the wavefunctions look. First of all, the Hamiltonian looks like

$$H = H_1 + H_2 + H_3 + H_4 + H_5,$$

where H_i is the harmonic oscillator Hamiltonian for the ith particle (assuming no spin-dependence), and we can label our states as $|n_1, n_2, n_3, n_4, n_5\rangle$ where $n_i \geq 0$. Then the energy is

$$E = \left(n_1 + n_2 + n_3 + n_4 + n_5 + \frac{5}{2}\right)\hbar\omega.$$

If we want to find the ground state energy, then we want to minimize the n_is, but we can't throw all of the electrons into the ground state because of the Pauli exclusion principle. Instead, we can fill the ground state with a spin-up and a spin-down electron, then fill the first excited state with a spin-up and a spin-down electron, and finally fill the second excited state with the final electron (so that we have $(n_1, n_2, n_3, n_4, n_5) = (0, 0, 1, 1, 2)$). This gives us an energy of

$E = \left(4 + \frac{5}{2}\right)\hbar\omega = \frac{13}{2}\hbar\omega$, and there is a two-fold degeneracy of the ground state because the final electron can be spin-up or spin-down.

Remark 209. *Note that just writing down the Hamiltonian H above does not uniquely determine our system – we wouldn't need the same constraints if we had bosons instead of fermions. So we need to specify what is in our Hamiltonian too!*

If we now think about the total spin of the ground state, notice that the first and second particles have identical (symmetric) spatial wavefunctions, so the spin wavefunction must be antisymmetric: this gives us an expression

$$\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right),$$

meaning that we get a total spin-0 state. Similarly, the third and fourth particles must be in a spin-0 state that looks as above, because of symmetric spatial wavefunctions. The final (outer) electron then must have $S = \frac{1}{2}$, and thus the ground state is in a state of total spin $S = \frac{1}{2}$.

From here, we can look at the first excited state: we can either raise n_5 from 2 to 3, or we can raise either n_3 or n_4 from 1 to 2, and in either case we get energy $\frac{15}{2}\hbar\omega$. This gives us two possible spin states for $(0, 0, 1, 1, 3)$ and two possible spin states for $(0, 0, 1, 2, 2)$, so there is a four-fold degeneracy at the first excited level.

But one thing we haven't looked at closely yet is the fact that the wavefunction must be **totally** antisymmetric: it must look the same under interchange of any two of the particles, not just those in the same energy level. And the way that we construct this wavefunction is to write as a determinant of the following form:

$$\psi = \frac{1}{\sqrt{5!}} \det \begin{bmatrix} \psi_0^\uparrow(x_1) & \psi_0^\downarrow(x_1) & \psi_1^\uparrow(x_1) & \psi_1^\downarrow(x_1) & \psi_2^s(x_1) \\ \psi_0^\uparrow(x_2) & \psi_0^\downarrow(x_2) & \psi_1^\uparrow(x_2) & \psi_1^\downarrow(x_2) & \psi_2^s(x_2) \\ \psi_0^\uparrow(x_3) & \psi_0^\downarrow(x_3) & \psi_1^\uparrow(x_3) & \psi_1^\downarrow(x_3) & \psi_2^s(x_3) \\ \psi_0^\uparrow(x_4) & \psi_0^\downarrow(x_4) & \psi_1^\uparrow(x_4) & \psi_1^\downarrow(x_4) & \psi_2^s(x_4) \\ \psi_0^\uparrow(x_5) & \psi_0^\downarrow(x_5) & \psi_1^\uparrow(x_5) & \psi_1^\downarrow(x_5) & \psi_2^s(x_5) \end{bmatrix},$$

where s is the spin of our particle with $n = 2$ (either up or down, so there are really two different wavefunctions of this form). Indeed, terms of the determinant always include only one term in each row, and indeed if we swap any two rows we get a negative sign (which is how we enforce the antisymmetry that we want). (This is known as a **Slater determinant**, and we'll talk more about it in lecture.)

We'll now discuss the **exchange force**, explaining how the antisymmetry can be physically enforced.

Example 210

Suppose we have an electron in Boston and an electron in Los Angeles: we want to know if we are required to think of the two electrons as indistinguishable, so that we need to antisymmetrize the wavefunction, and we want to understand what that antisymmetrization does.

If we started with two distinguishable particles, our wavefunction for these two particles would look like

$$\psi_d(x_1, x_2) = \psi_H(x_1)\psi_T(x_2),$$

where ψ_H is localized "here" and ψ_T is localized "there." If our particles become indistinguishable, we then have to look at wavefunctions of the form

$$\psi_\pm(x_1, x_2) = \frac{1}{\sqrt{2}}(\psi_H(x_1)\psi_T(x_2) \pm \psi_H(x_2)\psi_T(x_1)).$$

We'll see what this (anti-)symmetrization does by calculating the expectation value of $(\hat{x}_1 - \hat{x}_2)^2$ in both cases. In the distinguishable case, we have

$$\langle \psi_d | (\hat{x}_1 - \hat{x}_2)^2 | \psi_d \rangle = \int dx_1 dx_2 |\psi_d(x_1, x_2)|^2 (x_1 - x_2)^2,$$

and expanding out the square and noting that ψ_d is a product wavefunction gives us

$$= \left(\int dx_1 x_1^2 |\psi_H(x_1)|^2 \right) \left(\int dx_2 |\psi_T|^2 \right) - 2 \left(\int dx_1 x_1 |\psi_H(x_1)|^2 \right) \left(\int dx_2 x_2 |\psi_T|^2 \right) + \left(\int dx_1 |\psi_H(x_1)|^2 \right) \left(\int dx_2 x_2^2 |\psi_T|^2 \right),$$

and this simplifies to

$$= \langle x^2 \rangle_H + \langle x^2 \rangle_T - 2 \langle x \rangle_H \langle x \rangle_T.$$

But now if we instead use the $\psi_\pm$ states and find the expectation value, we find that (through a very similar calculation for each of the two terms)

$$\langle \psi_\pm | (\hat{x}_1 - \hat{x}_2)^2 | \psi_\pm \rangle = \langle x^2 \rangle_H + \langle x^2 \rangle_T - 2 \langle x \rangle_H \langle x \rangle_T \mp 2 \langle \psi_H | x | \psi_T \rangle \langle \psi_T | x | \psi_H \rangle .$$

In other words, we end up with an extra term which we can think of as an off-diagonal term $\mp 2 |\langle x \rangle_{HT}|^2$ of the matrix, and it's what we call the **exchange force**. This tells us then that the symmetric version ψ_+ has particles that tend to be closer together than distinguishable, and the antisymmetric version ψ_- has particles that tend to be farther apart.

But if we imagine our electrons that are in Boston and Los Angeles, respectively, the contribution of this exchange force will be very small:

$$\langle \psi_H | x | \psi_T \rangle = \int dx \psi_H^*(x) x \psi_T(x),$$

and if the electron wavefunctions are localized far apart, the effect will be negligibly small.

We'll close with a few facts that are useful to keep in mind:

Fact 211

Goldhaber's experiment tried to find out whether β-particles (coming from β-decay) are actually electrons. He did this by having particles bounce off of lead and looking at whether there were outgoing electrons that came from particles that went into the ground state.

Fact 212

The Δ^{++} particle has spin $\frac{3}{2}$ and is formed by three up-quarks (each spin 1/2 fermions). Then the ground state of Δ^{++} is spin-symmetric and also spatially-symmetric, but we know that Δ^{++} must be anti-symmetrizable. And that's what lead to the discovery of a new quantum number, which we call **color**.

Fact 213

The hydrogen molecule's rotation states can be classified by the $Y_{\ell,m}$s of the particles and also by the spin state. If we imagine a rotational mode of this hydrogen molecule and we attempt to do the antisymmetrization procedure, it turns out that for even ℓ we have a spatially even wavefunction and $S = 0$, and for odd ℓ we have a spatially odd wavefunction and $S = 1$. So there are two types of (stable) hydrogen gas with different spins, and this is what we call "ortho hydrogen" and "para hydrogen."

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We started talking about identical particles last time, thinking about the wavefunction when we have N such particles. The setup is to write the Hilbert space of a single particle V as being spanned by some orthonormal basis $|i\rangle$, so that the N-particle Hilbert space is $V \otimes V \otimes \cdots \otimes V$. If we then define the transposition operator $P_{(\ell m)}$ which swaps the states for the ℓth and mth particle, we require that our wavefunction is an eigenstate of $P_{(\ell m)}$ for all $\ell \neq m$, with eigenvalue 1 for bosons and -1 for fermions. (So the wavefunction $|\psi\rangle$ lives in the **symmetric subspace** for bosons and **antisymmetric subspace** for fermions.)

At the end of the last lecture, we noted that if we want to construct a symmetric version of a state $|i_1\rangle_1 |i_2\rangle_2 \cdots |i_N\rangle_N$, we can consider all permutations of $\{1, \cdots, N\}$ (there are $N!$ of them). The bosonic state can then be written as

$$|\psi\rangle_B = \sum_{\alpha \in S_N} \left|i_{\alpha(1)}\right\rangle_1 \left|i_{\alpha(2)}\right\rangle_2 \cdots \left|i_{\alpha(N)}\right\rangle_N .$$

Indeed, summing over all permutations means that we have $P_{(\ell m)} |\psi\rangle_B = |\psi\rangle_B$ (because the set of permutations forms a group).

Example 214

With $N = 3$, there are 6 permutations. If we start with a state $|i_1\rangle_1 |i_2\rangle_2 |i_3\rangle_3$, then we have the bosonic state

$$|\psi\rangle_B = |i_1\rangle_1 |i_2\rangle_2 |i_3\rangle_3 + |i_2\rangle_1 |i_1\rangle_2 |i_3\rangle_3 + |i_1\rangle_1 |i_3\rangle_2 |i_2\rangle_3 + |i_3\rangle_1 |i_2\rangle_2 |i_1\rangle_3 + |i_2\rangle_1 |i_3\rangle_2 |i_1\rangle_3 + |i_3\rangle_1 |i_1\rangle_2 |i_2\rangle_3 .$$

Note that the normalization factor can be slightly different depending on the values of i_1, i_2, i_3: if they are all distinct, then all $N!$ terms here are orthogonal, and thus our normalization factor is $\frac{1}{\sqrt{N!}}$. But things can look a little different if some of those state labels are the same.

But for fermions, we know that we want a negative sign coming out of transposition, so it turns out that basis states for the antisymmetric subspace will take a similar form but with some additional factors of -1.

Definition 215

Let $\alpha \in S_N$ be a permutation. The **sign** of α, denoted $\text{sgn}(\alpha)$, is defined as follows: if we can write α as a product (composition) of k transpositions, then it turns out k's parity is well-defined. We then let $\text{sgn}(\alpha) = (-1)^k$.

Example 216

For the case $N = 3$, the permutation 123 (identity) has sign 1, the permutations 213, 132, 321 (one transposition) have sign -1, and the permutations 231, 312 (cyclic) can be written as the product of transpositions (12)(23) and (23)(12), respectively, so they have sign 1.

It's important to note that we evaluate something like (12)(23) from right to left: for example, we can check that 2 gets sent to 3, because the transposition (23) sends 2 to 3 and then (12) keeps 3 where it is.

We can now define the fermionic state to be

$$|\psi\rangle_F = \sum_{\alpha \in S_N} \text{sgn}(\alpha) \left|i_{\alpha(1)}\right\rangle_1 \left|i_{\alpha(2)}\right\rangle_2 \cdots \left|i_{\alpha(N)}\right\rangle_N .$$

Indeed, acting by $P_{(\ell m)} |\psi\rangle_F$ will indeed give us an additional minus sign in $|\psi\rangle_F$, because we're essentially "adding one transposition" to each of our permutations. For the $N = 3$ case we've been explicitly analyzing, the fermionic state will look like

$$|\psi\rangle_B = |i_1\rangle_1 |i_2\rangle_2 |i_3\rangle_3 - |i_2\rangle_1 |i_1\rangle_2 |i_3\rangle_3 - |i_1\rangle_1 |i_3\rangle_2 |i_2\rangle_3 - |i_3\rangle_1 |i_2\rangle_2 |i_1\rangle_3 + |i_2\rangle_1 |i_3\rangle_2 |i_1\rangle_3 + |i_3\rangle_1 |i_1\rangle_2 |i_2\rangle_3 .$$

And in this case, we cannot have two of the state labels equal at all: if we let $i_1 = i_2$, then pairs of terms will cancel out with each other (specifically those which only differ by the transposition $P_{(12)}$), and we're left with the state 0, which is not valid. So the Pauli exclusion principle does show up as we expect, and this means that we will always have a normalization factor of $\frac{1}{\sqrt{N!}}$ because the $N!$ terms here are all orthonormal.

So far, we've been dealing only with countable bases, but we may also want to ask about situations like position-space wavefunctions with an uncountable basis. Our Hilbert space for single-particle wavefunctions is then $V = L^2(\mathbb{R}^3)$, and we can write our single-particle wavefunctions as $\psi(\vec{r})$, so that our N-particle wavefunctions look like

$$\psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N).$$

The constraint that we need to put on our wavefunction is then

$$\psi(\vec{r}_1, \cdots, \vec{r}_\ell, \cdots, \vec{r}_m, \cdots, \vec{r}_N) = \pm\psi(\vec{r}_1, \cdots, \vec{r}_m, \cdots, \vec{r}_\ell, \cdots, \vec{r}_N)$$

with ± depending on whether we have bosons or fermions. This time, if we work in a basis $\phi_m(\vec{r})$ where m labels our states, then we can replace our $|m_1\rangle_1 |m_2\rangle_2 \cdots |m_N\rangle_N$ notation with

$$\psi(\vec{r}_1, \cdots, \vec{r}_N) = \phi_{m_1}(\vec{r}_1)\phi_{m_2}(\vec{r}_2)\cdots\phi_{m_N}(\vec{r}_N).$$

And similarly to before, bosonic wavefunctions will be

$$\psi_B(\vec{r}_1, \cdots, \vec{r}_N) = \sum_{\alpha\in S_N} \phi_{m_{\alpha(1)}}(\vec{r}_1)\phi_{m_{\alpha(2)}}(\vec{r}_2)\cdots\phi_{m_{\alpha(N)}}(\vec{r}_N).$$

(We can also check that we can equivalently permute the $\vec{r}_i$s instead of the labels m_i, since we're summing over all permutations.) Our fermionic states again also just give us some additional factors of -1:

$$\psi_F(\vec{r}_1, \cdots, \vec{r}_N) = \sum_{\alpha\in S_N} \text{sgn}(\alpha)\phi_{m_{\alpha(1)}}(\vec{r}_1)\phi_{m_{\alpha(2)}}(\vec{r}_2)\cdots\phi_{m_{\alpha(N)}}(\vec{r}_N).$$

We can write this last wavefunction in a more compact manner as well: if we define an $N\times N$ matrix A via $A_{ij} = \phi_{m_i}(\vec{r}_j)$, meaning that

$$A = \begin{bmatrix} \phi_{m_1}(\vec{r}_1) & \phi_{m_1}(\vec{r}_2) & \cdots & \phi_{m_1}(\vec{r}_N) \\ \phi_{m_2}(\vec{r}_1) & \phi_{m_2}(\vec{r}_2) & \cdots & \phi_{m_2}(\vec{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{m_N}(\vec{r}_1) & \phi_{m_N}(\vec{r}_2) & \cdots & \phi_{m_N}(\vec{r}_N) \end{bmatrix},$$

then the fermionic wavefunction ψ_F is actually just the determinant of A (because the formula for the determinant also has us summing over permutations $A_{\alpha(i),i}$ with an additional $\text{sgn}(\alpha)$ factor in front). This is known as a **Slater determinant** (as mentioned in recitation), and it turns out that the **permanent** of A (which is like the determinant but without the sign factors) gives us the bosonic wavefunction as well.

More generally, particles can have both a position and a spin, and thus the Hilbert space for a single particle is

$$V = L^2(\mathbb{R}^3) \otimes \mathbb{C}^{2s+1},$$

where $\mathbb{C}^{2s+1}$ is the span of the $(2s+1)$ possible states for a spin s particle, $\{|\sigma\rangle : \sigma = -s, -s+1, \cdots, s-1s\}$. Our single-particle wavefunction then generally looks like

$$|\psi\rangle_{\text{particle}} = \sum_\sigma \psi_\sigma(\vec{r})\,|\sigma\rangle\,.$$

(For example, for a spin 1/2 particle, our system can be in the up state or the down state, so $|\psi\rangle = \psi(\vec{r},+)\,|+\rangle + \psi(\vec{r},-)\,|-\rangle$.) Therefore, states for the N-particle wavefunction can be written

$$|\psi\rangle_N = \sum_{\sigma_1,\cdots,\sigma_N} \psi(\vec{r}_1,\sigma_1;\vec{r}_2,\sigma_2;\cdots;\vec{r}_N,\sigma_n)\,|\sigma_1\rangle_1\,|\sigma_2\rangle_2\cdots|\sigma_N\rangle_N\,.$$

We now have symmetry or antisymmetry conditions, and the idea is that we must have

$$\psi(\vec{r}_1,\sigma_1;\cdots;\vec{r}_\ell,\sigma_\ell;\cdots;\vec{r}_m,\sigma_m;\cdots\vec{r}_N,\sigma_n) = \pm\psi(\vec{r}_1,\sigma_1;\cdots;\vec{r}_m,\sigma_m;\cdots;\vec{r}_\ell,\sigma_\ell;\cdots\vec{r}_N,\sigma_n)$$

for the position part of the wavefunction. But because we have both a spin and a position part, we can't immediately say something about the ± sign here.

Example 217

We'll look at the special case where we have two particles of spin 1/2.

In this situation, we can always decompose the spin wavefunction into symmetric states of the form

$$|\psi\rangle = \psi_+(\vec{r}_1,\vec{r}_2))\begin{cases}|+\rangle_1\,|+\rangle_2\\ \frac{1}{\sqrt{2}}(|+\rangle_1\,|-\rangle_2 + |-\rangle_1\,|+\rangle_2\\ |-\rangle_1\,|-\rangle_2\end{cases}$$

or the antisymmetric state

$$|\psi\rangle = \phi_-(\vec{r}_1,\vec{r}_2)\frac{1}{\sqrt{2}}(|+\rangle_1\,|-\rangle_2 - |-\rangle_1\,|+\rangle_2).$$

So now if we have fermions, then the combined wavefunction must be antisymmetric. Therefore, $\phi_+(\vec{r}_1,\vec{r}_2)$ must be **antisymmetric**, while $\phi_-(\vec{r}_1,\vec{r}_2)$ must be **symmetric**, because the corresponding spin parts are symmetric and antisymmetric, respectively. And if we have bosons, we must have ϕ_+,ϕ_- being symmetric and antisymmetric, respectively.

We'll now discuss a more economical way of representing these symmetric and antisymmetric states using **occupation numbers**. The idea is that if we have bosons and start in a state $|i_1\rangle_1\,|i_2\rangle_2\cdots|i_N\rangle_N$, then $|\psi\rangle_B$ and $|\psi\rangle_F$ essentially sum over permutations of those labels, and the same number of is will be present in each of those terms. So we can just specify how many $|1\rangle$s, $|2\rangle$s, $|3\rangle$s, and other states show up in our original $|i_1\rangle_1\,|i_2\rangle_2\cdots|i_N\rangle_N$: letting n_i be the number of particles in single-particle state i, we get the representation in the **number basis**

$$|\psi\rangle = |n_1,n_2,n_3,\cdots\rangle\,,$$

where $n_i \in \mathbb{Z}_{\geq 0}$ for bosons and $n_i \in \{0,1\}$ for fermions.

Example 218

Consider a Hilbert space for a single particle spanned by $|+\rangle$ and $|-\rangle$ (ignore spatial components, and pretend that this is valid for both bosons and fermions).

We described above that there are three symmetric basis wavefunctions for bosons, and they correspond to occupation numbers via

$$\begin{cases} |+\rangle_1 |+\rangle_2 & = |n_+ = 2, n_- = 0\rangle \,, \\ \frac{1}{\sqrt{2}}(|+\rangle_1 |-\rangle_2 + |-\rangle_1 |+\rangle_2 & = |n_+ = 1, n_- = 1\rangle \,, \\ |-\rangle_1 |-\rangle_2 & = |n_+ = 0, n_- = 2\rangle \,. \end{cases}$$

On the other hand, the only antisymmetric basis state is

$$\frac{1}{\sqrt{2}}(|+\rangle_1 |-\rangle_2 - |-\rangle_1 |+\rangle_2) = |n_+ = 1, n_- = 1\rangle \,.$$

(Note that the number basis is only defined within either the symmetric or antisymmetric basis, so there is no ambiguity between the two $|n_+ = 1, n_- = 1\rangle$s since we need to specify our subspace first.) This kind of notation is particularly useful when we have many particles, and it's cleaner conceptually because we know that the total sum of the numbers should always be N.

Remark 219. *Note that $|n+ = 1, n_- = 1\rangle$ can represent either $\frac{1}{\sqrt{2}}(|+\rangle_1 |-\rangle_2 - |-\rangle_1 |+\rangle_2)$ or $\frac{1}{\sqrt{2}}(|-\rangle_1 |+\rangle_2 - |+\rangle_1 |-\rangle_2)$ – this gives us an overall phase factor, and we need a convention for it. What we usually do is to order our single-particle states and choose the sign so that we have a coefficient of 1 in front of the one where $i_1 \le i_2 \le \cdots \le i_n$.*

We can now turn to a discussion of operators acting on these Hilbert spaces and how obserables behave. Because our setup can't distinguish between particles, the observables also shouldn't be able to do so, meaning that any observable A must satisfy $[A, P_{(\ell m)}] = 0$. In particular, we must have $[H, P_{(\ell m)}] = 0$.

Example 220

Suppose that we have a Hamiltonian of the form $H = \frac{\vec{p}_1^2}{2m} + \frac{\vec{p}_2^2}{2m} + U(\vec{r}_1) + U(\vec{r}_2) + V(\vec{r}_1 - \vec{r}_2)$. Then we have $[H, P_{12}] = 0$ as long as $V(\vec{r}) = V(-\vec{r})$.

More generally, if we have $H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \sum_{i=1}^N U(\vec{r}_i) + \sum_{i<j} V(\vec{r}_i - \vec{r}_j)$ (which describes a system of electrons in an atom or a solid), the easiest situation for us is when the particles do not interact at all, meaning that we can write

$$H = \sum_{i=1}^N H_{\text{sp}}^{(i)}$$

where $H_{\text{sp}}^{(i)} = I \otimes I \otimes \cdots \otimes H_{\text{sp}} \otimes \cdots \otimes I$ only acts on the ith particle. Then if the spectrum of H_{sp} can be described as

$$H_{\text{sp}} |m\rangle = E_m |m\rangle \,, \quad m \in \mathbb{Z}_+,$$

then eigenstates of the multiparticle Hamiltonian will look like

$$|\psi\rangle = |m_1\rangle_1 |m_2\rangle_2 \cdots |m_N\rangle_N \,, \quad E = E_{m_1} + \cdots + E_{m_N}.$$

If we now consider this state along with all of its permutations, all of those states will be eigenstates with the same energy, and thus the superposition will also be a superposition with said energy E. So this is how we can find bosonic and fermionic states for a non-interacting H: we symmetrize or antisymmetrize accordingly as we've already done. And just like before, we can use the occupation number representation using the single-particle eigenstates as basis: if it looks like $|n_1, n_2, n_3, \cdots\rangle$, then the energy of our eigenstate is

$$E_{n_1, n_2, n_3, \cdots} = \sum_i E_i n_i.$$

Finding the ground states of this system now depends on whether we have bosons or fermions: if we have bosons, we can just put all N of the particles into the ground state, and our energy is just N times the energy of the single-particle ground state (and this leads us to Bose-Einstein condensation). But if we have fermions, we can only have one particle per state, and thus the ground state in the number basis is $|1, 1, 1, 1, \cdots, 1, 0, 0, \cdots\rangle$.

And we can use this to explain the structure of atoms – ignoring the Coulomb repulsion between electrons and thinking of them as N independent particles, each electron has the Coulomb energy levels $E_m = -Z^2 \frac{13.6 \text{ eV}}{m^2}$, meaning that they can be in any of the $1s, 2s, 2p, \cdots$ states. But then we fill in electrons from lowest to highest energy: each of these levels can be doubly degenerate because the electron can have spin up or down. That's why the first shell has 2 electrons, the second has $2 + 6 = 8$ electrons, and so on! (The Coulomb repulsion will modify this, but the main features still remain.)