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1 Lecture 1: Blackbody Radiation

1.1 What is Physics?

Why do we need quantum mechanics? **The older (classical) theory was wrong!**

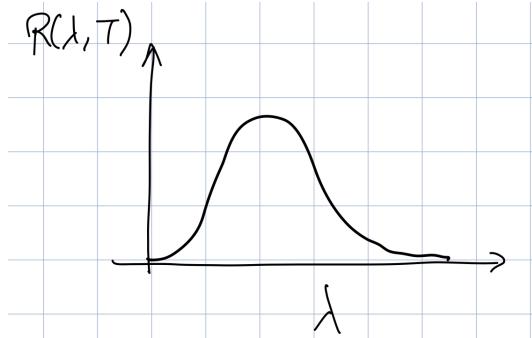
Physics doesn't tell you "why" things work—it tells you "how" things work. The reality is not observable, quantum mechanics "describes" observations rather than helping you "understand" some. By throwing away our philosophical concerns, we instead directly study the mathematics.

1.2 The Potter's Problem: Blackbody Radiation

Take a cube of some solid and heat it up to some temperature T . When you do this, it emits light (it glows). For a long time, no one knew how this phenomenon worked. Here are some observations through the ages:

- 1792: Wedgwood notes that all objects (at a certain T) glow the same color.
- 1800s: With improvements in spectroscopy, we can now measure the frequency content of light.
- 1859: Kirchoff proposes a model. R is the "emissive power/area", λ is wavelength of the light and T is the temperature.

$$R(\lambda, T)$$



The idea is that there are multiple collisions between the walls and the radiation field. The blackbody (as a perfect absorber) is absorbing all light at all frequencies. It looks something like this. The left side is near 0 because you have no wave at that wavelength. The right side must be bounded because we want total emissive power to be finite (or do we?).

- 1879: Stefan's Law

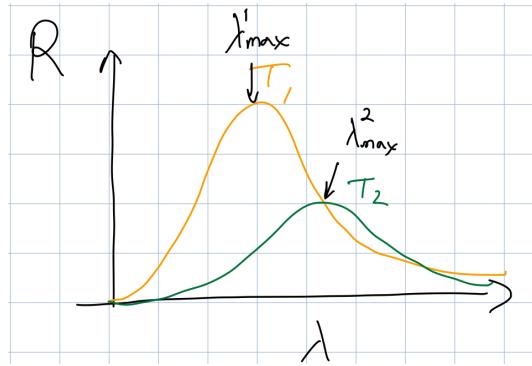
$$\int_0^{\infty} R(\lambda, T) d\lambda = \sigma T^4$$

i.e. the total radiation emitted is proportional to T^4 , which $\sigma \approx 5.67 \times 10^{-8} \frac{W}{m^2 K^4}$

- ??: Wien's Law

$$\lambda_{max} T \approx 2.898 \times 10^{-3} m \cdot K$$

i.e. these curves all have the same constant for the quantity. For example, in the following graph, $T_1 > T_2$.



- ????: Rayleigh-Jeans Law

$$R(\lambda, T) \propto \frac{8\pi k_B T}{\lambda^4}$$

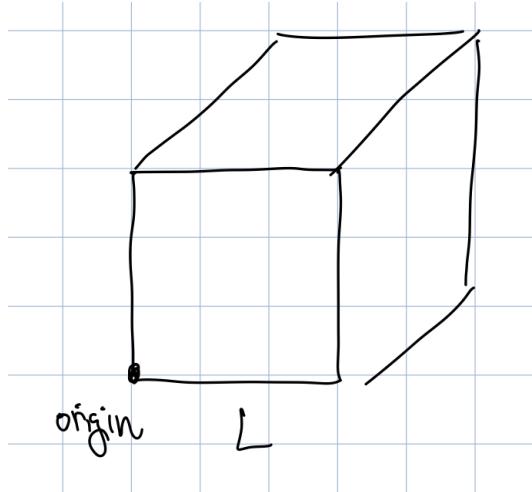
which only works at longer frequencies (the area is unbounded). The original derivation was similar to many observations in astronomy (guess a power law and add fudge factors).

1.3 A Formal Derivation

Let's derive the last law using thermodynamic principles and waves. We will analyze the energy density that the light trapped in the solid produces. The energy of a light wave increases with frequency, which in turn is proportional to the number of wave modes. In other words:

$$\text{Energy} = \text{Number of modes} \times \text{Energy per mode}$$

Suppose our blackbody is a cube of length L .



Let's find the waves that are stable in the cube. First, we write the wave equation.

$$\nabla^2 \Psi(\mathbf{r}, t) = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \Psi(\mathbf{r}, t)$$

where

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

In addition, we need boundary conditions—consider a standing wave in 1-d. At the ends it is fixed at 0. For 3-d this is:

$$\begin{aligned}\Psi(x = 0, y, z, t) &= \Psi(x = L, y, z, t) = 0, \forall y, z, t \\ \Psi(x, y = 0, z, t) &= \Psi(x, y = L, z, t) = 0, \forall x, z, t \\ \Psi(x, y, z = 0, t) &= \Psi(x, y, z = L, t) = 0, \forall x, y, t\end{aligned}$$

The solution is:

$$\Psi(\mathbf{r}, t) = A(t) \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

where $k_i = \frac{n_i \pi}{L}$ for $n_i \in \mathbb{N}$. n_i is the number of nodes along the i th axis. Each tuple of n_i is a valid mode (configuration) of the wave.

This looks like:

$$\Psi(\mathbf{r}, t) = A(t) B(x, y, z)$$

So we are modulating the space component of the wave with some $A(t)$ that changes over the time. This is true for any standing wave.

2 Lecture 2: Blackbody Radiation

2.1 Formal Blackbody Radiation, continued

To use our DE solution, we need a few partials:

$$\begin{aligned}\nabla^2 \Psi(\mathbf{r}, t) &= \left(A(t) \sin(k_y y) \sin(k_z z) \frac{\partial^2 \sin(k_x x)}{\partial x^2} \right) + \dots \\ &= -k_x^2 (A(t) \sin(k_x x) \sin(k_y y) \sin(k_z z)) + \dots \\ &= -\left(n_x^2 + n_y^2 + n_z^2\right) \frac{\pi^2}{L^2} A(t) B(x, y, z)\end{aligned}$$

Another one, letting $A(t) = A_0 \cos \omega t + \phi$.

$$\frac{\partial^2 \Psi(\mathbf{r}, t)}{\partial t^2} = -\omega^2 A(t) B(x, y, z)$$

Let's plug our solution back into the wave equation.

$$\begin{aligned}\nabla^2 \Psi(x, y, z, t) &= \frac{1}{c^2} \frac{\partial^2 \Psi(x, y, z, t)}{\partial t^2} \\ -\left(n_x^2 + n_y^2 + n_z^2\right) \frac{\pi^2}{L^2} A(t) B(x, y, z) &= \frac{-\omega^2}{c^2} A(t) B(x, y, z) \\ \omega^2 &= \frac{c^2 \pi^2}{L^2} \left(n_x^2 + n_y^2 + n_z^2\right)\end{aligned}$$

This equation relates the angular frequency of the wave to its mode configurations. To find the number of modes for a given wavelength we define notion of density of states:

$$g(\omega) = \frac{dN(\omega)}{d\omega}$$

We choose to work with densities since ω is a continuous quantity. Differentiating both sides yields:

$$N(\omega) = \int_0^\omega g(\omega) d\omega$$

This quantity will encapsulate all (n_x, n_y, n_z) such that:

$$n_x^2 + n_y^2 + n_z^2 \leq \frac{\omega^2 L^2}{c^2 \pi^2}$$

(because we are looking at frequencies less than ω). Note that this looks like a sphere equation (with $n_i \geq 0$). The volume of this first octant is

$$N(\omega) = \frac{1}{8} \left(\frac{4}{3} \pi \frac{\omega^3 L^3}{c^3 \pi^3} \right) = \frac{\omega^3 L^3}{6 c^3 \pi^3}$$

Let $V = L^3$ be the volume of the blackbody. Converting from angular to linear frequency:

$$\begin{aligned}N(f) &= \frac{(2\pi f)^3 V}{6 c^3 \pi^2} = \frac{4\pi f^3 V}{3 c^3} \\ g(f) &= \frac{dN(f)}{df} = \frac{4\pi f^2 V}{c^3}\end{aligned}$$

However, this is slightly incomplete. This assumes a certain polarization of the electric field. However, there are two degrees of freedom in which this field can polarize, so the amount of states is actually double. This means:

$$g(f) = \frac{8\pi f^2 V}{c^3}$$

In classical statistical mechanics, the equipartition each mode of a system is excited with energy equal to $k_B T$ (??), so the total energy for frequency f to $f + df$ is:

$$g(f) df \cdot k_B T = \frac{8\pi}{c^3} f^2 V k_B T df$$

This means the energy density (by volume) is:

$$d\kappa = \frac{8\pi}{c^3} f^2 k_B T df$$

and note since $f = \frac{c}{\lambda}$, $df = -\frac{c}{\lambda^2} d\lambda$ and:

$$\rho(\lambda, T) := \frac{d\kappa}{d\lambda} = \frac{8\pi}{\lambda^4} k_B T$$

where we dropped the negative sign (it just changes the order of integration). Note that our R is proportional to this density (the outward rate is just constant). We have produced the Rayleigh-Jean law (which is inaccurate!).

2.2 The Quantum Calculation

To solve our ultraviolet catastrophe, Planck postulated that light waves cannot have arbitrary energy values. Instead, for a fixed frequency f , he proposed that energy is quantized in discrete packets as

$$E_n = nhf$$

where hf is a quanta and $n \in \mathbb{N}$. He then calculated the expected energy of a wave as:

$$\bar{E} = \sum_{n=0}^{\infty} nhf \frac{\exp\left(-\frac{nhf}{k_B T}\right)}{\sum_{m=0}^{\infty} \exp\left(-\frac{mhf}{k_B T}\right)}$$

where the fraction term is the Boltzmann factor normalized to a probability. Can we simplify this? Let $x = \exp\left(-\frac{hf}{k_B T}\right)$.

$$\begin{aligned} \bar{E} &= hf \sum_{n=0}^{\infty} n \frac{x^n}{\sum_{m=0}^{\infty} x^m} \\ &= hf \frac{1 + x \sum_{n=0}^{\infty} (n+1)x^n}{\left(\frac{1}{1-x}\right)} \\ &= hf(1-x) \left(0 + x \frac{d \sum_{n=0}^{\infty} x^{n+1}}{dx}\right) \\ &= hf(1-x) \left(x \frac{d \frac{x}{1-x}}{dx}\right) \\ &= hfx(1-x) \left(\frac{(1-x)+x}{(1-x)^2}\right) \\ &= hf \frac{x}{1-x} \\ &= hf \frac{1}{x^{-1} - 1} \\ &= hf \frac{1}{\exp\left(\frac{hf}{k_B T}\right) - 1} \end{aligned}$$

Then, our energy is:

$$\frac{g(f) df}{V} \bar{E} = \frac{8\pi h f^3}{c^3} \frac{1}{\exp\left(\frac{hf}{k_B T}\right) - 1} df$$

By converting from f to λ , the correct formula is:

$$\rho(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

Quantum mechanics is all about things that can be *quantized*. How far can we take this idea? Planck successfully applied it to energy radiated from a blackbody. What about an atom? Bohr applied this concept to the model of the Hydrogen atom, as we will soon see.

3 Lecture 3: Matter as a wave

3.1 Everything is a wave (in Quantum Mechanics)

Whether we analyze something as a particle versus wave is really a question of system size versus wavelength. For example, for the de Broglie wavelength (for an electron orbital), angular momentum is quantized, so:

$$\lambda_{dB} = \frac{h}{p} \text{ nm}$$

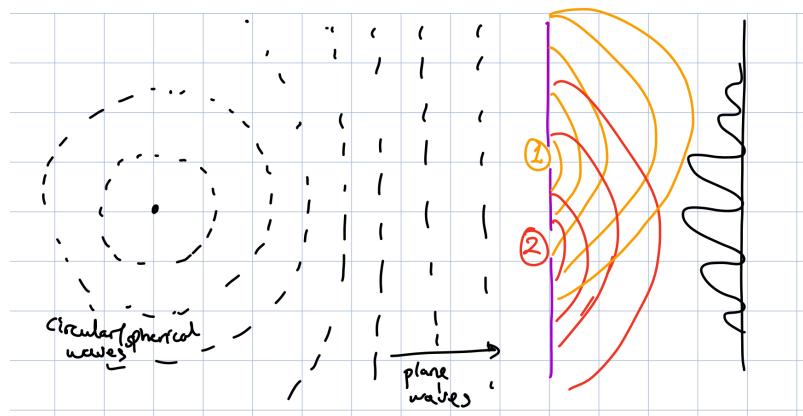
versus the size of an atom is on the order of an angstrom, much smaller.

However for a human

$$\lambda_{dB} = 10^{-36} \text{ m}$$

versus the size of a human is on the order of a meter.

Waves can interfere. Suppose you have a light wavefront like this.



We will focus on the case of a plane wave since the mathematics is simpler. We use complex exponentials to represent the waves. The electric field is:

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t + \phi)}$$

The amplitude is a vector (direction for which direction the wave wiggles in). The phase $\delta = (\mathbf{k} \cdot \mathbf{r} - \omega t + \phi)$ can be decomposed. \mathbf{k} is the spatial frequency and ω is the time frequency. Then ϕ is the wave phase at $(\mathbf{r}, t) = (\mathbf{0}, 0)$. We can get the total electric field by using simple superposition principle.

$$\begin{aligned} \mathbf{E}_{tot} &= \mathbf{E}_1 + \mathbf{E}_2 \\ &= \mathbf{E}_{01} e^{i\delta_1} + \mathbf{E}_{02} e^{i\delta_2} \end{aligned}$$

In practice, we measure a scalar quantity intensity I ,

$$\begin{aligned} I &\sim |\mathbf{E}|^2 = \mathbf{E} \cdot \mathbf{E}^* \\ &= E_{01}^2 + E_{02}^2 + \mathbf{E}_{01} \cdot \mathbf{E}_{02} (e^{i(\delta_2 - \delta_1)} + e^{-i(\delta_2 - \delta_1)}) \\ &= E_{01}^2 + E_{02}^2 + 2\mathbf{E}_{01} \cdot \mathbf{E}_{02} \cos(\delta_2 - \delta_1) \end{aligned}$$

However, they did the same experiment with electrons and got the same result. Matter must itself be a wave!

3.2 The Wavefunction

Now we want a wave description of matter. The \mathbf{E} is not sufficient for these purposes. We will use Ψ as this "wavefunction." Some weird properties of Ψ is:

- Ψ is a wave amplitude.
- It is not physical and cannot directly be measured.
- This function contains all the information about your system.

Max Born in 1926 gave the following interpretation to Ψ .

Theorem 3.1 (Born Rule)

If the wavefunction of a system is $|\Psi|^2$ is a probability (spatial) density to find the "particle" around \mathbf{r}, t .

With repeated measurements, the long-time probability for finding the particle within a cube $d\mathbf{r}$ becomes:

$$P(\mathbf{r}, t) d\mathbf{r} = |\Psi(\mathbf{r}, t)|^2 d\mathbf{r}$$

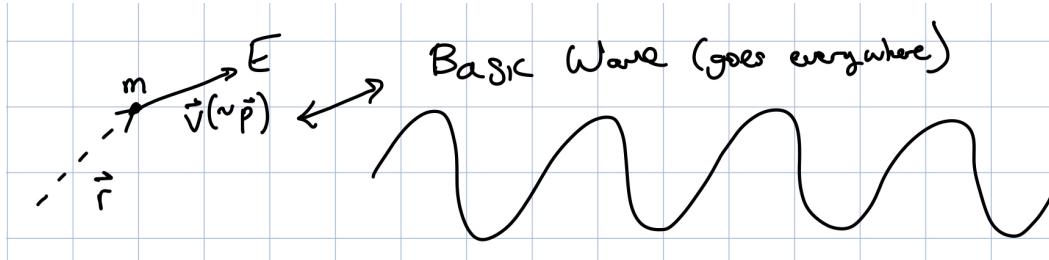
Theorem 3.2 (Superposition)

If Ψ_1, Ψ_2 are allowed waves (solutions), then:

$$\Psi = c_1 \Psi_1 + c_2 \Psi_2$$

is also a viable solution, $\{c_1, c_2\} \in \mathbb{C}$.

Think about your favorite particle. It looks something like this:



Unfortunately this basic wave spills everywhere in space. It is a good approximation for certain scales (say the double-slit setting), but not perfect. This is how our physics translates:

$$E = hf = \hbar\omega$$

$$p = \frac{h}{\lambda} = \hbar k$$

where $\hbar = \frac{h}{2\pi}$ and $k = \frac{2\pi}{\lambda}$.

Consider a 1-D particle with some x direction momentum p_x .

$$\Psi = Ae^{i(kx - \omega(k)t)}$$

$$\Psi = Ae^{i(p_x x - E(p_x)t)/\hbar}$$

Thus simply by derivative rules, the "momentum operator" p_x is:

$$-i\hbar \frac{\partial}{\partial x} \Psi = p_x \Psi$$

$$i\hbar \frac{\partial}{\partial t} \Psi = E \Psi$$

In 3-D, we have (using dot products):

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

which means that the operator looks like:

$$-i\hbar \nabla \Psi = \mathbf{p} \Psi$$

4 Lecture 4: Wave Packets

4.1 Aside: The Fourier Transform

First let us define the Discrete Fourier Transform.

Theorem 4.1 (Discrete Fourier Transform)

Suppose you have a periodic function f such that $f(x + 2\pi) = f(x)$ for all x . If we want to write

$$f(x) = \frac{1}{2}A_0 + \sum_{n=1}^{\infty} (A_n \cos(nx) + B_n \sin(nx))$$

We can do so by setting:

$$\begin{aligned} A_n &= \frac{1}{\pi} \int f(x) \cos(nx) dx \\ B_n &= \frac{1}{\pi} \int f(x) \sin(nx) dx \end{aligned}$$

How can we show this? Just like with a cartesian vector space, we can use inner products to project onto a basis of functions. What is the inner product for functions? It is the integral of the ordinary product:

$$\langle f(x), g(x) \rangle = \frac{1}{\pi} \int f(x)g(x) dx$$

Thus:

$$\begin{aligned} A_m &= \langle f(x), \cos(mx) \rangle \\ B_m &= \langle f(x), \sin(mx) \rangle \end{aligned}$$

Now, suppose you want to decompose your function as:

$$f(x) = \frac{1}{\sqrt{2\pi}} \sum_{n=-\infty}^{\infty} c_n e^{inx}$$

Then (by a similar projection argument):

$$c_m = \frac{1}{\sqrt{2\pi}} \int_{-\pi}^{\pi} f(x) e^{-imx} dx$$

Definition 4.1 (Kronecker Delta)

The kronecker delta δ_{mn} is the indicator:

$$\delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{otherwise} \end{cases}$$

Thus we must have,

Theorem 4.2

The basis functions e^{inx} are orthonormal, i.e.

$$\frac{1}{2\pi} \int_{-\pi}^{\pi} e^{i(n-m)x} dx = \delta_{mn}$$

Theorem 4.3 (Continuous Fourier Transform)

If you wish to write:

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{ikx} dx$$

(where $g(k)$ is the continuous fourier transform of $f(x)$), then we have:

$$g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx$$

We call these fourier transforms unitary transforms since they change basis but do not lose information. Let us now explore the continuous version of the delta, the Dirac delta. Plugging in the Fourier transform into the synthesis equation:

$$\begin{aligned} f(x) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \left(\int_{-\infty}^{\infty} f(x') e^{-ikx'} dx' \right) e^{ikx} dk \\ &= \int_{-\infty}^{\infty} f(x') \delta(x - x') dx \end{aligned}$$

where we define:

Definition 4.2 (Dirac Delta)

The dirac delta distribution is defined as:

$$\delta(y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{iky} dk$$

Some wacky properties:

- $\delta(x - x') = 0$ if $x \neq x'$
- $\int_{\text{region including } 0} \delta(x) dx = 1$ otherwise

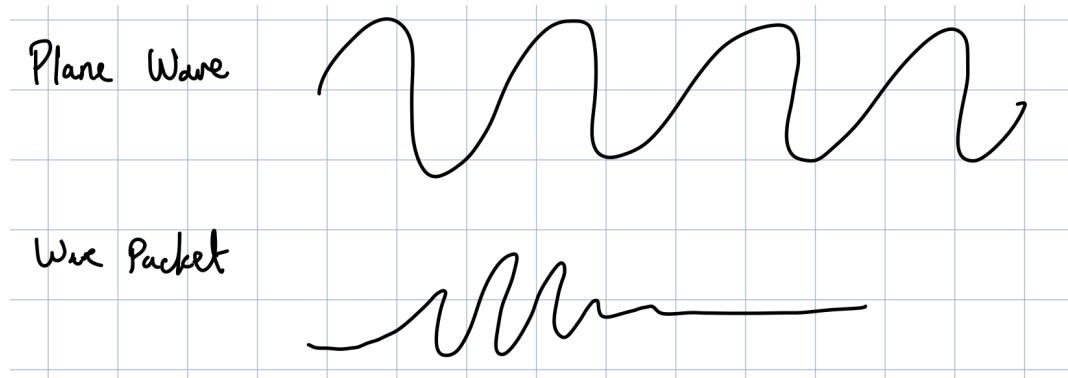
Notice something interesting, a single frequency, a single δ is infinitely thin! But if you take up more frequencies in the frequency domain, add together more and more δ s, the time and space components of the wave will be thinner!

4.2 Wave Packets and Normalization

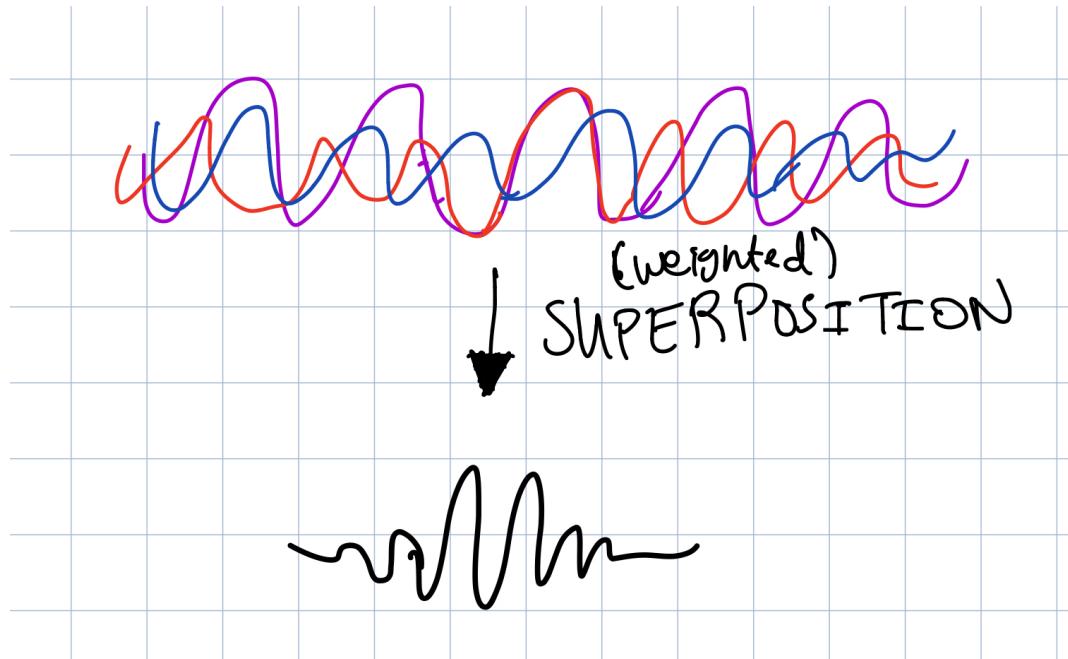
By probability density laws,

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

but for this basic wave that spans all of space, this diverges! (Or the wavefunction is zero everywhere). Instead we have wave packets that are much more localized.



Suppose we have some waves indexed by j : $A_j e^{i(k_j x - \omega t)}$. We want to pick them and add them up to get this localized shape.



For a 1-D wavepacket, the wave function is as follows (our index j has become continuous p_x).

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int e^{\frac{i(p_x x - Et)}{\hbar}} \phi(p_x) dp_x$$

Let us assume $\phi(p_x)$ is a sharp (non-delta) function that is centered p_0 and has half-max width $2\Delta p_x$.

Let

$$\beta(p_x) = p_x x - E(p_x)t$$

Then

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int e^{\frac{i\beta(p_x)}{\hbar}} \phi(p_x) dp_x$$

In the vicinity of p_0 is the only place where the integral does not vanish. Furthermore, we also do not want the exponential to rapidly oscillate (this will kill the integral) so we only get nonzero components in places where $\beta(p_x)$ doesn't vary much. Thus we look for the stationary phase condition

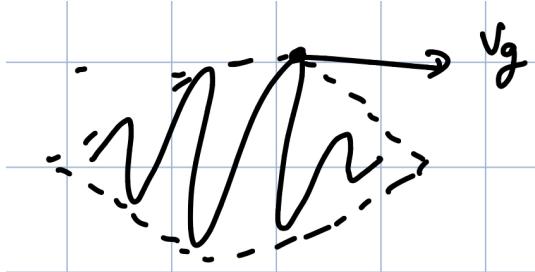
$$\left. \frac{d\beta(p_x)}{dp_x} \right|_{p_x=p_0} = 0$$

So, doing this yields:

$$x - t \frac{d}{dp_x} E(p_x) = 0$$

$$\frac{x}{t} = \frac{dE(p_x)}{dp_x}$$

where this quantity is defined as the group velocity v_g . This is how fast the highest amplitude part of the wave packet moves:



We can also find the phase velocity, the velocity of each component. Each component is:

$$e^{i(k_0 x - \omega(k_0)t)}$$

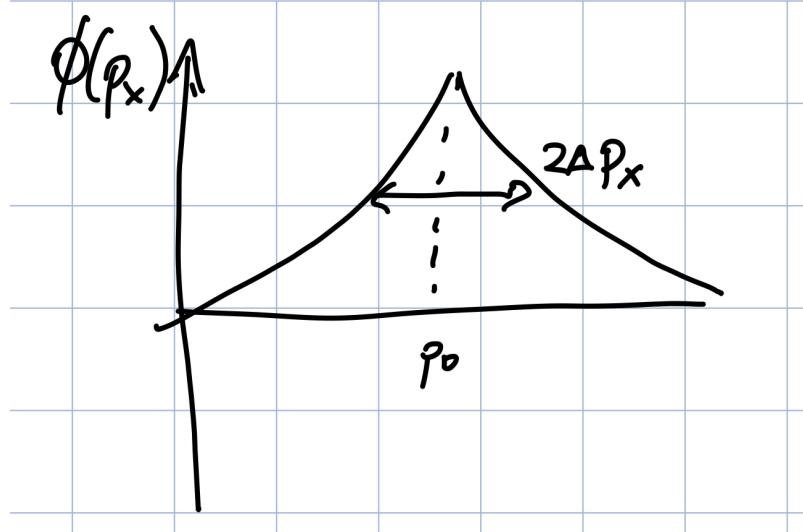
$$k_0 x - \omega(k_0)t = 0$$

$$v_p = \frac{x}{t} = \frac{E(p_0)}{p_0}$$

5 Lecture 5: Heisenberg Uncertainty

5.1 Wave Packet Envelopes

Consider our thin-in-momentum wave packet from before.



Recall

$$v_g = \frac{\partial \omega}{\partial k} \sim \frac{\partial E}{\partial p}$$

Suppose the velocity (for e.g. a point object) is:

$$v = v_g = \frac{p_x}{m}$$

Then since v_g is $\frac{\partial E}{\partial p}$, the energy can be integrated to be $E = \frac{p_x^2}{2m}$ and we recover the kinetic energy!

Now we Taylor expand:

$$E(p_x) = \frac{p_0^2}{2m} + \frac{p_0}{m}(p_x - p_0) + \frac{1}{2m}(p_x - p_0)^2$$

The first term is $E(p_0)$ and the $\frac{p_0}{m}$ is the group velocity.

So we can write the wavefunction integral:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \exp\left(i[p_x x - (E(p_0)t + v_g t(p_x - p_0) + \frac{(p_x - p_0)^2}{2m}t)]/\hbar\right) \phi(p_x) dp_x$$

We can drop that second order term when:

$$\frac{(p_x - p_0)^2 t}{2m\hbar} \ll 1$$

So the wave will disperse (at later time t) and spread out! Removing the term yields:

$$\begin{aligned} \Psi(x, t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \exp(i[p_x x - E(p_0)t - v_g t(p_x - p_0)]/\hbar) \phi(p_x) dp_x \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \exp(i[p_x x - p_0 x + p_0 x - E(p_0)t - v_g t(p_x - p_0)]/\hbar) \phi(p_x) dp_x \\ &= \frac{e^{i[p_0 x - E(p_0)t]}}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \exp(i(p_x - p_0)(x - v_g t)/\hbar) \phi(p_x) dp_x \end{aligned}$$

The beginning is a plane wave and the integral is a modulating envelope that moves at the group velocity, v_g . Calling

$$F(x, t) = \int_{-\infty}^{\infty} \exp(i(p_x - p_0)(x - v_g t)/\hbar) \phi(p_x) dp_x$$

The probability density becomes:

$$|\Psi(x, t)|^2 = |F(x, t)|^2$$

5.2 Gaussian Wave Packets

Now consider the Gaussian wave packet, which in momentum space looks like:

$$\phi(p_x) = ce^{-(p_x - p_0)^2} 2(\Delta p_x)^2$$

Note that $|\phi|^2$ falls to $\frac{1}{e}$ at $p_0 \pm \Delta p_x$. Here is a good Gaussian identity:

$$\int_{-\infty}^{\infty} e^{-\alpha u^2} e^{-\beta u} du = \left(\frac{\pi}{\alpha}\right)^{1/2} e^{\beta^2/4\alpha}$$

Let us take $\Psi(x) = \Psi(x, 0)$:

$$\begin{aligned} \Psi(x) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{ip_xx/\hbar} \phi(p_x) dp_x \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{ip_xx/\hbar} \cdot ce^{-(p_x - p_0)^2} 2(\Delta p_x)^2 dp_x \\ &= \frac{\pi^{-\frac{1}{4}} \sqrt{\Delta p_x}}{\sqrt{\hbar}} e^{ip_0x/\hbar} e^{-(\Delta p_x)^2 x^2 / 2\hbar^2} \end{aligned}$$

Note that the magnitude is a Gaussian. This function falls to $\frac{1}{e}$ of the maximum at $x = \pm\Delta_x$, where $\Delta x = \frac{\hbar}{\Delta p_x}$. It turns out this is the best you can do.

Theorem 5.1 (Heisenberg Uncertainty Principle)

The Gaussian wave packet is the minimum uncertainty state. That is,

$$\Delta p_x \Delta x \geq \hbar$$

for any wave packet.

Furthermore, there is an interplay between frequency and time. Since $E = \hbar\omega$:

$$\Delta E \delta t \geq \hbar$$

There is a very nice physical interpretation of this principle. If you measure x to an accuracy $\Delta x = a$, then immediately measuring p would give you an uncertainty at least $\Delta p \geq \frac{\hbar}{\Delta x}$.

5.3 Heisenberg Microscope

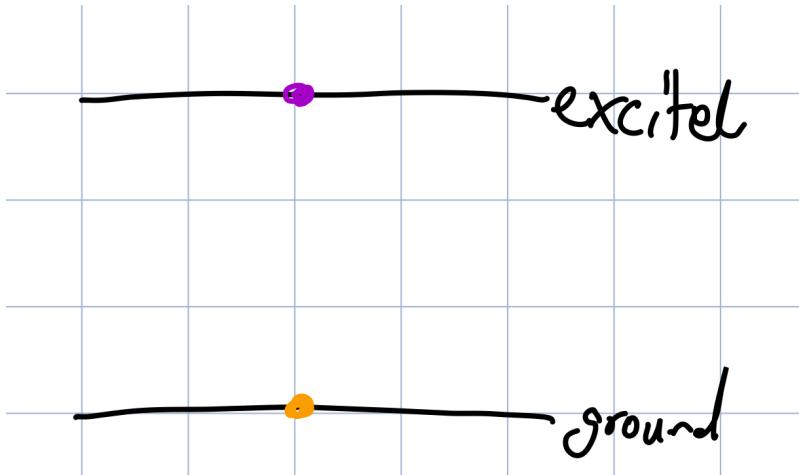
Suppose you're doing a double-slit experiment and you want to observe what slit the electron went through. We would need to shine some gamma rays on the electron to look at it. In order for us to measure which slit the electron went to,

we definitely need the wavelength to be smaller than the gap between the slits, $\lambda_\gamma < d$. Then:

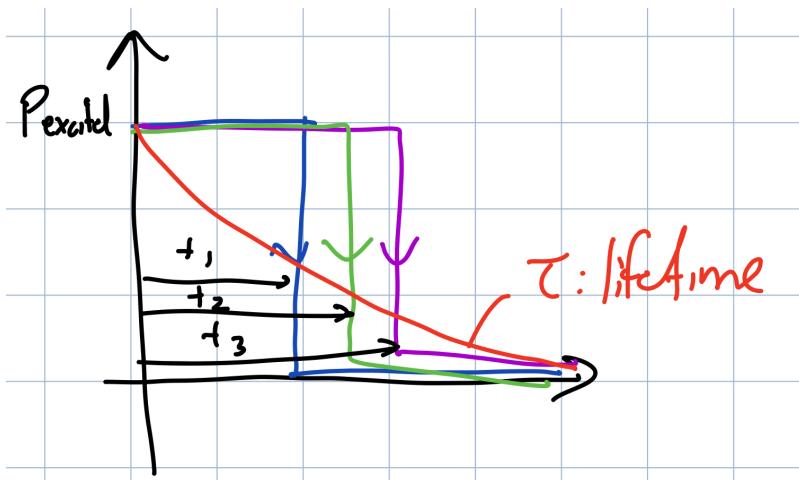
$$\begin{aligned} p_\gamma &= \frac{h}{\lambda_\gamma} \\ \Delta p_{e^{-1}} &\sim \frac{h}{\lambda_\gamma} \\ \Delta p_{e^{-1}} &\sim \frac{h}{\lambda_\gamma} \geq \frac{h}{d} \\ d\Delta p_{e^{-1}} &\geq h \\ \Delta\theta &= \frac{\Delta p_{e^{-1}}}{p_{e^{-1}}} = L\Delta\theta \end{aligned}$$

6 Lecture 6: Heisenberg Uncertainty Continued, Schrodinger's Equation

In the quantum theory of an atom, electrons have defined energy levels.



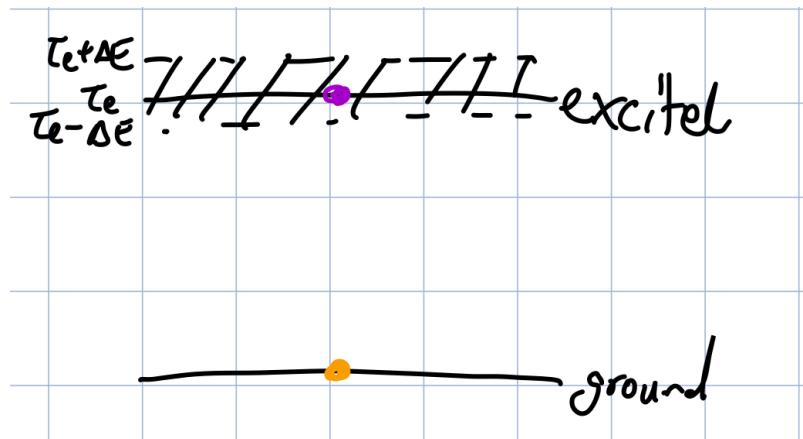
Consider an electron in the ground state—it can stay there for basically an infinite amount of time. When an electron is in the excited state, then it will drop down at some indeterminate time. If you average this together, you get a half life decay like this:



Because this is really a probability distribution, you actually see a small band of frequencies. The uncertainty is:

$$\Delta E = \frac{\hbar}{\tau}$$

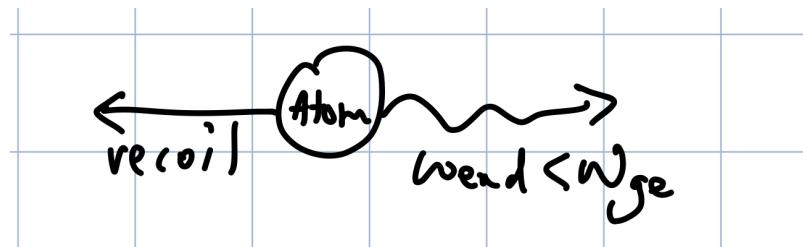
The diagram now more accurately looks like this:



and the photon emission spectrum looks like this.



Imagine now a fluorescent tube. Once you excited an atom on the edge of the tube, how do the atoms in the middle shine? Well, the atoms emit photons which are absorbed by neighboring atoms. However, by conservation of momentum, the atom must recoil backwards when emitting a photon.



But since the atom spectra is actually a probability distribution and not pointwise, if the recoil is less than the line width, then you can still get this resonance with high probability. This is decidedly not true for nuclei and γ rays, except if the entire lattice resonates, distributing the recoil over many particles. This is called the Mossbauer Effect, and allows the bulb to work.

6.1 Schrodinger's Wave Equation

Now we want an equation that can give us the wave function. We want the following nice properties:

- Linear (permits superposition, since superposition is done to waves)
- Should “agree” with classical physics
- There should be only one time derivative, because if there were two you would need two snapshots in time, i.e. causality reasons.

Suppose the wave function is:

$$\Psi(x, t) = A e^{i(p_x x - Et)\hbar}$$

Then we know that the energy is:

$$E = \frac{p_x^2}{2m} \implies \omega = \frac{\hbar k^2}{2m}$$

which is called the dispersion relation for a free particle. Furthermore, by the eigenfunction properties of the exponential:

$$\begin{aligned} \frac{\partial \Psi(x, t)}{\partial t} &= A(-i\omega)e^{i(kx - \omega t)} \\ &= -i\omega\Psi = \frac{-i}{\hbar}E\Psi \\ \frac{\partial^2 \Psi(x, t)}{\partial x^2} &= -k^2 A e^{i(kx - \omega t)} \\ &= \frac{-p_x^2}{\hbar^2}\Psi \\ &= \frac{-2Em}{\hbar^2}\Psi \end{aligned}$$

Setting the E s equal yields:

Theorem 6.1 (Schrodinger's Wave Equation - 1D Free Particle)

The wave equation is

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

Where we can define operators:

$$\begin{aligned} \hat{E} &= i\hbar \frac{\partial}{\partial t} \\ \hat{p}_x &= -i\hbar \frac{\partial}{\partial x} \end{aligned}$$

So the wave equation is just relating energy and momentum! However, we need to bring in potential energy into our model. Let's do it for a conservative force, since the mathematics is simpler.

Definition 6.1 (Potential Operator)

The potential operator is for a scalar potential $V(\mathbf{r}, t)$ is:

$$\hat{V}(\mathbf{r}, t)\Psi(\mathbf{r}, t) = V(\mathbf{r}, t)\Psi(\mathbf{r}, t)$$

Then note that for a conservative force:

$$\mathbf{F}(\mathbf{r}, t) = -\nabla V(\mathbf{r}, t)$$

So we can write down the full Schrodinger equation:

Theorem 6.2 (Time-Independent Schrodinger Equation)

We have for a wave function Ψ :

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

Where the sum in the brackets is often denoted \hat{H} , the **Hamiltonian operator**.

Let's look at some properties of the \hat{H} operator.

$$\begin{aligned} \int |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} &= 1 \\ \frac{\partial}{\partial t} \int \Psi(\mathbf{r}, t)^* \Psi(\mathbf{r}, t) d\mathbf{r} &= 0 \\ &= \int \Psi(\mathbf{r}, t)^* \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} + \frac{\partial \Psi(\mathbf{r}, t)^*}{\partial t} \Psi(\mathbf{r}, t) d\mathbf{r} \\ &= \int \frac{1}{i\hbar} [\Psi^*(\hat{H}\Psi) - (\hat{H}\Psi)^*\Psi] d\mathbf{r} \end{aligned}$$

which means:

$$\begin{aligned} \int \Psi^*(\hat{H}\Psi) d\mathbf{r} &= \int (\hat{H}\Psi)^*\Psi d\mathbf{r} \\ \int \Psi^* \hat{H} \Psi d\mathbf{r} &= \int \Psi^* \hat{H}^* \Psi d\mathbf{r} \end{aligned}$$

This means that $\hat{H} = \hat{H}^*$, i.e. \hat{H} is a **Hermitian operator**. This means that E is a real number, which makes sense, since it is observable! In fact, all observables will have associated Hermitian operators.

7 Lecture 7: Hermitian Operators

7.1 Probability Current

Like we stated before, Hermitian operators have all real eigenvalues, and any operator that is observable is Hermitian! Now continuing from last lecture, we had (substituting the spatial part and assuming a real valued potential):

$$\begin{aligned}\frac{\partial}{\partial t} \int |\Psi|^2 d\mathbf{r} &= \int \frac{1}{i\hbar} [\Psi^* (\hat{H}\Psi) - (\hat{H}\Psi)^*\Psi] d\mathbf{r} \\ &= \int \frac{i\hbar}{2m} [\Psi^* (\nabla^2\Psi) - (\nabla^2\Psi)^*\Psi] d\mathbf{r} \\ &= - \int \frac{i\hbar}{2m} \int \nabla \cdot [\Psi^* \nabla\Psi - (\nabla\Psi^*)\Psi] d\mathbf{r} \\ &= - \int \nabla \cdot \mathbf{j} d\mathbf{r}\end{aligned}$$

Where we define:

$$\mathbf{j} = \Psi^* \nabla\Psi - (\nabla\Psi^*)\Psi$$

the "probability current." Using Stokes' theorem:

$$\begin{aligned}\frac{\partial}{\partial t} \int |\Psi|^2 d\mathbf{r} &= - \int \mathbf{j} \cdot d\mathbf{s} \\ \frac{\partial P(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r}, t) &= 0\end{aligned}$$

So now the name of \mathbf{j} makes sense! This quantifies how much the current moves away from a given point.

7.2 Expectation Values

In classical mechanics, we have the average as:

$$\langle \mathbf{r} \rangle = \int_{\mathbb{R}^3} \mathbf{r} P(\mathbf{r}, t) d\mathbf{r}$$

Now suppose we have an operator \hat{r} that gives position as $\hat{r}\Psi = \mathbf{r}\Psi$.

$$\langle \hat{r} \rangle = \int_{\mathbb{R}^3} \mathbf{r} |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = \int_{\mathbb{R}^3} \Psi^* \hat{r} \Psi d\mathbf{r}$$

Now let's say we want the average of the momentum:

$$\begin{aligned}\langle \hat{p} \rangle &= \int \Psi^* \hat{p} \Psi d\mathbf{r} \\ &= -i\hbar \int \Psi^* \nabla \Psi d\mathbf{r}\end{aligned}$$

Note that \hat{p} is Hermitian but $\hat{p} = -i\hbar \nabla$ and so its conjugate gives you a positive sign? That's because we only give the complex conjugate guarantees on the operator acting on a wave function! We will see more in homework.

If you come across two Hermitian operators, the product is Hermitian only if the two operators commute. However, operators (even Hermitian ones) do not commute in general. For example, \hat{x} and \hat{p}_x do not commute.

Definition 7.1

The commutator (bracket) is defined as:

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

Clearly the commutator is 0 if and only if the two operators commute. This means they are unrelated and can be measured simultaneously!

$$\begin{aligned} [\hat{x}, \hat{p}_x] &= \hat{x}\hat{p}_x - \hat{p}_x\hat{x} \\ [\hat{x}, \hat{p}_x]\Psi &= \hat{x}\hat{p}_x\Psi - \hat{p}_x\hat{x}\Psi \\ &= -i\hbar x \frac{\partial}{\partial x}\Psi + i\hbar \frac{\partial}{\partial x} \\ &= -i\hbar x \frac{\partial}{\partial x}\Psi + i\hbar \left(\Psi + x \frac{\partial \Psi}{\partial x}\right) \\ &= i\hbar\Psi \end{aligned}$$

So the commutator is $i\hbar I \neq 0$. In fact, in general, the commutator of a canonical Fourier pair will always be this.

8 Lecture 8: Solving the Schrodinger Equation

We return to the Schrodinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + \hat{V} \right] \Psi$$

We want to look for specific solutions: the separable stationary, eigen, or standing wave solutions.

$$\Psi(\mathbf{r}, t) = f(t)\Psi(\mathbf{r})$$

We will assume the potential is time-independent. Let us substitute into the Schrodinger equation:

$$\begin{aligned} i\hbar \Psi(\mathbf{r}) \frac{df(t)}{dt} &= \left[-\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}) + \hat{V}(\mathbf{r}) \right] f(t) \\ i\hbar \frac{\frac{df(t)}{dt}}{f(t)} &= \frac{\left[-\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}) + \hat{V}(\mathbf{r}) \Psi(\mathbf{r}) \right]}{\Psi(\mathbf{r})} \end{aligned}$$

Since these are both independent, they must be both equal to some constant E . For the time portion:

$$\begin{aligned} i\hbar \frac{df}{dt} &= Ef \\ f(t) &= Ce^{-iEt/\hbar} \end{aligned}$$

When $\hat{V} = 0$ the other differential equation similarly gives: $C_2 e^{-i\mathbf{k} \cdot \mathbf{r}/\hbar}$. For $\hat{V} \neq 0$, then the spatial eigenfunctions of the Hamiltonian can be found using the time-independent Schrodinger equation (plugging into \mathbf{r}):

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(\mathbf{r}) \right] \Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

Definition 8.1 (Eigenfunctions)

The **eigenfunctions** of an operator \hat{H} is a solution to the equation:

$$\hat{H}\Psi_E = E\Psi_E$$

for some $E \in \mathbb{R}$. They represent stationary states with time dependence $e^{-iEt/\hbar}$. You can find $\Psi_E(\mathbf{r})$ by solving the time-independent Schrodinger Equation.

Let us find the expectation of the Hamiltonian, i.e. the energy of such a stationary state

$$\begin{aligned} \langle \hat{H} \rangle_{\Psi_E} &= \int \Psi_E^*(\hat{H})\Psi_E d\mathbf{r} \\ &= \int \Psi_E^* E \Psi_E d\mathbf{r} \\ &= E \end{aligned}$$

Let's find the probability density of one of these states:

$$\begin{aligned} P(\mathbf{r}, t) &= \Psi_E^*(\mathbf{r}, t)\Psi_E(\mathbf{r}, t) \\ &= \Psi_E^*(\mathbf{r})f^*(t)f(t)\Psi_E(\mathbf{r}) \\ &= \Psi_E^*(\mathbf{r})\Psi_E(\mathbf{r}) \end{aligned}$$

which means the probability density is not time dependent!

8.1 Solving Quantum Problems

This gives us a nice roadmap to solving quantum problems.

1. Specify $\hat{V}(\mathbf{r})$
2. Solve the time-independent Schrodinger Equation for $\Psi_E(\mathbf{r})$, E .
3. Put together the full eigensolution: $\Psi_E(\mathbf{r}, t) = \Psi_E(\mathbf{r})e^{-iEt/\hbar}$.
4. The general solution is a linear combination of these $\Psi_E(\mathbf{r})$.

It can be shown easily that $\Psi_E(\mathbf{r})$ are orthonormal. We postulate that (E, Ψ_E) found by solving the Schrodinger Equation represents all possible energies.

$$\Psi(\mathbf{r}, t) = \sum_E c_E(t) \Psi_E(\mathbf{r})$$

where

$$c_{E'}(t) = \int_{-\infty}^{\infty} \Psi_{E'}^*(\mathbf{r}) \Psi(\mathbf{r}, t) d\mathbf{r}$$

So:

$$\Psi(\mathbf{r}, t) = \sum_E c_E(0) \Psi_E(\mathbf{r}) e^{-iEt/\hbar}$$

and we can find the initial condition with:

$$c_E(0) = \int_{-\infty}^{\infty} \Psi_E^*(\mathbf{r}) \Psi(\mathbf{r}, 0) d\mathbf{r}$$

The c_E also have a physical interpretation: the magnitude squared is the probability of finding the system at the energy E and

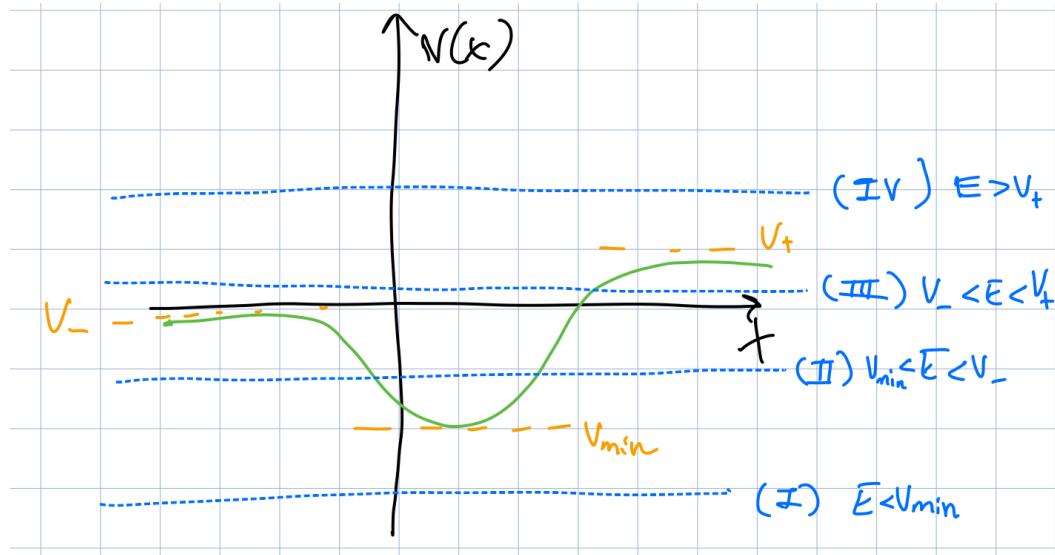
$$\sum_E |c_E|^2 = 1$$

Now we can decompose

$$\begin{aligned} \langle \hat{H} \rangle_{\Psi} &= \int \Psi^*(\mathbf{r}, t) \hat{H} \Psi(\mathbf{r}, t) d\mathbf{r} \\ &= \int \left(\sum'_{E'} c_{E'}^* e^{iE't/\hbar} \Psi_{E'}^*(\mathbf{r}) \right) \hat{H} \left(\sum_E c_E e^{-iEt/\hbar} \Psi_E(\mathbf{r}) \right) d\mathbf{r} \\ &= \sum_E \sum_{E'} c_{E'}^* c_E e^{-i(E-E')t/\hbar} E \int \Psi_{E'}^*(\mathbf{r}) \Psi_E(\mathbf{r}) d\mathbf{r} \\ &= \sum_E |c_E|^2 E \end{aligned}$$

9 Lecture 9: Different Potentials

Consider the following potential:



Let us try solving the Schrodinger equation:

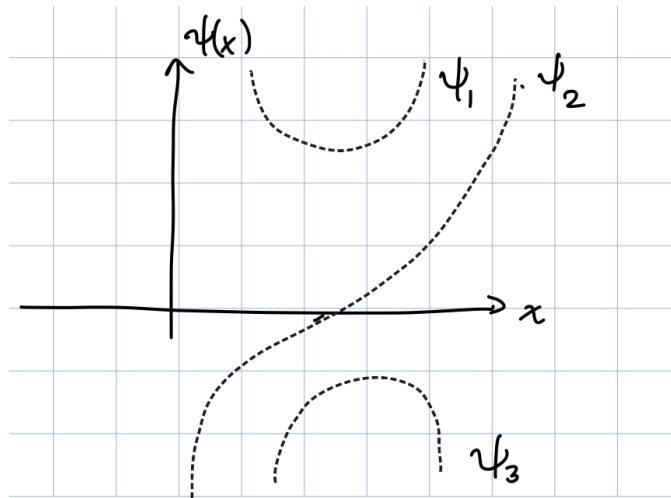
$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \Psi_E(x) = E \Psi_E(x)$$

We will work through the marked cases on the diagram.

1. Doing a simple subtraction:

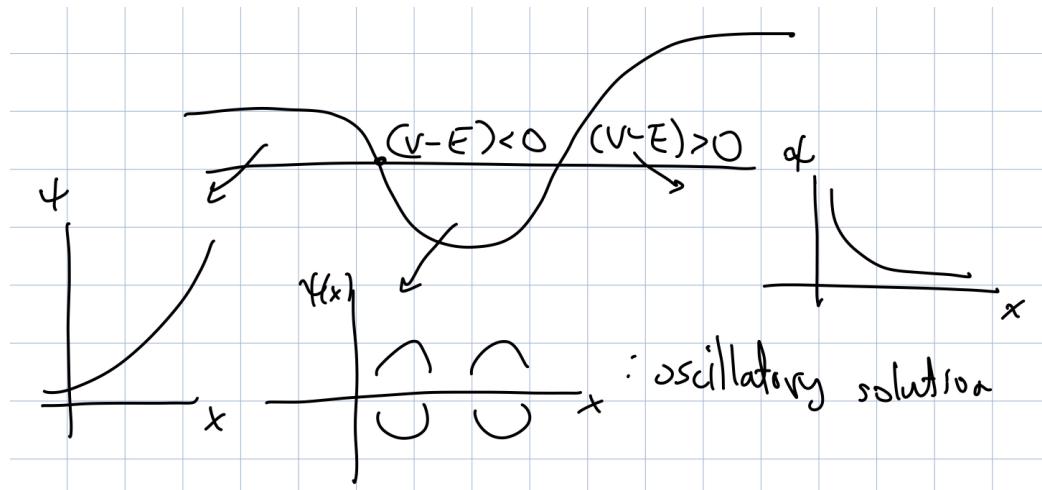
$$\frac{d^2}{dx^2} \Psi(x) = \frac{2m}{\hbar^2} (V(x) - E) \Psi(x)$$

Since $V(x) - E > 0$, this means that $\frac{d^2\Psi}{dx^2}$ and Ψ have the same sign. But look at some candidate solutions. These all diverge, which would contradict normalization!

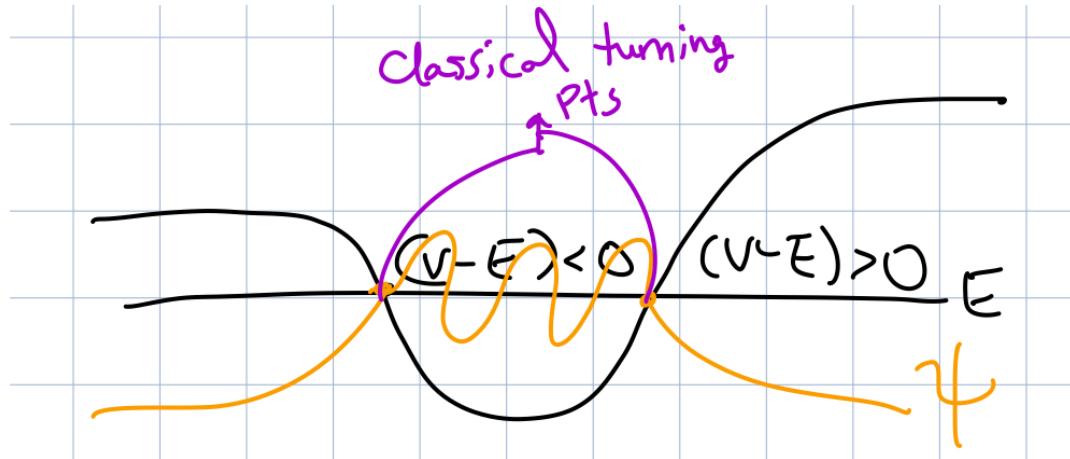


No solutions for $E < V_{min}$, which makes sense—you can't allow states lower than the lowest energy.

2. We detail some possibilities considering curvature:



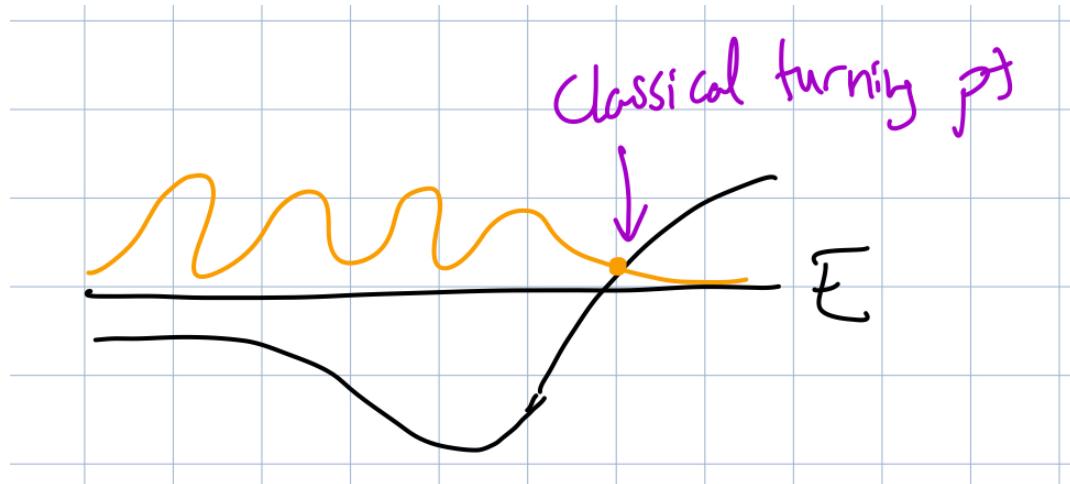
However, Ψ and $\frac{d\Psi}{dx}$ must be continuous by a probabilistic interpretation of $|\Psi|^2$. Thus a stitched solution must be like



Notice that at the ends there is an exponential decay! So there is a small (but vanishing) probability that we have the wavefunction at a lower energy than the potential!

The oscillatory wave in the middle quantizes the allowed values of E (you can only have energies that fit the boundary conditions). These are called bound states.

- With similar reasoning, this case looks like:



However, since you only have one boundary condition for a second-order equation, there is no energy quantization! Any energy in between can be allowed.

4. Lastly, the second-derivative is proportional to the difference, so oscillatory solutions will be faster wiggling in the lower potential reasons. They are called scattering states.

9.1 Free Particle, Revisited

Let us walk through the case of a free particle ($V = 0$). We write the Time-Independent Schrodinger Equation:

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

let $k = \left(\frac{2mE}{\hbar}\right)^{1/2}$

$$\frac{d^2\Psi(x)}{dx^2} + k^2\Psi(x) = 0$$

$$\Psi(x) = Ae^{ikx} + Be^{-ikx}$$

Degeneracy in E (i.e. Ψ with $\pm k$ has same energy). So the eigenfunction is:

$$\Psi_E(x, t) = (Ae^{ikx} + Be^{-ikx})e^{-iEt/\hbar}$$

Case 1: Suppose $B = 0$, then:

$$\Psi(x, t) = Ae^{i(kx - \omega t)}$$

which is a traveling wave moving to the right. Probability density is $|\Psi|^2 = |A|^2$. What's the probability current?

$$j = \frac{\hbar}{2mi} \left[\Psi^* \frac{\partial\Psi}{\partial x} - \Psi \frac{\partial\Psi^*}{\partial x} \right]$$

$$= \frac{\hbar k}{m} |A|^2 = v|A|^2$$

Case 2: Suppose $A = 0$, then the analysis is the same, but the traveling wave is moving to the left.

Case 3: Suppose $A = B$, then:

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

This is a standing wave with nodes at $x_n = \pm \frac{\pi/2 + n\pi}{k}$ for $n \in \mathbb{Z}$.

How can we normalize such a wave function? We use the good old Delta Trick:

$$\int e^{i(k-k')x} dx = 2\pi\delta(k - k')$$

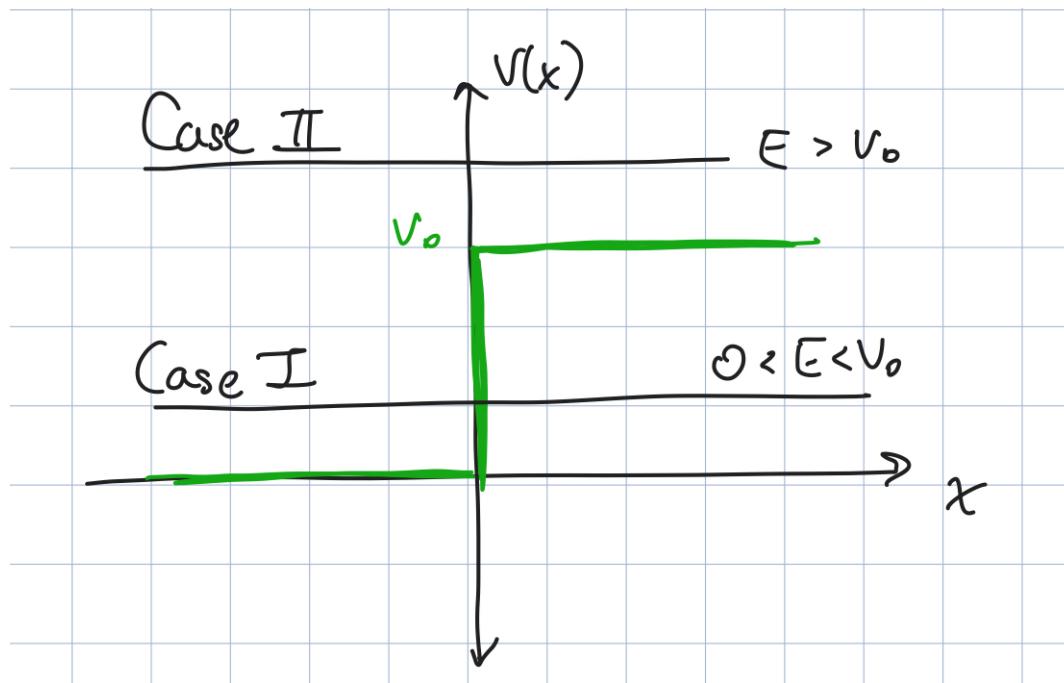
which means $\Psi(x) = \frac{1}{\sqrt{2\pi}}e^{ikx}$.

10 Lecture 10: Step Potential

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

Take the following potential:

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x > 0 \end{cases}$$



There is no possible solution where $E < 0$. In general, the solution is oscillatory in regions where "it should exist" and dies out as an exponential in places where "it shouldn't exist".

Suppose we are in Case I. For $x < 0$, the equation is, for $k = (2mE/\hbar^2)^{1/2}$

$$\frac{d^2\Psi(x)}{dx^2} + k^2\Psi(x) = 0$$

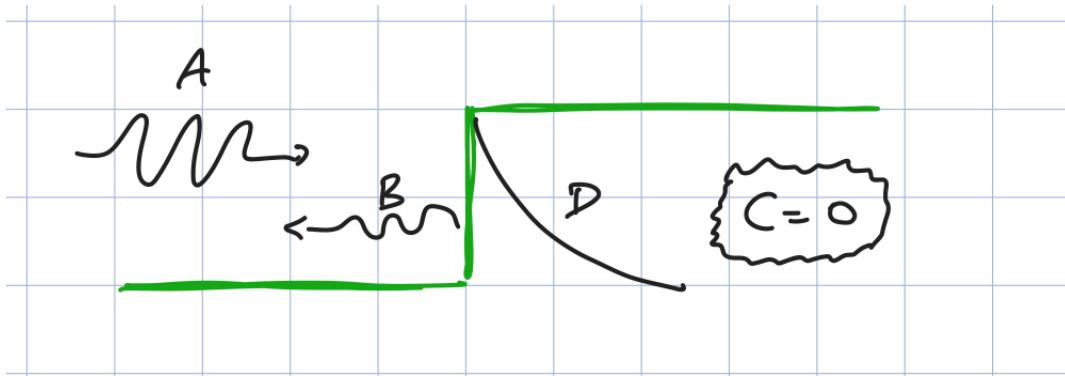
For $x > 0$, the equation is, for $\kappa = (2m(V_0 - E)/\hbar^2)^{1/2}$.

$$\frac{d^2\Psi(x)}{dx^2} - \kappa^2\Psi(x) = 0$$

The equations have solutions, as we have seen previously, has solution:

$$\Psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{\kappa x} + De^{-\kappa x} & x > 0 \end{cases}$$

Now consider the problem of a particle incident from the left. This creates boundary conditions to find the coefficients:



At the sharp interface, we can approximate the wave packet as a plane wave, which is exactly what our solutions do! We need to enforce continuity of Ψ, Ψ' at $x = 0$. So for $\Psi(0)$ we get the equation $A + B = D$. For $\Psi'(0)$ we get $ik(A - B) = -\kappa D$. Note that this doesn't uniquely determine the equation since we don't know how high the input amplitude is! So $\frac{B}{A}$ might be a better variable to define (it is the amplitude fraction). Solving our system yields:

$$A = \left(\frac{1 + i\kappa/k}{2} \right) D, B = \left(\frac{1 - i\kappa/k}{2} \right) D$$

So:

$$\frac{B}{A} = \frac{1 - i\kappa/k}{1 + i\kappa/k} = e^{i\alpha}$$

where $\alpha = 2 \operatorname{atan} \left(-\sqrt{\frac{V_0}{E} - 1} \right)$ This has modulus 1! This makes sense because we said none of the wave makes it through and it is all reflected. Furthermore, $\frac{D}{A} = 1 + e^{i\alpha}$. This means:

$$\Psi(x) = \begin{cases} 2Ae^{i\alpha/2} \cos(kx - \frac{\alpha}{2}), & x < 0 \\ 2Ae^{i\alpha/2} \cos(\frac{\alpha}{2})e^{-\kappa x}, & x > 0 \end{cases}$$

We define the reflection coefficient as the ratio of the probability currents:

$$\mathfrak{R} = \frac{|B|^2}{|A|^2} = 1$$

There is a little bit of probability on the right side, but we don't consider evanescent solutions as actually transmitting the wave. So there is 0 transmittivity.

$$P(x) = \begin{cases} 4|A|^2 \cos^2(kx - \frac{\alpha}{2}), & x < 0 \\ |D|^2 e^{-2\kappa x}, & x > 0 \end{cases}$$

The probability density to the left of the barrier is oscillatory, despite it being a plane wave. This is because there is self-interference between the wave and its reflected version!

10.1 Uncertain in the Barrier

Now we ask, can we observe the particle in the region $x > 0$? For this potential, the decay length is $\frac{1}{\kappa}$. This observation means we've made a measurement of $\Delta x \sim \frac{1}{\kappa}$. By Heisenberg, this induces an uncertainty in the momentum!

$$\Delta P_x \geq \frac{\hbar}{\Delta x} \sim [2m(V_0 - E)]^{1/2}$$

But, then $\Delta E = \frac{(\Delta P_x)^2}{2m} \geq V_0 - E$. Which means that we CANNOT SAY the energy is above the barrier.

What happens if the barrier step approaches infinity? The evanescent part disappears. As $V_0 \rightarrow \infty$, then $\Psi \rightarrow 0$ at the boundary.

Let's step back and take Case II, where $E > V_0$. Similarly,

$$\Psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{ik'x} + De^{-ik'x} & x > 0 \end{cases}$$

where $k = (2mE/\hbar^2)^{1/2}$ and $k' = (2m(E - V_0)/\hbar^2)^{1/2}$. Let's again take the case of a left incident wave. $D = 0$ because there is no back transmission (no other potential barriers), but $A, B, C \neq 0$ since there is the original piece, a reflected piece, and a transmitted piece. Solving the boundary conditions gets you:

$$\frac{B}{A} = \frac{k - k'}{k + k'}, \quad \frac{C}{A} = \frac{2k}{k + k'}$$

and we have:

$$\Re = \frac{\left[1 - (1 - \frac{V_0}{E})^{1/2}\right]^2}{\left[1 - (1 + \frac{V_0}{E})^{1/2}\right]^2}$$

So the transmittivity is:

$$\tau = \frac{v'|C|^2}{v|A|^2} = \frac{4kk'}{(k + k')^2}$$

Note QM always has partial reflection.

11 Lecture 11: Potential Barrier

Aside: Solving Eigenfunction Problems

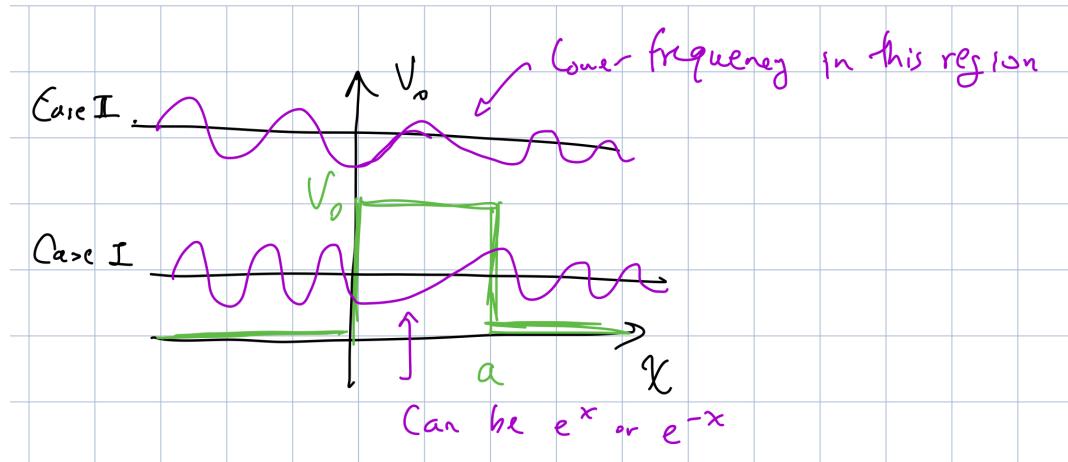
There are two problems we are primarily interested in:

1. $\Psi(\mathbf{r}, t)$ is given, find the decomposition into $\sum_E c_E \Psi_E(\mathbf{r})$
2. Tailor the most general solution to a given problem, i.e. find the c_E

Now we consider the case of a potential barrier:

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & 0 < x < a \\ 0 & x > a \end{cases}$$

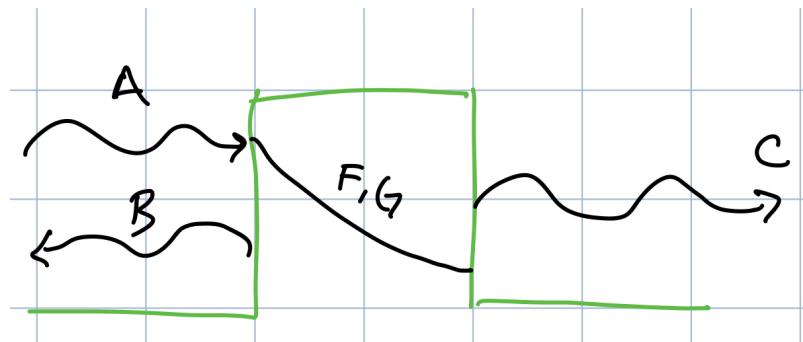
By the intuition we build up last time, we see:



So our solutions are, with $k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$ and $\kappa = \left(\frac{2m}{\hbar}(V_0 - E)\right)^{1/2}$.

$$\Psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Fe^{\kappa x} + Ge^{-\kappa x} & 0 < x < a \\ Ce^{ikx} + De^{-ikx} & x > a \end{cases}$$

Now let's impose some boundary conditions. Consider a particle incident from the left.



We do not need to remove F because the positive solution doesn't blow up in the $[0, a]$ region. If we take $v = \frac{\hbar k}{m}$, we have

$$\mathbf{j} = \begin{cases} v[|A|^2 - |B|^2] \\ v|C|^2 \end{cases}$$

with again:

$$\Re = \frac{|B|^2}{|A|^2}, \tau = \frac{|C|^2}{|A|^2}$$

Let's match the boundary conditions. At $x = 0$:

$$\begin{aligned}\Psi : A + B &= F + G \\ \Psi' : ik(A - B) &= \kappa(F - G)\end{aligned}$$

and then at $x = a$:

$$\begin{aligned}\Psi : Ce^{ika} &= Fe^{\kappa a} + Ge^{-\kappa a} \\ \Psi' : ikCe^{ika} &= \kappa(Fe^{ika} - Ge^{ika})\end{aligned}$$

Our goal is to eliminate F, G to make our lives easier and try doing things in terms of B/A and C/A . This yields:

$$\begin{aligned}\frac{B}{A} &= \frac{(k^2 + \kappa^2)(e^{2\kappa a} - 1)}{e^{2\kappa a}(k + i\kappa)^2 - (k - i\kappa)^2} \\ \frac{C}{A} &= \frac{4ik\kappa e^{-ika}e^{\kappa a}}{e^{2\kappa a}(k + i\kappa)^2 - (k - i\kappa)^2} \\ \Re &= \left[1 + \frac{4E(V_0 - E)}{V_0^2 \sinh^2(\kappa a)} \right]^{-1} \\ \tau &= \left[1 + \frac{V_0^2 \sinh^2(\kappa a)}{4E(V_0 - E)} \right]^{-1}\end{aligned}$$

Note that the transmittance is nonzero, which means some amount of the particle makes it through the potential barrier! This is the phenomenon known as quantum tunneling. Suppose $\frac{mV_0a^2}{\hbar^2} = \frac{1}{4}$.

This is the reason fusion is possible. Although there is a Coulomb repulsion between two Hydrogen nuclei, there is a strong force attraction when they are close together. Instead, it doesn't take as much energy as you actually need to overcome the barrier classically. You can tunnel below the barrier at some point, so the sun is much colder than classical physics predicts!

Let us Taylor expand the transmittance:

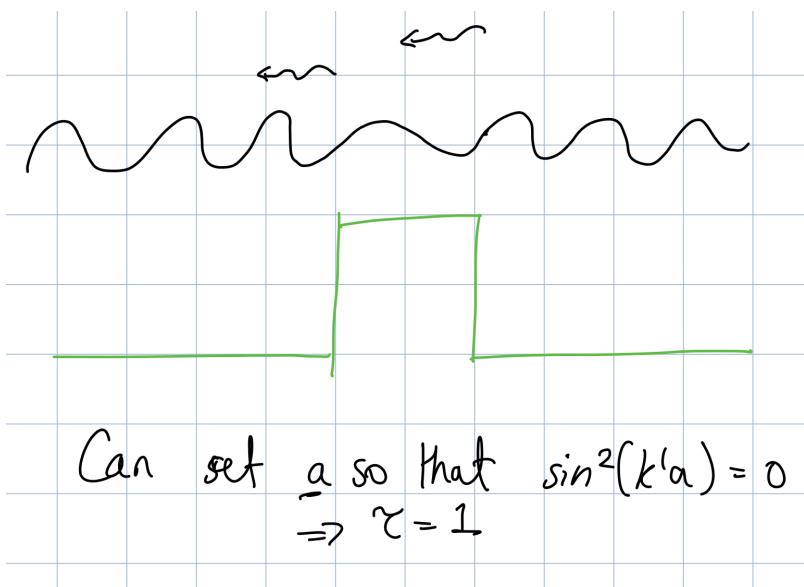
$$\lim_{E \rightarrow V_0} \tau = \left(1 + \frac{mV_0a^2}{2\hbar} \right)^{-1}$$

where the second term is known as the "opacity" of the barrier.

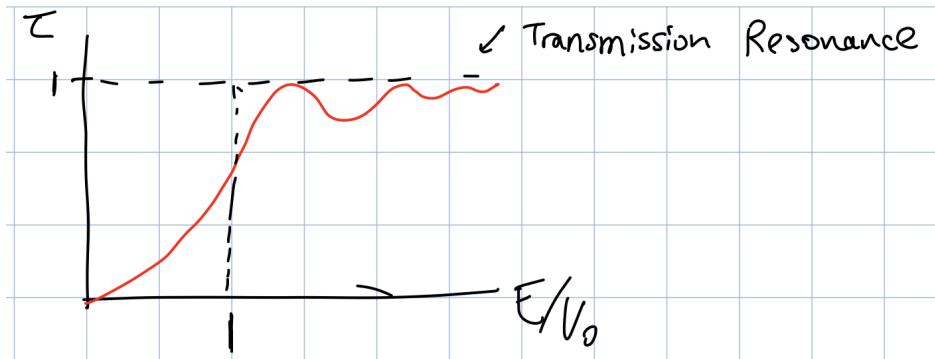
Let's take Case II now. The wave is still the same for $x < 0$ and $x > a$ (but A, B, C, D are different). Instead the barrier we have some ik' instead (similar to last lecture).

$$\begin{aligned}\Re &= \left(1 + \frac{4E(E - V_0)}{V_0^2 \sin^2(k'a)} \right)^{-1} \\ \tau &= \left(1 + \frac{V_0^2 \sin^2(k'a)}{4E(E - V_0)} \right)\end{aligned}$$

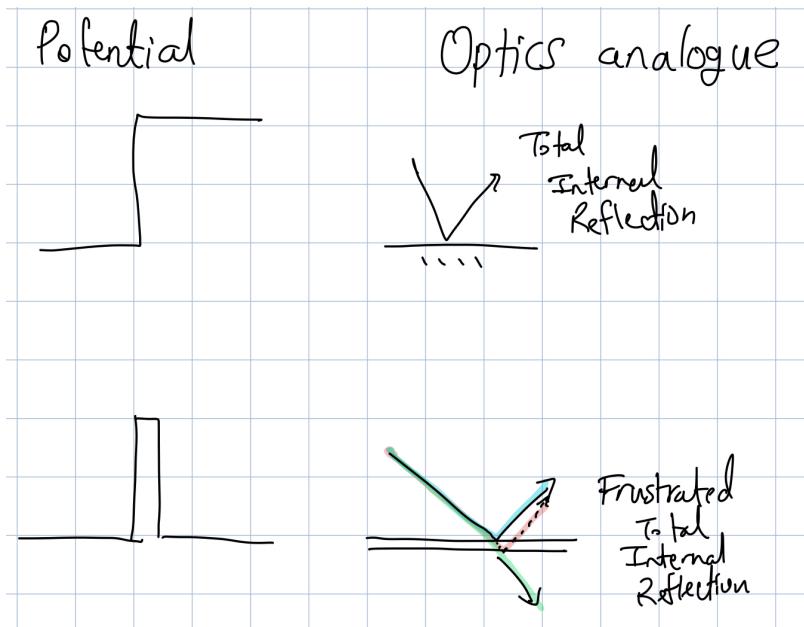
Here is the last point of the potential barrier, explained through pictures. There is a reflection on both ends of the barrier like so:



So, if we align the phases perfectly of the two reflections, they cancel and we don't lose any energy.



This is analogous to optics (another wave theory!).



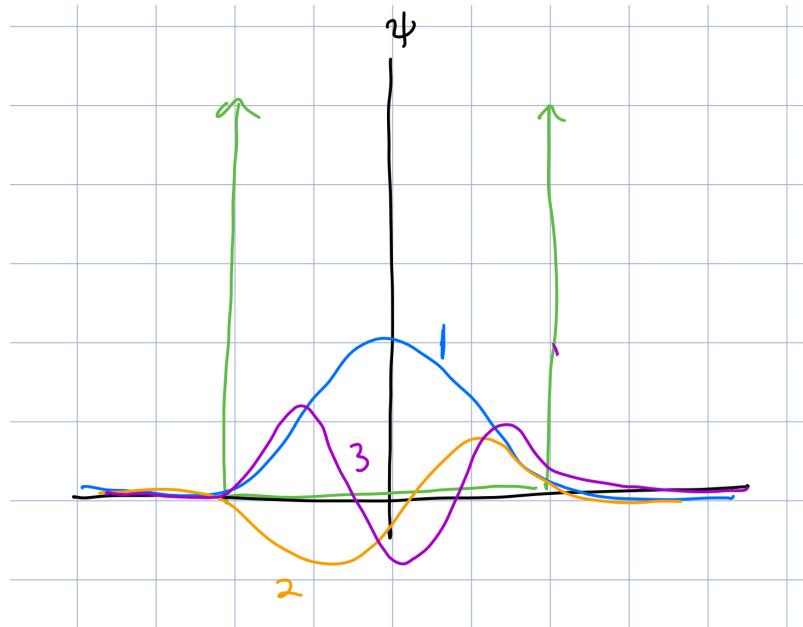
12 Lecture 12: Square Wells

12.1 Infinite Square Well

We have been considering scattering states in potentials. Now let us consider some kind of bound state in the Infinite Square Well:

$$\Psi(x) = \begin{cases} 0 & |x| > a \\ +\infty & \text{otherwise} \end{cases}$$

We can only match the boundary conditions for Ψ at $x = \pm a$; we cannot match Ψ' . This can only happen at certain energies:



For $|x| < a$, the general solution for a free particle is the superposition of plane waves with $k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$

$$\Psi(x) = A e^{ikx} + B e^{-ikx} = A \cos(kx) + B \sin(kx)$$

Theorem 12.1

With a potential with even symmetry, there are only even and odd solutions for Ψ .

The boundary conditions end up being:

$$\begin{aligned} A \cos(ka) + B \sin(ka) &= 0 \\ A \cos(ka) - B \sin(ka) &= 0 \end{aligned}$$

which means: $A \cos(ka) = B \sin(ka) = 0$

Suppose $B = 0$ for even solutions. Then: $\cos(ka) = 0$, so $k_n = \frac{n\pi}{2a} = \frac{n\pi}{L}$ for $n = 1, 3, \dots$ and our solution is $\Psi_n(x) = A_n \cos(k_n x)$ and:

$$\int \Psi_n^* \Psi_n dx = 1 \implies A = \frac{1}{\sqrt{a}}$$

So the general solution is:

$$\Psi_n(x) = \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right)$$

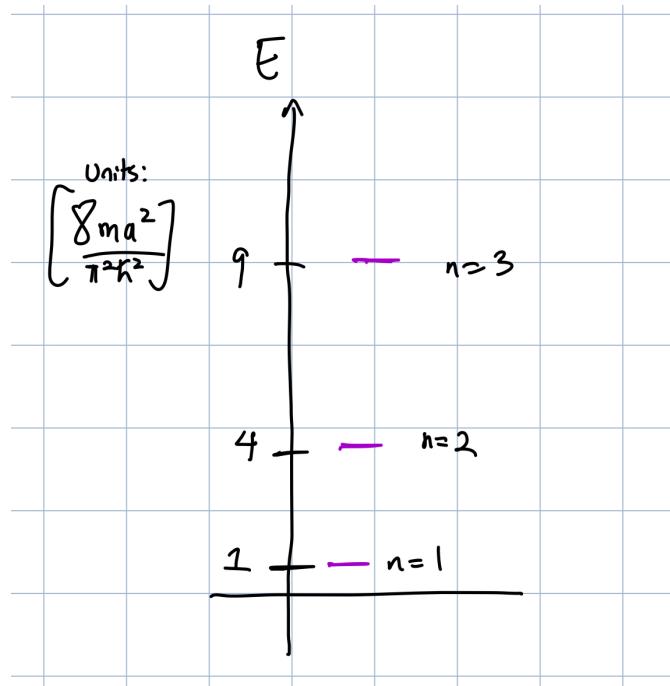
Similarly for $A = 0$, we can quantize for $n = 2, 4, 6, \dots$

$$\Psi_n(x) = \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right)$$

For all $n \in \mathbb{N}$, $k_n = \frac{n\pi}{L}$. Whenever you can fit a half-wavelength between the boundaries, you get a bound state.

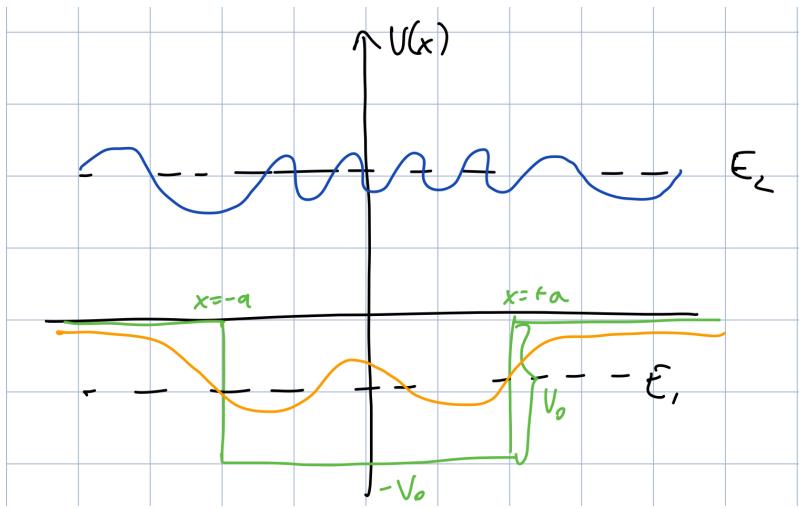
$$E_n = \frac{p^2}{2m} = \frac{\hbar^2 k_n^2}{2m} = \frac{k^2 \pi^2 n^2}{2m L^2}$$

This is a decent approximation to an atom for low n states. There are an infinite number of bound states, though, which is unrealistic. The ground state energy E_1 is not 0. $E_n \propto n^2$.



12.2 Finite Square Well

Now consider a finite version of the above.



Consider case 1, $-V_0 < E < 0$. Take $\alpha = \left[\frac{2m}{\hbar^2} (V_0 + E) \right]^{1/2} = \left[\frac{2m}{\hbar^2} (V_0 - |E|) \right]^{1/2}$. Then we know

$$\frac{d^2\Psi(x)}{dx^2} + \alpha^2\Psi(x) = 0$$

inside the well.

Now suppose you are outside the well: you have $\beta = (\frac{2m|E|}{\hbar^2})^{1/2}$.

$$\frac{d^2\Psi(x)}{dx^2} - \beta^2\Psi(x) = 0$$

So the even solutions look like:

$$\Psi(x) = \begin{cases} A \cos(\alpha x) & |x| < a \\ Ce^{-\beta x} & |x| > a \end{cases}$$

Matching boundary conditions:

$$\begin{aligned} \Psi : A \cos(\alpha a) &= Ce^{-\beta a} \\ \Psi' : -\alpha A \sin(\alpha a) &= -\beta C e^{-\beta a} \\ \alpha \tan(\alpha a) &= \beta C e^{-\beta a} \end{aligned}$$

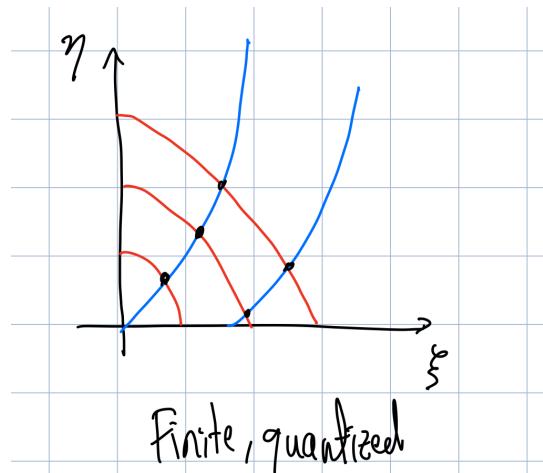
For the odd solutions:

$$\Psi(x) = \begin{cases} B \sin(\alpha x) & |x| < a \\ Ce^{-\beta x} & |x| > a \end{cases}$$

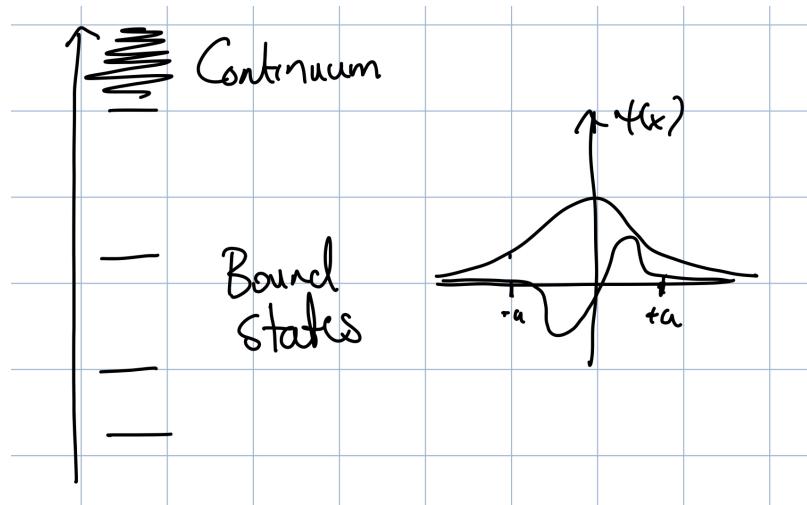
Now matching boundary conditions yields $\alpha \cot(\alpha a) = -\beta$. Solving these two transcendental equations is kinda tricky. Define $\xi = \alpha a$, $\eta = \beta a$, meaning that:

$$\begin{aligned} \xi \tan \xi &= \eta \\ \xi \cot \xi &= -\eta \end{aligned}$$

Note that $\xi^2 + \eta^2 = \delta^2$ where $\delta = \left(\frac{2mV_0a^2}{\hbar^2} \right)^{1/2}$. The solutions are the intersections here:



which are a finite number of quantized bound states. The spectrum and wave function look like this:



which seems like a much better approximation of an atom (since you can “pull off” electrons and have non-bound states).

Finally, case 2 is really easy, it's the same traveling wave.

$$\Psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < -a \\ Ce^{ikx} & x > a \\ Fe^{i\alpha x} + Ge^{-i\alpha x} & |x| < a \end{cases}$$

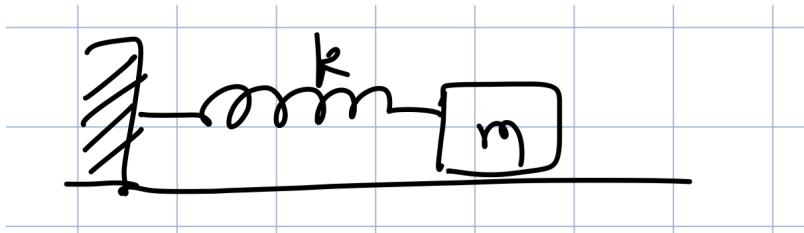
where k and α are found the same way as always.

$$\Re = \left[1 + \frac{4E(V_0 + E)}{V_0^2 \sin^2(\alpha L)} \right]^{-1}$$

etc.

13 Lecture 13: Quantum Harmonic Oscillator

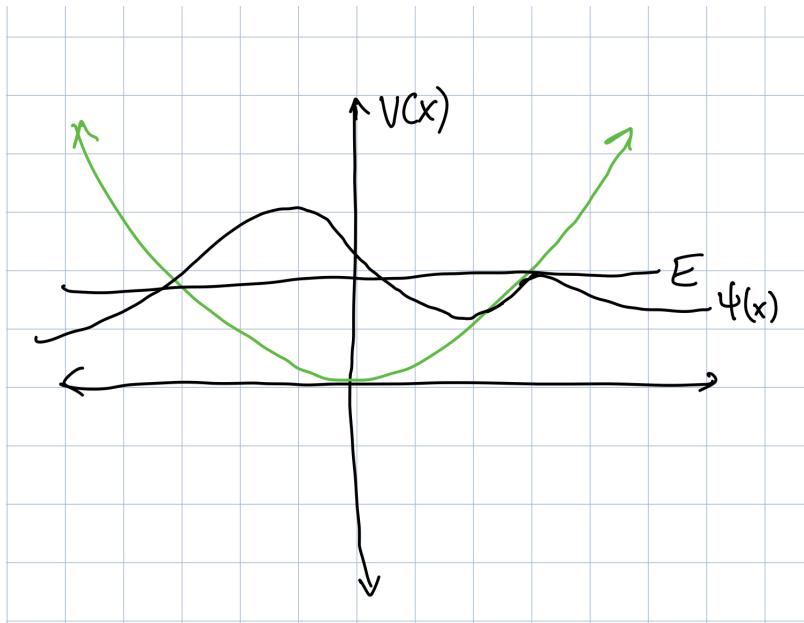
Consider a classical oscillator.



We know

$$\mathbf{F} = -k\mathbf{x}, V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2$$

where $\omega = \sqrt{\frac{k}{m}}$. The potential looks like



The time-independent Schrodinger equation looks like:

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + \frac{1}{2}kx^2\Psi = E\Psi$$

Let's go to dimensionless variables to make our lives easier. Let $\lambda = \frac{2E}{\hbar\omega}$ (a redimensioned energy), $\xi = \left(\frac{m\omega}{\hbar}\right)^{1/2}x$, so:

$$\frac{d^2}{d\xi^2}\Psi(\xi) + (\lambda - \xi^2)\Psi(\xi) = 0$$

we are going to consider the asymptotic solution for large values of $\xi \gg \lambda$.

$$\left(\frac{d^2}{d\xi^2} - \xi^2\right)\Psi(\xi) = 0$$

The solution to this is $\Psi(\xi) = e^{\pm\xi^2/2}$, but we want something that doesn't bother you at large arguments and applying normalization (boundary conditions at infinity must be 0), $\Psi(\xi) \approx \xi^p e^{-\xi^2/2}$ for some power p . More generally,

$$\Psi(\xi) = e^{-\xi^2/2}H(\xi)$$

for some function H which respects the asymptotic behavior at large arguments. Substituting our candidate back in, we get:

$$\frac{d^2H}{d\xi^2} - 2\xi \frac{dH}{d\xi} + (\lambda - 1)H = 0$$

This is a well-studied equation called the Hermite equation. The solutions for H are called the Hermite polynomials. Let's solve by power-series expansion. Since the parity of $\Psi(x)$ is definite for a symmetric potential and the Gaussian is even, $H(\xi)$ must also have definite parity. First look at the even solutions

$$H(\xi) = \sum_{\ell=0}^{\infty} c_{\ell} \xi^{2\ell}$$

where $c_0 \neq 0$. Substituting into the equation, we have:

$$\begin{aligned} \sum_{\ell=0}^{\infty} [(2\ell)(2\ell-1)c_{\ell}\xi^{2(\ell-1)} + (\lambda - 1 - 4\ell)c_{\ell}\xi^{2\ell}] &= 0 \\ \sum_{\ell=0}^{\infty} [2(\ell+1)(2\ell+1)c_{\ell+1} + (\lambda - 1 - 4\ell)c_{\ell}]\xi^{2\ell} &= 0 \\ 2(\ell+1)(2\ell+1)c_{\ell+1} + (\lambda - 1 - 4\ell)c_{\ell} &= 0 \\ c_{\ell+1} &= \frac{(4\ell+1-\lambda)}{2(\ell+1)(2\ell+1)}c_{\ell} \end{aligned}$$

But we still need c_0 and we are unsure if this series even converges. By the ratio test, let's look at:

$$\lim_{\ell \rightarrow \infty} \frac{c_{\ell+1}}{c_{\ell}} = \lim_{\ell \rightarrow \infty} \frac{(4\ell+1-\lambda)}{2(\ell+1)(2\ell+1)} \sim \frac{1}{\ell}$$

What if H were an exponential? Then:

$$e^{\xi^2} = \sum_{\ell} \frac{(\xi^2)^{\ell}}{\ell!} \implies \frac{c_{\ell+1}}{c_{\ell}} = \frac{1}{\ell}$$

But this would diverge the wave function! $\Psi \sim e^{\xi^2} \xi^p e^{-\xi^2/2}$ so $\Psi \sim \xi^p e^{\xi^2/2}$ which is non-normalizable. Let the highest power be ξ^{2N} where $N = 0, 1, 2, \dots$. This means $c_N \neq 0$ but $c_{N+1} = 0$, which means the rest of the terms are 0. This means:

$$4(N+1) + 1 - \lambda = 0 \implies \lambda = 4N + 1$$

$\lambda = 1, 5, 9, \dots$, so energy is quantized!

For the odd solution, we could do exactly the same thing, just for the odd power series instead. Here is the flow:

1. Make a power series: $d_0 \neq 0$

$$\sum_{\ell=0}^{\infty} d_{\ell} \xi^{2\ell+1}$$

2. Find a recurrence relation:

$$d_{\ell+1} = \frac{4\ell+3-\lambda}{2(\ell+1)(2\ell+3)}$$

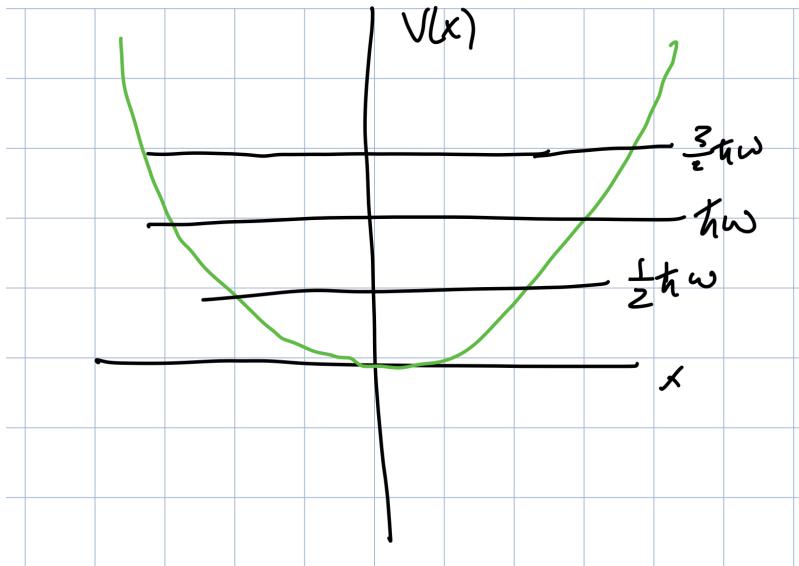
3. Solve for

$$\lambda = 4N + 3, \lambda = 3, 7, 11, \dots$$

Together, λ can quantized be any odd natural. So for any $n = 0, 1, 2, \dots$:

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

Let's take a look at the energy spectrum.



Note that the minimum energy is not 0, this would violate Heisenberg Uncertainty Principle. In fact, any oscillatory mode must have some minimum energy. The vacuum has some (tiny) energy always! This is called “zero-point motion”.

Furthermore, the levels are equally spaced.

14 Lecture 14: Quantum Harmonic Oscillator, Dirac Notation

Recall that from last lecture, we found the general wavefunction as:

$$\Psi_n(\xi) = e^{-\xi^2/2} H_n(\xi)$$

where $\xi = \alpha x$, $\alpha = (\frac{m\omega}{\hbar})^{1/2}$ and H_n is the n th Hermite polynomial. There are two ways to get these polynomials: either use a table or a generating function. Here are the first few:

$$H_0(\xi) = 1$$

$$H_1(\xi) = 2\xi$$

$$H_2(\xi) = 4\xi^2 - 2$$

$$H_3(\xi) = 8\xi^3 - 12\xi$$

$$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$$

⋮

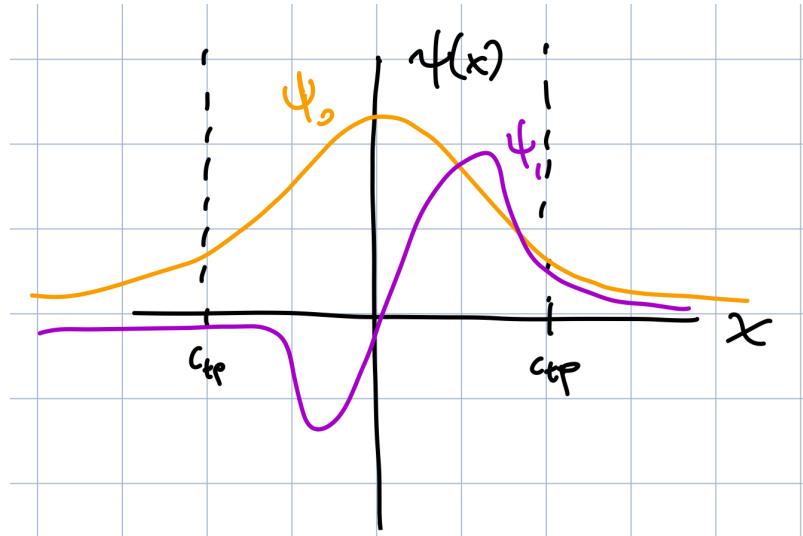
$$\begin{aligned} H_n(\xi) &= (-1)^n e^{\xi^2} \frac{d^n e^{-\xi^2}}{d\xi^n} \\ &= e^{\xi^2/2} \left(\xi - \frac{d}{d\xi} \right)^n e^{-\xi^2/2} \end{aligned}$$

This means the wave function is:

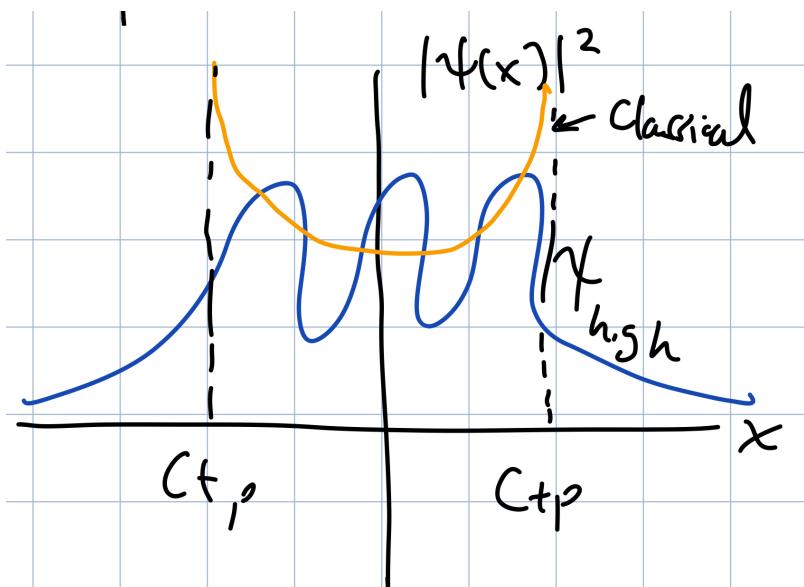
$$\Psi_n(x) = \left(\frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{1/2} e^{-\alpha^2 x^2/2} H_n(\alpha x)$$

with $E_n = (n + 1/2)\hbar\omega$ (as we remember from last time).

This is what they look like, marking the “classical turning points” of a particle as ctp:



In a classical setting, a particle in an oscillator will spend most of its time near the ends. But the probability density of a high-energy wave looks like this:



14.1 Dirac Notation

Now, having this wavefunction representation is really useful for plotting and visualizing the wave function. But, we would like to do algebra on this object. So, we identify vectors and their adjoints as:

$$\Psi(x) \leftrightarrow \langle \Psi |, \Psi^*(x) \leftrightarrow | \Psi \rangle$$

To write an inner product, we say:

$$\langle \Psi | \Psi \rangle = \int \Psi^* \Psi dx$$

Schrodinger's equation now becomes:

$$\hat{H} |\Psi_E\rangle = E |\Psi_E\rangle$$

And now to denote the expectation value, we write

$$\langle x \rangle_\Psi = \langle \Psi | \hat{x} | \Psi \rangle$$

Definition 14.1 (Adjoint)

The adjoint of an operator \hat{A} is \hat{A}^\dagger such that:

$$\langle \hat{A}x, y \rangle = \langle x, \hat{A}^\dagger y \rangle$$

Hermitian, or self-adjoint operator corresponds to some observable because it has real eigenvalues.

14.2 Revisiting the QHM

Now, let us try to make an operator that transitions between our QHM eigenstates. Define the state step up and down operator:

$$\hat{a}_\pm = \frac{1}{\sqrt{2}} \left[\left(\frac{m\omega}{\hbar} \right)^{1/2} \hat{x} \mp i \frac{\hat{p}_x}{(m\hbar\omega)^{1/2}} \right]$$

Note that the two operators adjoints are exactly each other.

$$\hat{a}_+^\dagger = \hat{a}_-$$

Furthermore their commutator $[\hat{a}_-, \hat{a}_+] = 1$. This means

$$\begin{aligned} \hat{H} &= \frac{\hat{p}_x^2}{2m} + \frac{1}{2} m \omega^2 x \\ &= \frac{\hbar\omega}{2} (\hat{a}_- \hat{a}_+ + \hat{a}_+ \hat{a}_-) \\ &= \hbar\omega \left(\hat{a}_- \hat{a}_+ - \frac{1}{2} \right) \\ &= \hbar\omega \left(\hat{a}_+ \hat{a}_- + \frac{1}{2} \right) \end{aligned}$$

This means that if we define $\hat{N} = \hat{a}_+ \hat{a}_-$, it is the number operator, which is exactly equivalent to our length Hermite derivation! Note that from the above statement, the commutator

$$[\hat{H}, \hat{a}_\pm] = \pm \hbar\omega \hat{a}_\pm$$

What is $\hat{a}_\pm |E\rangle$? Well we can act \hat{H} on this, so:

$$\begin{aligned} \hat{H} \hat{a}_\pm |E\rangle &= (\hat{a}_\pm \hat{H} \pm \hbar\omega \hat{a}_\pm) |E\rangle \\ &= (E \pm \hbar\omega) \hat{a}_\pm |E\rangle \end{aligned}$$

So this operator adds or subtracts a quantum of energy.

15 Lecture 15: Dirac Notation, continued

We saw last time how dirac notation of bras and kets can be useful. We saw that we can represent the vector $\Psi_n(x)$ however we want:

$$\Psi_n(x) \leftrightarrow |n\rangle, |E\rangle, |E_n\rangle, |\Psi_n\rangle$$

Recall that we defined operators:

$$\hat{a}_{\pm} = \frac{1}{\sqrt{2}} \left[\left(\frac{m\omega}{\hbar} \right)^{1/2} \hat{x} \mp i \frac{\hat{p}_x}{(m\hbar\omega)^{1/2}} \right]$$

In fact, this ladder operator can always be written with any Fourier pair of operators (instead of \hat{x}, \hat{p}).

We said that $\hat{H} = \hbar\omega(\hat{N} + \frac{1}{2})$. We also have:

$$\hat{a}_- |E_0\rangle = 0$$

because acting on the ground state should annihilate it. Now acting with $\hbar\omega\hat{a}_+$ on the left:

$$\begin{aligned} \hbar\omega\hat{a}_+\hat{a}_- |E_0\rangle &= 0 \\ \hbar\omega \left(\frac{\hat{H}}{\hbar\omega} - \frac{1}{2} \right) |E_0\rangle &= 0 \\ \left(\hat{H} - \frac{1}{2}\hbar\omega \right) |E_0\rangle &= 0 \\ \hat{H} |E_0\rangle &= \left(\frac{1}{2}\hbar\omega \right) |E_0\rangle \end{aligned}$$

this means we know the energy of the ground state is $\frac{1}{2}\hbar\omega$. Furthermore, suppose we want the raising operator to increase the energy with

$$|E_{n+1}\rangle = c_{n+1}\hat{a}_+ |E_n\rangle$$

To satisfy normalization we need $\langle E_{n+1}|E_{n+1}\rangle = 1$.

$$\begin{aligned} \langle E_{n+1}|E_{n+1}\rangle &= (c_{n+1}^* \hat{a}_+^\dagger \langle E_n|)(c_{n+1} \hat{a}_+ |E_n\rangle) \\ 1 &= |c_{n+1}|^2 \langle E_n| \hat{a}_+^\dagger \hat{a}_- |E_n\rangle \\ 1 &= |c_{n+1}|^2 \langle E_n| \hat{a}_- \hat{a}_+ |E_n\rangle \\ 1 &= |c_{n+1}|^2 \langle E_n| (\hat{N} + 1) |E_n\rangle \\ 1 &= |c_{n+1}|^2 (n + 1) \langle E_n|E_n\rangle \\ c_{n+1} &= \frac{1}{\sqrt{n+1}} \end{aligned}$$

We take c_{n+1} real for simplicity. So:

$$\hat{a}_+ |E_n\rangle = \sqrt{n+1} |E_{n+1}\rangle$$

And similarly,

$$\hat{a}_- |E_n\rangle = \sqrt{n} |E_{n-1}\rangle$$

Chaining together reveals:

$$|E_n\rangle = \frac{1}{\sqrt{n!}} \hat{a}_+^n |E_0\rangle$$

Let's write \hat{x} and \hat{p} as:

$$\hat{x} = \left(\frac{\hbar}{2m\omega} \right)^{1/2} (\hat{a}_+ + \hat{a}_-)$$

Suppose we wanted to calculate

$$\langle E_0 | \hat{x}^4 | E_0 \rangle = \frac{\hbar^2}{4m^2\omega^2} \langle E_0 | \hat{a}_+^4 + \hat{a}_+^3\hat{a}_- + \dots + \hat{a}_-^4 | E_0 \rangle$$

Since all the states are orthogonal, any raising and lowering will cancel with the $\langle E_0 |$. Thus, only the terms with the same amount of raising and lowering remain.

$$\langle E_0 | \hat{x}^4 | E_0 \rangle = \frac{\hbar^2}{4m^2\omega^2} \langle E_0 | \hat{a}_-\hat{a}_+\hat{a}_-\hat{a}_+ + \hat{a}_-\hat{a}_-\hat{a}_+\hat{a}_+ | E_0 \rangle$$

One can then apply the raising and lowering rules to find the final value.

16 Lecture 16: QHO from Dirac Notation, Quantum Postulates

Let's choose a basis $\{|n\rangle\}_{n=0}^{\infty}$ for our transforms. We will define the infinite matrix:

$$[\hat{H}]_{ij} = \begin{bmatrix} \hbar\omega/2 & 0 & \dots \\ 0 & 3\hbar\omega/2 & \dots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

Because the matrix element $\langle i | \hat{H} | j \rangle = 0$ when $i \neq j$ and $\langle i | \hat{H} | i \rangle = E_i$. It's very obvious that this matrix will be diagonal because we chose the eigenbasis. Let's write down the matrices for \hat{a}_+ and \hat{a}_-

$$\begin{aligned} [\hat{a}_+]_{kn} &= \sqrt{n+1} \delta_{k,n+1} \\ [\hat{a}_-]_{kn} &= \sqrt{k+1} \delta_{k+1,n} \end{aligned}$$

So for example the \hat{a}_+ operator looks like:

$$[\hat{a}_+] = \begin{bmatrix} 0 & 0 & 0 & 0 & \dots \\ \sqrt{1} & 0 & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & 0 & \dots \\ 0 & 0 & \sqrt{3} & 0 & \dots \\ \vdots & \vdots & \vdots & \ddots & \end{bmatrix}$$

Remember the zero-indexing!

Now, we return to our dimensionless variable $\xi = (\frac{m\omega}{\hbar})^{1/2}x = \alpha x$. Then our operators are:

$$\hat{a}_{\pm} = \frac{1}{\sqrt{2}} \left(\xi \mp \frac{d}{d\xi} \right)$$

We know by the annihilation of the ground state:

$$\begin{aligned} \hat{a}_- |0\rangle &= 0 \\ \left(\xi + \frac{d}{d\xi} \right) \Psi_0(\xi) &= 0 \\ \Psi_0(\xi) &= \left(\frac{\alpha}{\sqrt{\pi}} \right)^{1/2} e^{-\xi^2/2} \end{aligned}$$

Applying the raising operator n times:

$$\Psi_n(\xi) = \frac{1}{\sqrt{n!}} \left[\frac{1}{\sqrt{2}} \left(\xi - \frac{d}{d\xi} \right) \right]^n \Psi_0(\xi)$$

which is exactly the generating function we derived for Hermite polynomials!

16.1 The Fundamental Postulates of Quantum Mechanics

We now precisely define the assumptions of quantum mechanics. There are chiefly 8 of these postulates:

1. To an ensemble of physical systems (a bunch of identical copies of the same system), one can assign a wavefunction Ψ which contains all the information that can be known about the ensemble.

For example take a system of N particles. Then we have a function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, then $\Psi^* \Psi$ is the probability to find particle 1 at \mathbf{r}_1 , particle 2 at \mathbf{r}_2 , etc.

In general, Ψ is complex.

2. The superposition principle.

If Ψ_1, Ψ_2 are solutions, then $\Psi = c_1\Psi_1 + c_2\Psi_2$ is a solution.

3. With every dynamical variable \mathcal{A} there is an associated linear operator \hat{A} .

For example, in position space $\mathcal{A} = \hat{A}(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N, t)$.

4. The result of an infinitely precise measurement of \mathcal{A} is one of the eigenvalues of \hat{A} . Upon instantaneous remeasurement of the operator, the measurement is that same eigenvalue.

$$\hat{A} |\Psi_n\rangle = a_n |\Psi_n\rangle$$

If \hat{A} is Hermitian, $a_n \in \mathbb{R}$.

5. If a series of measurements are made on \hat{A} , the result is called the expectation value:

$$\langle \hat{A} \rangle = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Note that $\langle \hat{A} \rangle$ is not the average of a classical statistical distribution.

6. A wavefunction representing any dynamical state can be expressed as a linear combination of the eigenstates of an operator \hat{A} .

$$|\Psi\rangle = \sum_n c_n |\Psi_n\rangle$$

7. The time evolution of a system is given by the time-dependent Schrodinger equation:

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

Some notes surrounding the discussion of the postulates.

Quantum vs Classical uncertainty: In a classical setup, the apparatus gives you some kind of uncertainty, i.e. a meterstick with not enough lines. The value is still a fixed, deterministic quantity. The expectation value is not sharp because there is actually a probability of being in one state or the other, and such "uncertainty" is irreducible.

17 Lecture 17: Operator Properties

Recall that $|\Psi\rangle$ is a state vector and $\langle\Psi|$ is its adjoint. Furthermore, recall the adjoint of an operator, where if

$$|\phi\rangle = \hat{A} |x\rangle$$

then

$$\langle\phi| = \langle x| \hat{A}^\dagger$$

Note 17.1 (Adjoint/Inner product properties)

Here are some properties of the inner product.

$$\langle\Psi_1|\Psi_2\rangle = \int \Psi_1^*(\mathbf{r})\Psi_2(\mathbf{r})$$

$$\langle\Psi_1|\Psi_2\rangle^* = \langle\Psi_2|\Psi_1\rangle$$

$$\langle\Psi_1|c\Psi_2\rangle = c \langle\Psi_1|\Psi_2\rangle$$

$$\langle c\Psi_1|\Psi_2\rangle = c^* \langle\Psi_1|\Psi_2\rangle$$

For orthonormal Ψ_1, Ψ_2 ,

$$\langle\Psi_1|\Psi_2\rangle = \delta_{12}$$

Also, taking the adjoint of a scalar function is just:

$$f(\hat{A})^\dagger = f^*(\hat{A}^\dagger)$$

Definition 17.1 (Inverses/Identity)

The identity operator is defined as

$$\hat{I} |\Psi\rangle = |\Psi\rangle$$

If $\hat{B}\hat{A} = \hat{A}\hat{B} = \hat{I}$, then $\hat{B} = \hat{A}^{-1}$.

Then we can also define a unitary operator.

Definition 17.2 (Unitary Operator)

A linear operator is said to be unitary if $\hat{U}^{-1} = \hat{U}^\dagger$, i.e.

$$\hat{U}\hat{U}^\dagger = \hat{U}^\dagger\hat{U} = \hat{I}$$

These can be said to be like rotations: they do not change things like commutators, inner products, and all the physics we have done until this point.

Definition 17.3 (Projection Operator)

The projection operator $\hat{\Lambda}$ does the following. If we have $|\Psi\rangle = |\phi\rangle + |x\rangle$, then

$$|\phi\rangle = \hat{\Lambda} |\Psi\rangle, |x\rangle = (\hat{I} - \hat{\Lambda}) |\Psi\rangle$$

Here is an incredibly useful theorem. It uses the sum of an outer product $|u\rangle\langle v|$.

Theorem 17.1

The following is true:

$$\sum_n |\Psi_n\rangle \langle \Psi_n| = \hat{I}$$

Proof

$$\begin{aligned} |\Psi\rangle &= \sum_n c_n |\Psi_n\rangle \\ \langle \Psi_m | \Psi \rangle &= \sum_n c_n \langle \Psi_m | \Psi_n \rangle = c_m \\ \Psi(\mathbf{r}, t) &= \sum_n \int \Psi_n^*(\mathbf{r}') \Psi(\mathbf{r}', t) \Psi_n(\mathbf{r}) d\mathbf{r}' \\ \Psi(\mathbf{r}, t) &= \int \Psi(\mathbf{r}', t) \left(\sum_n \Psi_n^*(\mathbf{r}') \Psi_n(\mathbf{r}) \right) d\mathbf{r}' \end{aligned}$$

So we must have $\sum_n \Psi_n^*(\mathbf{r}') \Psi_n(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}')$, since it acts like a delta under the integral sign.
Note that

$$\begin{aligned} \langle x | \Psi \rangle &= \int x^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) d\mathbf{r} \\ \langle x | \Psi \rangle &= \int \int x^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) \delta(\mathbf{r} - \mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ \langle x | \Psi \rangle &= \sum_n \int x^*(\mathbf{r}, t) \Psi_n(\mathbf{r}) d\mathbf{r} \int \Psi_n^*(\mathbf{r}') \Psi(\mathbf{r}', t) d\mathbf{r}' \\ \langle x | \Psi \rangle &= \sum_n \langle x | \Psi_n \rangle \langle \Psi_n | \Psi \rangle \\ \langle x | \Psi \rangle &= \langle x | \left(\sum_n |\Psi_n\rangle \langle \Psi_n| \right) |\Psi\rangle \end{aligned}$$

The only operator that always satisfies this is the identity, so $\sum_n |\Psi_n\rangle \langle \Psi_n| = \hat{I}$.

18 Lecture 18: Calculations with Dirac Notation

Suppose you want to find the expectation value of some operator:

$$\langle \hat{A} \rangle_{\Psi} = \langle \Psi | \hat{A} | \Psi \rangle$$

We know if $|\Psi\rangle = |\Psi_a\rangle$, then it's easy to act \hat{A} on $|\Psi\rangle$ with a decomposition.

$$|\Psi\rangle = \sum_n c_n |\Psi_n\rangle, \langle \Psi | = \sum_m c_m^* \langle \Psi_m |$$

So:

$$\begin{aligned} \langle \hat{A} \rangle_{\Psi} &= \sum_{m,n} c_m^* c_n \langle \Psi_m | \hat{A} | \Psi_n \rangle \\ &= \sum_{m,n} c_m^* c_n a_n \langle \Psi_m | \Psi_n \rangle \\ &= \sum_m \sum_n c_m^* c_n a_n \delta_{mn} \\ &= \sum_n |c_n|^2 a_n \end{aligned}$$

Where again $|c_n|^2$ is the probability you are in state n . This means that $\sum_n |c_n|^2 = 1$.

Suppose you have degeneracy, where there are multiple linearly independent Ψ such that they have the same eigenvalue a_n . We index them $\Psi_{n,1}, \Psi_{n,2}, \dots$. If it is α times degenerate, then Ψ_{nr} ranges from $r = 1, \dots, \alpha$. The probability to observe a_n is:

$$P_n = \sum_{r=1}^{\alpha} |c_{nr}|^2 = \sum_{r=1}^{\alpha} |\langle \Psi_{nr} | \Psi \rangle|^2$$

After measurement

$$|\Psi\rangle_{\text{after}} = \sum_{r=1}^{\alpha} c_{nr} |\Psi_{nr}\rangle$$

this quantum effect is called entanglement of measurement.

You can be in a superposition of continuum and bound state. The most general state is:

$$|\Psi\rangle = \sum_n c_n |\Psi_n\rangle + \int c(a) |\Psi_a\rangle da$$

Remember that for wave packets, $c(a)$ would be the Fourier transform $\phi(k)$ of the wave packet, and $|\Psi_a\rangle$ was the basis of plane waves. In this way, we can find:

$$\langle \hat{A} \rangle_{\Psi} = \sum_n |c_n|^2 a_n + \int |c(a)|^2 a da$$

18.1 Commuting Operators

\hat{A}, \hat{B} "commute" if $[\hat{A}, \hat{B}] = 0$. This also means that there exists a common set of eigenfunctions for both of them, $\{|\Psi_n\rangle\}$, where

$$\hat{A} |\Psi_n\rangle = a_n |\Psi_n\rangle, \hat{B} |\Psi_n\rangle = b_n |\Psi_n\rangle$$

Recall for the free particle:

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

So this means that $[\hat{H}, \hat{p}] = 0$ (just express everything in terms of \hat{p}). We found in the past a common eigenbasis for them, the plane wave basis $|\Psi_k\rangle = e^{ikx}$.

$$\hat{p} |\Psi_k\rangle = \hbar k |\Psi_k\rangle, \hat{H} |\Psi_k\rangle = \frac{\hbar^2 k^2}{2m} |\Psi_k\rangle$$

18.2 Formalizing Heisenberg Uncertainty

Define

$$\begin{aligned}\delta \hat{A} &= [\langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle]^{1/2} \\ &= \sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2}\end{aligned}$$

Then we can state the formal version of Heisenberg Uncertainty:

Theorem 18.1 (Heisenberg Uncertainty Principle)

For any two operators \hat{A}, \hat{B} we have:

$$\delta \hat{A} \delta \hat{B} \geq \frac{1}{2} |\langle [\hat{A}, \hat{B}] \rangle|$$

18.3 Unitary Transforms

Suppose you have

$$\hat{A} |\Psi\rangle = |x\rangle$$

for some linear Hermitian operator \hat{A} . Consider \hat{U} unitary. Define $|\Psi'\rangle = \hat{U} |\Psi\rangle$. Then:

$$|x'\rangle = \hat{U} |x\rangle = \hat{U} \hat{A} |\Psi\rangle = \hat{U} \hat{A} \hat{U}^\dagger |\Psi'\rangle$$

This means if we want an \hat{A}' to transform vectors in that other basis, it is just $\hat{U} \hat{A} \hat{U}^\dagger$. Or in other words, $\hat{A} = \hat{U}^\dagger \hat{A}' \hat{U}$.

We have now the following facts about Unitary transforms, which correspond well to a physical change of coordinates.

- If \hat{A} is Hermitian, then \hat{A}' is Hermitian.
- Operator equations are unchanged,

$$\hat{A} = c_1 \hat{B} + c_2 \hat{C} \hat{D} \implies \hat{A}' = c_1 \hat{B}' + c_2 \hat{C}' \hat{D}'$$

- The eigenfunctions and eigenvalues of \hat{A}' and \hat{A} are the same.
- Matrix elements are unchanged, e.g. $\langle x | \hat{A} | \Psi \rangle = \langle x' | \hat{A}' | \Psi' \rangle$.

Theorem 18.2

In fact, can always express a unitary \hat{U} in terms of any Hermitian operator \hat{A}

$$\hat{U} = e^{i\hat{A}} = \sum_{j=0}^{\infty} \frac{(i\hat{A})^j}{j!}$$

\hat{A} is dubbed the generator of the Unitary.

Proof 18.1 (Heuristic)

Why is this true? Well, consider an infinitesimal unitary operator

$$\hat{U} = e^{i\hat{F}} \approx \hat{I} + i\epsilon\hat{F}$$

for some small $\epsilon > 0$. Then take some function

$$|\Psi'\rangle = |\Psi\rangle + |\delta\Psi\rangle$$

where $|\delta\Psi\rangle = i\epsilon\hat{F}|\Psi\rangle$.

Now take some operator:

$$\begin{aligned}\hat{A}' &= \hat{A} + \delta\hat{A} \\ &= \hat{U}\hat{A}\hat{U}^\dagger \\ &= \hat{A} + i\epsilon\hat{F}\hat{A} - i\epsilon\hat{A}\hat{F} + O(\epsilon^2)\end{aligned}$$

This means $\delta A = i\epsilon[\hat{F}, \hat{A}]$.

19 Lecture 19: Unitary Change of Bases, Angular Momentum

Suppose you have some unitary time evolution, $\hat{U}(t, t_0)$ that advances the system from $t = t_0$ to $t = t$. Clearly $\hat{U}(t_0, t_0) = \hat{I}$.

$$|\Psi(t)\rangle = \hat{U}(t, t_0) |\Psi(0)\rangle$$

Consider that $\hat{U}^{-1}(t, t_0) = \hat{U}(t_0, t)$. We know for time elements: $\hat{U}(t, t_0) = \hat{U}(t, t')\hat{U}(t', t_0)$.

Note the Schrodinger Equation becomes:

$$i\hbar \frac{\partial \hat{U}}{\partial t} = \hat{H}\hat{U}(t, t_0)$$

By formal integration, the solution is simply:

$$\hat{U}(t, t_0) = \hat{I} - \frac{i}{\hbar} \int_{t_0}^t \hat{H}\hat{U}(t', t_0) dt'$$

Consider the first order behavior for a small timestep δt .

$$\begin{aligned} i\hbar [\hat{U}(t_0 + \delta t, t_0) - \hat{U}(t_0, t_0)] &= \hat{H}\hat{U}(t_0, t_0)\delta t \\ \hat{U}(t_0 + \delta t, t_0) &= \hat{I} - \frac{i}{\hbar} \hat{H} \cdot \delta t \end{aligned}$$

this means that the Hamiltonian is the generator of time translation. Similarly, \hat{p} is the generator of space translations.

Consider a time-independent Hamiltonian. Then:

$$\begin{aligned} \frac{d}{dt} \langle \hat{A} \rangle &= \frac{d}{dt} \langle \Psi | \hat{A} | \Psi \rangle \\ &= \left\langle \frac{\partial \Psi}{\partial t} \middle| \hat{A} | \Psi \rangle + \langle \Psi | \frac{\partial \hat{A}}{\partial t} | \Psi \rangle + \langle \Psi | \hat{A} \middle| \frac{\partial \Psi}{\partial t} \right\rangle \\ &= -\frac{1}{i\hbar} \langle \hat{H}\Psi | \hat{A} | \Psi \rangle + \frac{1}{i\hbar} \langle \Psi | \hat{A} | \hat{H}\Psi \rangle + \langle \Psi | \frac{\partial \hat{A}}{\partial t} | \Psi \rangle \\ &= -\frac{1}{i\hbar} \langle \Psi | \hat{H}^\dagger \hat{A} | \Psi \rangle + \frac{1}{i\hbar} \langle \Psi | \hat{A} \hat{H} | \Psi \rangle + \langle \Psi | \frac{\partial \hat{A}}{\partial t} | \Psi \rangle \\ &= \frac{1}{i\hbar} \langle [A, H] \rangle + \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle \end{aligned}$$

In the special case of an time-independent \hat{A} , then

$$\frac{d}{dt} \langle \hat{A} \rangle = \frac{1}{i\hbar} \langle [\hat{A}, \hat{H}] \rangle$$

If \hat{A} commutes with \hat{H} , then \hat{A} is a constant of motion, e.g. conserved.

19.1 Angular Momentum

We know in classical mechanics, $\mathbf{L} = \mathbf{r} \times \mathbf{p}$:

$$\begin{aligned} L_x &= yp_z - zp_y \\ L_y &= zp_x - xp_z \\ L_z &= xp_y - yp_x \end{aligned}$$

Turning these into Quantum mechanic operators:

$$\begin{aligned}\hat{L}_x &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ \hat{L}_y &= -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\ \hat{L}_z &= -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)\end{aligned}$$

which can be succinctly written as $\hat{\mathbf{L}} = -i\hbar(\mathbf{r} \times \nabla)$. Do the components commute?

$$\begin{aligned}[\hat{L}_x, \hat{L}_y] &= [yp_z - zp_y, zp_x - xp_z] \\ &= [yp_z, zp_x] + [zp_y, xp_z] - [yp_z, xp_z] - [zp_y, zp_x]\end{aligned}$$

Consider the first term:

$$[yp_z, zp_x] = yp_z zp_x - zp_x yp_z = yp_x [p_z, z] = -i\hbar y p_x$$

because any momentums in orthogonal directions commute and any spacial coordinates in orthogonal directions commute. We can resolve the rest of the components similarly.

$$\begin{aligned}[\hat{L}_x, \hat{L}_y] &= i\hbar(xp_y - yp_x) \\ &= i\hbar \hat{L}_z\end{aligned}$$

Similarly, $[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x$ and $[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$. So you cannot know all three components simultaneously! However, we can know the length.

$$\begin{aligned}[L^2, L_x] &= [L_x^2 + L_y^2 + L_z^2, L_x] \\ &= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x] \\ &= 0 + L_y [L_y, L_x] + [L_y, L_x] L_y + L_z [L_z, L_x] + [L_z, L_x] L_z \\ &= -i\hbar (L_y L_z - L_z L_y) + i\hbar (L_y L_z - L_z L_y) \\ &= 0\end{aligned}$$

So we can write a simultaneous eigenbasis for both the quantities.

Note that the vector cannot point towards \hat{z} , because then you would know \hat{L}_x and \hat{L}_y . $|\hat{L}|$ must be at least $\hbar \hat{L}_z$ in order to satisfy the uncertainty relation.

20 Lecture 20: Angular Momentum, Part 2

It is obvious that:

$$[\hat{p}_i, \hat{p}_j] = i\hbar\delta_{ij}, [\hat{x}_i, \hat{x}_j] = [\hat{p}_i, \hat{p}_j] = 0$$

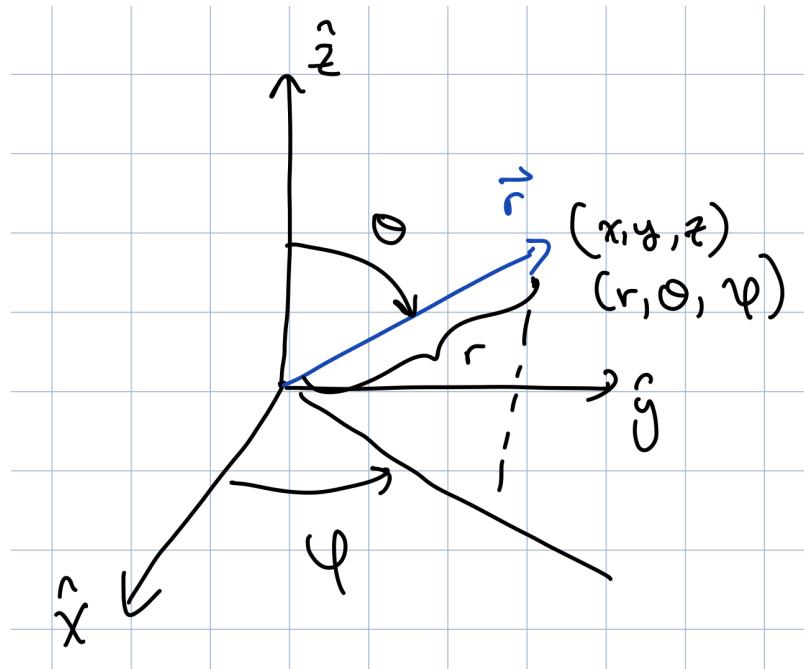
We showed last time that:

$$[\hat{L}_i, \hat{L}_j] = i\hbar\hat{L}_k\delta_{ij}, [\hat{L}^2, \hat{L}_z] = 0$$

We typically describe the state with two quantum numbers:

$$\hat{L}^2, \hat{L}_z \rightarrow |\ell m\rangle$$

Use a right-handed coordinate system to define polar coordinate system.



The ranges of these coordinates are:

$$(r, \theta, \varphi) \in [0, \infty] \times [0, \pi] \times [0, 2\pi]$$

The angular momentum operators look like:

$$\begin{aligned}\hat{L}_x &= -i\hbar \left(-\sin \varphi \frac{\partial}{\partial \theta} - \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \\ \hat{L}_y &= -i\hbar \left(-\cos \varphi \frac{\partial}{\partial \theta} - \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \\ \hat{L}_z &= -i\hbar \frac{\partial}{\partial \varphi} \\ \hat{L}^2 &= -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]\end{aligned}$$

where notice r is missing, i.e.:

$$[\hat{L}_i, f(r)] = 0$$

Theorem 20.1 (Generators of Rotations)

To generate a finite rotation α about a unit vector \hat{n} :

$$\hat{U}_{\hat{n}}(\alpha) = \exp\left(-\frac{i}{\hbar}\alpha\hat{n} \cdot \hat{L}\right)$$

To generate an infinitesimal rotation $\delta\alpha$, we can linearize to:

$$\hat{U}_{\hat{n}}(\delta\alpha) = \hat{I} - \frac{i}{\hbar}\delta\alpha\hat{L}_z$$

20.1 Eigenfunctions and Eigenvalues of Angular Momentum

Niels Bohr told us that angular momentum was quantized for atomic orbitals, i.e. $mvr = n\hbar$ for mass m and integral n

Call an eigenfunction of the \hat{L}_z operator: $\Phi_m(\varphi)$ with eigenvalue $m\hbar$.

$$\hat{L}_z\Phi_m(\varphi) = m\hbar\Phi_m(\varphi)$$

This yields a differential equation:

$$\begin{aligned} -i\frac{\partial}{\partial\varphi}\Phi_m(\varphi) &= m\Phi_m(\varphi) \\ \Phi_m(\varphi) &= \frac{1}{\sqrt{2\pi}} \end{aligned}$$

A clear boundary condition is:

$$\begin{aligned} \Phi_m(2\pi + \varphi) &= \Phi_m(\varphi) \\ e^{2\pi im} &= 1 \\ m &\in \mathbb{Z} \end{aligned}$$

So angular momentum must be quantized! Furthermore, Φ_m form a complete orthonormal basis for functions of φ .

$$f(\varphi) = \sum_{m \in \mathbb{Z}} a_m \Phi_m(\varphi)$$

Employing Fourier's trick:

$$a_m = \int_0^{2\pi} \Phi_m^*(\varphi) f(\varphi) d\varphi$$

Call a separable eigenfunction of the \hat{L}^2 as $Y_{\ell m}(\theta, \varphi) = \Theta_{\ell m}(\theta)\Phi_m(\varphi)$, the spherical harmonic. Note that this is also an eigenfunction for \hat{L}_z .

21 Lecture 21: Angular Momentum, Part 3

As we did last time, call a separable eigenfunction of the \hat{L}^2 as $Y_{\ell m}(\theta, \varphi) = \Theta_{\ell m}(\theta)\Phi_m(\varphi)$, the spherical harmonic. Note that this is also an eigenfunction for \hat{L}_z . We can call the eigenvalue a , but calling it $\ell(\ell + 1)\hbar^2$ makes our life easier (and makes ℓ integer-valued). The eigenequation writes

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

Solving this is hard, but we shall do it:

$$\begin{aligned} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] Y_{\ell m}(\theta, \varphi) &= -\ell(\ell + 1) Y_{\ell m}(\theta, \varphi) \\ \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \left[\ell(\ell + 1) - \frac{m^2}{\sin^2 \theta} \right] \right] Y_{\ell m}(\theta, \varphi) \Theta_{\ell m}(\theta) &= 0 \end{aligned}$$

where this is because $Y = \Theta\Phi$. Let $w = \cos \theta$ and $F_{\ell m}(w) = \Theta_{\ell m}(\theta)$.

$$\left[(1 - w^2) \frac{d^2}{dw^2} - 2w \frac{d}{dw} + \ell(\ell + 1) - \frac{m^2}{1 - w^2} \right] F_{\ell m}(w) = 0$$

Let's start with $m = 0$, which is no angular momentum in the z .

$$\left[(1 - w^2) \frac{d^2}{dw^2} - 2w \frac{d}{dw} + \ell(\ell + 1) \right] F_{\ell 0}(w) = 0$$

This is a well-known equation called the Legendre equation. Their solutions are the Legendre polynomials P_ℓ . These are not necessary to know by heart, but are useful to look up.

$$\begin{aligned} P_0(w) &= 1 \\ P_1(w) &= w \\ P_2(w) &= \frac{1}{2}(3w^2 - 1) \\ &\vdots \end{aligned}$$

Their generating function is:

$$P_\ell(w) = 2^{-\ell} (\ell!)^{-1} \frac{d^\ell}{dw^\ell} (w^2 - 1)^\ell$$

For general m , these are associated legendre polynomials

$$P_\ell^{|m|}(w) = (1 - w^2)^{|m|/2} \frac{d^{|m|}}{dw^{|m|}} P_\ell(w)$$

We have a restriction that $m = -\ell, -\ell + 1, \dots, \ell$. This can be seen by simplifying

$$\langle L^2 \rangle \geq \langle L_z^2 \rangle$$

This step was omitted since it was similar enough to the Hermite derivation.

This means our solution becomes:

$$\Theta_{\ell m}(\theta) = \begin{cases} (-1)^m \left[\frac{(2\ell+1)(\ell-m)!}{2(\ell+m)!} \right]^{1/2} P_\ell^m(\cos \theta) & m \geq 0 \\ (-1)^m \Theta_{\ell, -m}(\theta) & m < 0 \end{cases}$$

Eventually we yield the **Spherical Harmonics**.

$$Y_{\ell m}(\theta, \varphi) = \begin{cases} (-1)^m \left[\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!} \right]^{1/2} P_\ell^m(\cos \theta) e^{im\varphi} & m \geq 0 \\ (-1)^m Y_{\ell, -m}^*(\theta, \varphi) & m < 0 \end{cases}$$

these are the simultaneous eigenfunctions of L^2 and L_z . We only allow $\ell = 0, 1, 2, \dots$ and $m = -\ell, -\ell + 1, \dots, \ell$.

In chemistry, the magnetic quantum number ℓ determines the type of orbital. If $\ell = 0$, the orbital is s , $\ell = 1$ means p , $\ell = 2$ means d and $\ell = 3$ means f . We know there are $2\ell + 1$ values of m . Each of these corresponds to a "lobe" of the orbital. And the orbital shape is exactly the $|Y_{\ell m}|^2$!

21.1 Spherical Harmonics as a Basis

These $Y_{\ell m}$ form a orthonormal basis set, i.e.:

$$\int Y_{\ell' m'}^*(\theta, \varphi) Y_{\ell m}(\theta, \varphi) d\Omega = \delta_{\ell\ell'} \delta_{mm'}$$

where $d\Omega = \sin \theta d\theta d\varphi$. They are also complete so:

$$f(\theta, \varphi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} a_{\ell m} Y_{\ell m}(\theta, \varphi)$$

And we can recover:

$$a_{\ell m} = \int Y_{\ell m}^*(\theta, \varphi) f(\theta, \varphi) d\Omega$$

22 Lecture 22: The Harmonic Oscillator with Angular Momentum

Recall that the Hamiltonian of the Harmonic Oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$

Solving this in Cartesian coordinates gives 3 independent differential equations with solution:

$$\Psi_n \sim e^{-x^2} H_n(x)$$

But let's take an operator perspective. Recall the raising and lowering operators:

$$\hat{a}_\pm = \frac{1}{\sqrt{2}} \left(\left(\frac{m\omega}{\hbar} \right)^{1/2} \mp \frac{i\hat{p}_x}{(m\hbar\omega)^{1/2}} \right)$$

These act on the energy eigenstates by doing:

$$\begin{aligned}\hat{a}_+ |\Psi_n\rangle &= \sqrt{n+1} |\Psi_{n+1}\rangle \\ \hat{a}_- |\Psi_n\rangle &= \sqrt{n} |\Psi_{n-1}\rangle\end{aligned}$$

We can draw parallels with the angular momentum operator.

$$\begin{aligned}L_x &= y p_z - z p_y \\ L_y &= z p_x - x p_z \\ L_z &= x p_y - y p_x\end{aligned}$$

We derived last time the simultaneous eigenfunctions of \hat{L}^2, \hat{L}_z as $\Psi_{\ell m} \sim Y_{\ell m}(\theta, \varphi)$. This is how the operators act:

$$\begin{aligned}\hat{L}^2 |\ell m\rangle &= \ell(\ell+1)\hbar^2 |\ell m\rangle \\ \hat{L}_z |\ell m\rangle &= m\hbar |\ell m\rangle\end{aligned}$$

Now let's develop some ladder operators:

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$$

this is our guess—let's see how they interact.

$$\begin{aligned}[\hat{L}^2, \hat{L}_\pm] &= 0 \\ \hat{L}_\pm \hat{L}_\mp &= \hat{L}_x^2 + \hat{L}_y^2 \pm \hbar \hat{L}_z = \hat{L}^2 - \hat{L}_z^2 \pm \hbar \hat{L}_z \\ [\hat{L}_+, \hat{L}_-] &= 2\hbar \hat{L}_z \\ [\hat{L}_z, \hat{L}_\pm] &= \pm \hbar \hat{L}_\pm\end{aligned}$$

Let's try applying the operator now:

$$\begin{aligned}\hat{L}_z |\ell m\rangle &= m\hbar |\ell m\rangle \\ \hat{L}_\pm \hat{L}_z |\ell m\rangle &= \hat{L}_\pm(m\hbar |\ell m\rangle) \\ (\hat{L}_z \hat{L}_\pm \mp \hbar \hat{L}_\pm) |\ell m\rangle &= m\hbar \hat{L}_\pm |\ell m\rangle \\ \hat{L}_z \hat{L}_\pm &= (m \pm 1)\hbar \hat{L}_\pm |\ell m\rangle\end{aligned}$$

So, the raising/lowering operator increases/decreases the eigenvalue by \hbar . This means the z projection of the vector is changed.

Further,

$$\begin{aligned}\hat{L}^2 |\ell m\rangle &= \ell(\ell+1)\hbar^2 |\ell m\rangle \\ \hat{L}_\pm \hat{L}^2 |\ell m\rangle &= \ell(\ell+1)\hbar^2 \hat{L}_\pm |\ell m\rangle \\ \hat{L}^2 \hat{L}_\pm |\ell m\rangle &= \ell(\ell+1)\hbar^2 \hat{L}_\pm |\ell m\rangle\end{aligned}$$

This raising/lowering does not change the total angular momentum. Since the z component was changed but the total length was not changed, this is just an orientation change of the momentum. There is also normalization which we can omit. We can summarize this as:

Theorem 22.1

The raising and lowering operators for the z component angular momentum act as:

$$\hat{L}_\pm |\ell m\rangle = \hbar[\ell(\ell+1) - m(m \pm 1)]^{1/2} |\ell, m \pm 1\rangle$$

Note we can also write \hat{L}_x in terms of the raising/lowering:

$$\begin{aligned}\hat{L}_x &= \frac{1}{2}(\hat{L}_+ + \hat{L}_-) \\ \hat{L}_y &= \frac{1}{2i}(\hat{L}_+ - \hat{L}_-)\end{aligned}$$

But now we find the average position:

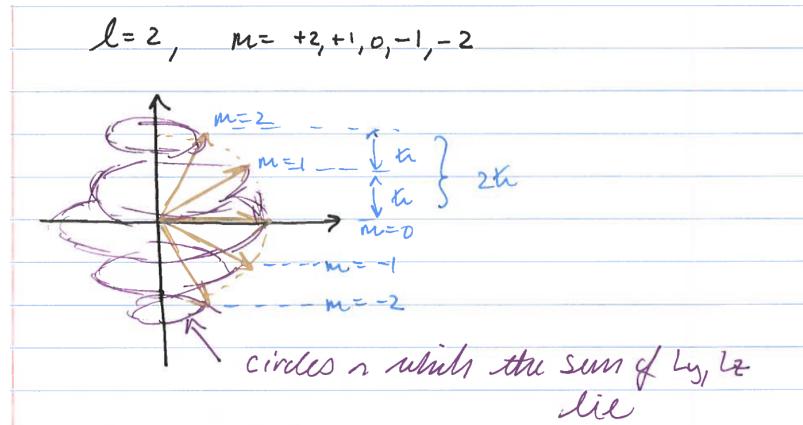
$$\begin{aligned}\langle L_x \rangle &= \langle \ell m | \hat{L}_x | \ell m \rangle \\ &= \frac{1}{2} \langle \ell m | \hat{L}_+ + \hat{L}_- | \ell m \rangle \\ &= 0\end{aligned}$$

Similarly $\langle L_y \rangle = 0$. But we think that the actual angular momentum shouldn't be identically 0. We check the expectation of its square:

$$\begin{aligned}\langle L_x^2 \rangle &= \langle L_y^2 \rangle = \frac{1}{2} \langle L^2 - L_z^2 \rangle \\ &= \frac{1}{2} (\ell(\ell+1) - m^2) \hbar^2 \geq \frac{\ell \hbar^2}{2}\end{aligned}$$

Even when you have maximum z component, $m^2 = \ell^2$, there is still a piece of the vector in other directions! To avoid violating Heisenberg uncertainty, the vector is still a bit longer than the z component.

For example take the case of $\ell = 2$. We know $m \in \{-2, -1, 0, +1, +2\}$. Note that: $|L| = \sqrt{6}\hbar$. We can then plot different vectors for different values of m .



Consider a particle of mass μ . The kinetic energy is:

$$\begin{aligned}\hat{T} &= \frac{\hat{p}^2}{2\mu} \\ &= -\frac{\hbar^2}{2\mu} \nabla^2 \\ &= -\frac{\hbar^2}{2\mu} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \varphi^2} \right) \\ &= -\frac{\hbar^2}{2\mu} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\hat{L}^2}{\hbar^2 r^2} \right)\end{aligned}$$

If we constrain the particle to live on sphere of $r = a$:

$$\begin{aligned}\hat{T} &= \frac{\hat{L}^2}{2\mu a^2} \\ &= \frac{\hat{L}^2}{2I}\end{aligned}$$

where I is the moment of inertia. Thus:

$$\hat{H} = \frac{\hat{L}^2}{2I} + \hat{V}(\theta, \varphi)$$

The simplest problem is that of the rigid rotor, when $\hat{V} = 0$.

$$\hat{H} = \frac{\hat{L}^2}{2I} \implies E_\ell = \frac{\hbar^2}{2\pi} \ell(\ell+1)$$

This immediately gives you the rotation energy of diatomic molecules.

23 Lecture 23: Generalized Angular Momentum, Spin

We wish to generalize angular momentum, not just the orbital case (which was enforced to be 2π -periodic). We'll call it \mathbf{J} . We preserve commutators but remove the original circle definition:

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

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$$

$$[\hat{J}^2, \hat{J}_z] = 0$$

which means that \hat{J}^2, \hat{J}_z have a simultaneous eigenfunctions $|jm\rangle$, where the eigenvalues are:

$$\hat{J}^2 |jm\rangle = j(j+1)\hbar^2 |jm\rangle$$

$$\hat{J}_z |jm\rangle = m\hbar |jm\rangle$$

Since $\langle \hat{J}^2 \rangle \geq \langle \hat{J}_z^2 \rangle$, this must mean:

$$j(j+1) \geq m^2$$

which characterizes the allowable values of m . We can define the raising and lowering operators similarly to last time:

$$\hat{J}_{\pm} = \hat{J}_x \pm i\hat{J}_y, \hat{J}_{\pm}^{\dagger} = \hat{J}_{\mp}$$

Finally we have:

$$\begin{aligned} [\hat{J}^2, \hat{J}_{\pm}] &= 0 \\ \hat{J}_{\pm} \hat{J}_{\mp} &= \hat{J}^2 - \hat{J}_z^2 \pm \hbar \hat{J}_z \\ [\hat{J}_+, \hat{J}_-] &= 2\hbar \hat{J}_z \\ [\hat{J}_z, \hat{J}_{\pm}] &= \pm \hbar \hat{J}_{\pm} \\ \hat{J}_{\pm} |jm\rangle &= [j(j+1) - m(m \pm 1)]^{1/2} |j, m \pm 1\rangle \end{aligned}$$

We know $j = 0, 1, 2, \dots$ since it must be a length. Call m_T the top of the ladder. We know:

$$\begin{aligned} \hat{J}_+ |jm_T\rangle &= 0 \\ \hat{J}_- \hat{J}_+ |jm_T\rangle &= 0 \\ \hat{J}^2 |jm_T\rangle - \hat{J}_z^2 |jm_T\rangle - \hbar \hat{J}_z |jm_T\rangle &= 0 \\ j(j+1)\hbar^2 - m_T^2 \hbar^2 - m_T \hbar^2 |jm_T\rangle &= 0 \\ j(j+1) &= m_T^2 + m_T \end{aligned}$$

Similarly, we can apply this at the bottom of the ladder m_B to get:

$$j(j+1) = m_B^2 - m_B$$

Equating them, we get

$$m_T^2 + m_T = m_B^2 - m_B$$

Either $m_T = -m_B$ or $m_T = m_B - 1$, discarding the second one because it's non-physical (the top of the ladder can't be below the bottom). This means that $m_T = j$ and $m_B = -j$. So $m_T - m_B = 2j$ for $j = 0, 1, 2, \dots$. But if we only care about m being integer, so we must conclude $j = 0, 1/2, 1, 3/2, \dots$: half-integer valued!

23.1 Spin Matrices

To ensure orthonormality:

$$\langle j'm'|jm\rangle = \delta_{jj'}\delta_{mm'}$$

We can work out matrix elements:

$$\begin{aligned} [\hat{J}^2]_{j'm'jm} &= \langle j'm'|\hat{J}^2|jm\rangle \\ &= j(j+1)\hbar^2\delta_{jj'}\delta_{mm'} \end{aligned}$$

Note that such a matrix is a 4-dimensional tensor, so we can't draw it out very nicely. Let's work out another one:

$$\begin{aligned} [\hat{J}_z]_{j'm'jm} &= \langle j'm'|\hat{J}_z|jm\rangle \\ &= m\hbar\delta_{jj'}\delta_{mm'} \\ [\hat{J}_{\pm}]_{j'm'jm} &= \langle j'm'|\hat{J}_{\pm}|jm\rangle \\ &= \sqrt{j(j+1)-m(m\pm 1)}^{1/2}\langle j'm'|j,m\pm 1\rangle \\ &= \sqrt{j(j+1)-m(m\pm 1)}^{1/2}\delta_{jj'}\delta_{m\pm 1,m'} \end{aligned}$$

We can find the matrix for \hat{J}_x using $\frac{1}{2}(\hat{J}_+ + \hat{J}_-)$.

Now let's take $j = 0$. Then $m = 0$, so:

$$J_x = 0, J_y = 0, J_z = 0, J^2 = 0$$

The first interesting case is $j = \frac{1}{2}$. Then: $m = \pm\frac{1}{2}$

$$\begin{aligned} \hat{J}_x &= \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ \hat{J}_y &= \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ \hat{J}_z &= \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ \hat{J}^2 &= \frac{3\hbar}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{aligned}$$

The next interesting case is $j = 1$. Then $m = 1, 0, -1$

$$\begin{aligned} \hat{J}_x &= \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \\ \hat{J}_y &= \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \\ \hat{J}_z &= \hbar \cdot \text{diag}(1, 0, -1) \\ \hat{J}^2 &= 2\hbar^2 \cdot \text{diag}(1, 1, 1) \end{aligned}$$

We can also use a block diagonal matrix formalism:

$$\begin{pmatrix} (j = 0) & & & \\ & (j = 1/2) & & \\ & & (j = 1) & \\ & & & \ddots \end{pmatrix}$$

We call these different values of j "spin-states." Spin is a fundamental vector label of a particle, that behaves like angular momentum and is intrinsic to matter (i.e. charge, mass).

24 Lecture 24: Spin

Definition 24.1 (Spin)

Elementary particles ahve an internal degree of freedom that behaves as an angular momentum and is called spin. The operator that gives you the spin of a state is $\hat{\mathbf{S}}$.

Since spin is angular momentum, we have:

$$\begin{aligned} [\hat{S}_x, \hat{S}_y] &= i\hbar \hat{S}_z \\ [\hat{S}_y, \hat{S}_z] &= i\hbar \hat{S}_x \\ [\hat{S}_z, \hat{S}_x] &= i\hbar \hat{S}_y \end{aligned}$$

Also, the simultaneous eigenbasis of \hat{S}^2, \hat{S}_z called $|sm_s\rangle = \chi_{s,m_s}$ acts

$$\begin{aligned} \hat{S}^2 |sm_s\rangle &= s(s+1)\hbar^2 |sm_s\rangle \\ \hat{S}_x |sm_s\rangle &= m_s \hbar |sm_s\rangle \end{aligned}$$

s can be $0, 1/2, 1, 3/2, \dots$. m_s has $(2s+1)$ allowed values: $(-s, -s+1, \dots, s)$. Recall the matrix representations of these operators. Let's take $s = 1$.

$$\begin{aligned} \hat{S}_z &= \hbar \begin{pmatrix} 1 & & \\ & 0 & \\ & & -1 \end{pmatrix} \\ \hat{S}^2 &= 2\hbar^2 \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix} \\ \hat{S}_{\pm} &= \hat{S}_x \pm i\hat{S}_y \end{aligned}$$

The eigenvectors in this basis are just the elementary basis vectors over \mathbb{R}^3 . The eigenvalues of \hat{S}_z are $\hbar, 0, -\hbar$ respectively. All the eigenvalues of \hat{S}^2 are $2\hbar^2$.

24.1 Wave Function with Spin

Let's add another argument to the wavefunction $\Psi(\mathbf{r}, t, \sigma)$. We can write a general state as:

$$\sum_{m_s=-s}^s \Psi_{m_s}(\mathbf{r}, t) \chi_{s, m_s}$$

Then naturally, $|\Psi_{m_s}(\mathbf{r}, t)|^2 d\mathbf{r}$ is the probability of being in a ball of volume $d\mathbf{r}$ around \mathbf{r} at time t at spin state $S_z = m_s \hbar$. Then

$$\sum_{m_s=-s}^s |\Psi_{m_s}(\mathbf{r}, t)|^2 d\mathbf{r} \neq 1$$

gives you the probability irrespective of spin (i.e. for all spins)

$$\int |\Psi_{m_s}(\mathbf{r}, t)|^2 d\mathbf{r} \neq 1$$

gives you the probability is a particle with $m_s \hbar$ at time t .

In our above discussion, we assumed that position and spin s are independent. This may not necessarily be the case (as we will see in entanglement).

24.2 Spin = 1/2

Some examples of systems with spin 1/2 are: electrons, protons, qubits. We take $s = \frac{1}{2}$, $m_s = -\frac{1}{2}, +\frac{1}{2}$. Note that the length of the vector is $\sqrt{\text{e-val of } \hat{S}^2}$. The eigenvalue $s(s+1)\hbar^2 = \frac{3}{4}\hbar^2$, so the length is $\frac{\sqrt{3}}{2}\hbar$. The z projection can be $\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$.

We can write this $\chi_{1/2,1/2}, \chi_{1/2,-1/2}$ or $|\uparrow\rangle, |\downarrow\rangle$ or $|+\rangle, |-\rangle$. In a sense, this algebra describes anything that can take two states perfectly!

$$\begin{aligned} S^2 |+\rangle &= \frac{3\hbar^2}{4} |+\rangle \\ S^2 |-\rangle &= \frac{3\hbar^2}{4} |-\rangle \\ S_z |+\rangle &= \frac{\hbar}{2} |+\rangle \\ S_z |-\rangle &= -\frac{\hbar}{2} |-\rangle \\ S_{\pm} |\mp\rangle &= \hbar |\pm\rangle \\ S_{\pm} |\pm\rangle &= 0 \\ S_x |+\rangle &= \frac{\hbar}{2} |-\rangle \\ S_y |-\rangle &= \frac{-i\hbar}{2} |+\rangle \end{aligned}$$

Let's write the matrices:

$$\begin{aligned} [S_z] &= \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ [S_x] &= \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ [S_y] &= \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \end{aligned}$$

If you have some state:

$$|\chi\rangle = a |+\rangle + b |-\rangle$$

The probability of being spin up $|a|^2$ and being spin down $|b|^2$ where:

$$|a|^2 + |b|^2 = 1$$

(this made Patrick very happy). For spin 1/2:

$$\begin{aligned} S^2 &= \frac{3}{4}\hbar^2 I \\ S_x^2 &= S_y^2 = S_z^2 = \frac{\hbar^2}{4} I \\ S_{\pm}^2 &= 0 \end{aligned}$$

Definition 24.2 (Anticommutator)

The Anticommutator for two operators \hat{A}, \hat{B} is:

$$[\hat{A}, \hat{B}]_+ = \hat{A}\hat{B} + \hat{B}\hat{A}$$

This means:

$$[S_x, S_y]_+ = 0$$

Note that the Pauli matrices (the matrices above without the \hbar) combined with the identity forms a basis for all 2 by 2 matrices.

25 Lecture 25: Conservation of Angular Momentum

Consider a particle with revolutional and spin angular momentum.

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

Note that \mathbf{L} is a function of θ, ϕ and \mathbf{S} only operators on spin variables. Thus we know $[\mathbf{L}, \mathbf{S}] = 0$. If we want a unitary transform for an angle α about an axis $\hat{\mathbf{n}}$ is:

$$\hat{U}_{\hat{\mathbf{n}}}(\alpha) = \exp\left(-\frac{i}{\hbar}\alpha\hat{\mathbf{n}} \cdot \mathbf{J}\right)$$

For an isolated system, total angular momentum is conserved! This means $[\mathbf{J}, \hat{H}] = 0$. There must be simultaneous eigenfunctions for $\hat{H}, \hat{J}^2, \hat{J}_z$.

This also means the energy only depends on j (i.e. not m) because spatial orientation doesn't matter. Let's consider the addition of \mathbf{J} for two particles.

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$$

We can describe \mathbf{J}_i as $|j_i, m_i\rangle$ as operators $\hat{J}_i^2, \hat{J}_{iz}$. Note that $[\mathbf{J}_1, \mathbf{J}_2] = 0$ for two independent particles. This means the general state is a product state:

$$|j_1 j_2 m_1 m_2\rangle = |j_1 m_1\rangle |j_2 m_2\rangle$$

We need 4 quantum numbers to describe two particles. For a given pair of (j_1, j_2) there are a total of $(2j_1+1)(2j_2+2)$ states. We can also describe the system as a combination of the two, using the total angular momentum. This is described by \hat{J}^2, \hat{J}_z , but this is only two quantum numbers, so this is not enough information to describe our system. We can supplement to get $|jm j_1 j_2\rangle$ OR $|jm m_1 m_2\rangle$. However, the last one doesn't actually work. Let's see this.

We know $j_{max} = j_1 + j_2$ and $j_{min} = |j_1 - j_2|$.

$$\begin{aligned} \hat{J}_z |j_1 j_2 m_1 m_2\rangle &= \hat{J}_z |j_1 m_1\rangle |j_2 m_2\rangle \\ &= (\hat{J}_{1z} \otimes \hat{I} + \hat{I} \otimes \hat{J}_{2z}) |j_1 m_1\rangle |j_2 m_2\rangle \\ &= (m_1 + m_2)\hbar |j_1 j_2 m_1 m_2\rangle \end{aligned}$$

Let's also consider the squared operator:

$$\begin{aligned} \hat{J}^2 &= (\mathbf{J}_1 + \mathbf{J}_2)^2 \\ &= J_1^2 + J_2^2 + 2\mathbf{J}_1 \cdot \mathbf{J}_2 \\ &= J_1^2 + J_2^2 + 2J_{1x}J_{2x} + 2J_{1y}J_{2y} + 2J_{1z}J_{2z} \end{aligned}$$

From the above, note J^2 commutes with J_1^2, J_2^2 but does not commute with J_{1z} or J_{2z} .

So, $|jm j_1 j_2\rangle$ is a complete description and $|jm m_1 m_2\rangle$ does not. There is a unitary transformation between the former and $|j_1 j_2 m_1 m_2\rangle$. Again note the sum on the right is finite.

$$|jm j_1 j_2\rangle = \sum_{m_1, m_2} \langle j_1 j_2 m_1 m_2 | jm \rangle |j_1 j_2 m_1 m_2\rangle$$

The coefficients $\langle j_1 j_2 m_1 m_2 | jm \rangle$ are termed Clebsch-Gordon coefficients.

Let's consider the addition of two particles with $S = \frac{1}{2}$. Particle one has states $\chi_{1/2, 1/2}^{(1)}, \chi_{1/2, -1/2}^{(1)}$. Similar for particle two. We shall abbreviate this as: $|i \uparrow\rangle, |i \downarrow\rangle$.

Now for state $|s_1 s_2 m_{s_1} m_{s_2}\rangle$:

m_{s_1}	m_{s_2}	total state	total m_s
$ 1 \uparrow\rangle$	$ 2 \uparrow\rangle$	$ \uparrow\uparrow\rangle$	1
$ 1 \uparrow\rangle$	$ 2 \downarrow\rangle$	$ \uparrow\downarrow\rangle$	0
$ 1 \downarrow\rangle$	$ 2 \uparrow\rangle$	$ \downarrow\uparrow\rangle$	0
$ 1 \downarrow\rangle$	$ 2 \downarrow\rangle$	$ \downarrow\downarrow\rangle$	-1

For $s = 0$, m_s must be 0, so we must subtract the two

$$\chi_{s=0, m=0} = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

This is the anti-symmetric spin singlet. We subtract because we want $m = 0$ and the only way to do this

For $s = 1$ there are $m_s = -1, 0, 1$.

$$\begin{aligned}\chi_{1,1} &= |\uparrow\uparrow\rangle \\ \chi_{1,0} &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ \chi_{1,-1} &= |\downarrow\downarrow\rangle\end{aligned}$$

This spin-1 state is a symmetric spin triplet.

Note that the final basis we get at the end still has size four, as we expect.