Contents

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 throw the ages:

- 1792: Wedgewood 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.

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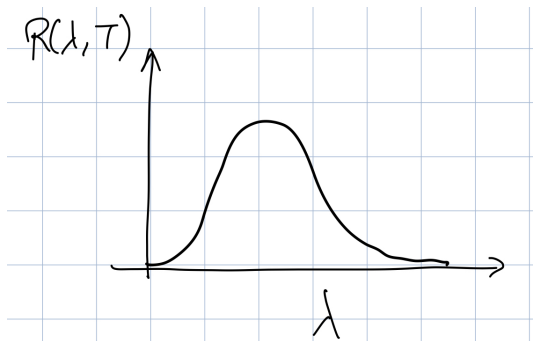
The idea is that there are multiple collisions between the walls and the radiation field. The blackbody (as a perfect absorber) is absorbing all light at all frequencies. It looked something like this. The left-side is near 0 because you have no wave at that wavelength. The right side must be bounded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

- 1879: Stefan's Law

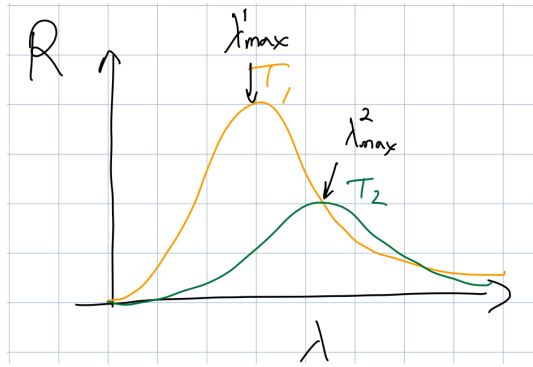$$\int_0^\infty R(\lambda, T)\, d\lambda = \sigma T^4$$

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

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

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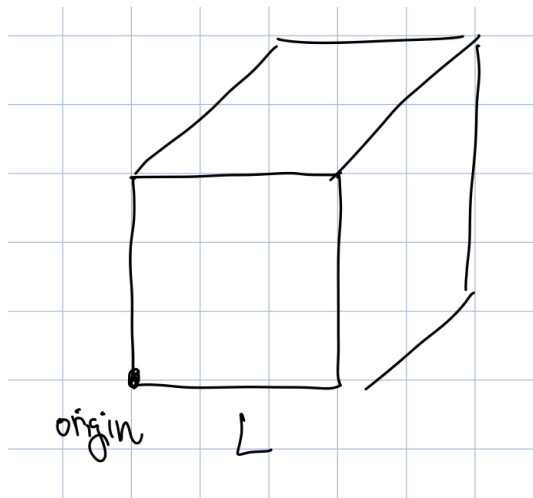
Let's find the waves that are stable in the cube. First, we write the wave equation.

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

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:

$$\Psi(x = 0, y, z, t) = \Psi(x = L, y, z, t) = 0, \forall y, z, t$$
$$\Psi(x, y = 0, z, t) = \Psi(x, y = L, z, t) = 0, \forall x, z, t$$
$$\Psi(x, y, z = 0, t) = \Psi(x, y, z = L, t) = 0, \forall x, y, t$$

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 ith 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:

$$\nabla^2 \Psi(\mathbf{r}, t) = \left(A(t) \sin(k_y y) \sin(k_z z) \frac{\partial^2 \sin(k_x x)}{\partial x^2} \right) + \dots$$

$$= -k_x^2 (A(t) \sin(k_x x) \sin(k_y y) \sin(k_z z)) + \dots$$

$$= -\left(n_x^2 + n_y^2 + n_z^2 \right) \frac{\pi^2}{L^2} A(t) B(x, y, z)$$

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.

$$\nabla^2 \Psi(x, y, z, t) = \frac{1}{c^2} \frac{\partial^2 \Psi(x, y, z, t)}{\partial t^2}$$

$$-\left(n_x^2 + n_y^2 + n_z^2 \right) \frac{\pi^2}{L^2} A(t) B(x, y, z) = \frac{-\omega^2}{c^2} A(t) B(x, y, z)$$

$$\omega^2 = \frac{c^2 \pi^2}{L^2} \left(n_x^2 + n_y^2 + n_z^2 \right)$$

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:

$$N(f) = \frac{(2\pi f)^3 V}{6 c^3 \pi^2} = \frac{4\pi f^3 V}{3 c^3}$$

$$g(f) = \frac{dN(f)}{df} = \frac{4\pi f^2 V}{c^3}$$

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:

$$\frac{g(f)\,\mathrm{d}f}{V}\bar{E} = \frac{8\pi h f^3}{c^3}\frac{1}{\frac{hf}{k_B T}) - 1}\,\mathrm{d}f$$

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:

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

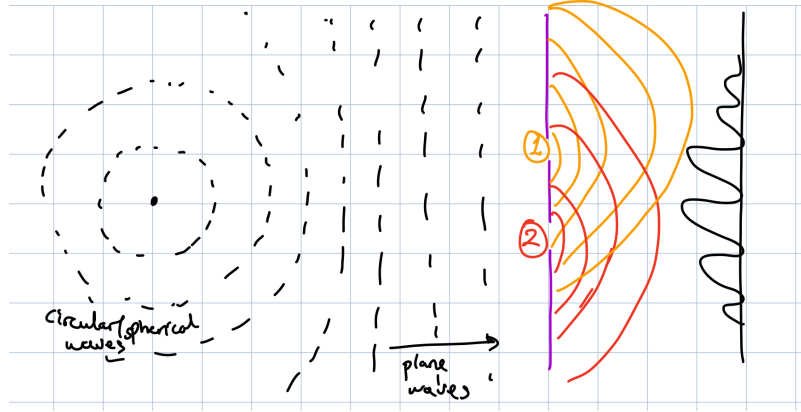versus the size of an atom is on the order of an angstrom, much smaller.

However for a human

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

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,

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

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 $\mathrm{d}\mathbf{r}$ becomes:

$$P(\mathbf{r}, t)\, \mathrm{d}\mathbf{r} = |\Psi(\mathbf{r}, t)|^2\, \mathrm{d}\mathbf{r}$$
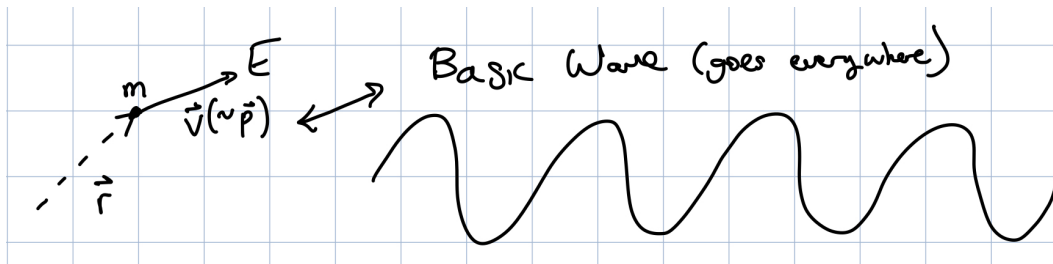
Theorem 3.2 (Superposition)
If Ψ_1, Ψ_2 are allowed waves (solutions), then:

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

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.

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

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

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:

$$A_n = \frac{1}{\pi}\int f(x)\cos(nx)\,\mathrm{d}x$$

$$B_n = \frac{1}{\pi}\int f(x)\sin(nx)\,\mathrm{d}x$$

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:

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

Thus:

$$A_m = \langle f(x), \cos(mx)\rangle$$

$$B_m = \langle f(x), \sin(mx)\rangle$$

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):

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

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:

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

$$= \int_{-\infty}^{\infty} f(x') \delta(x - x') \, dx$$

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 δs, 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.

Plane Wave
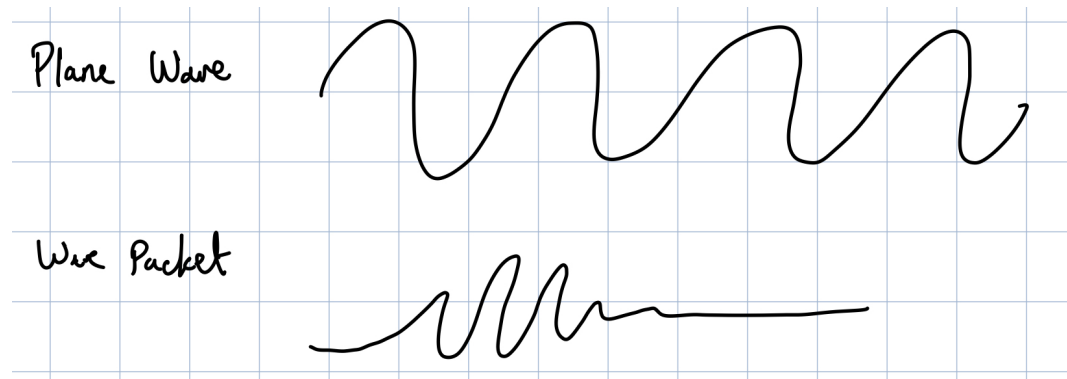
Wave Packet

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.

(weighted)

SUPERPOSITION

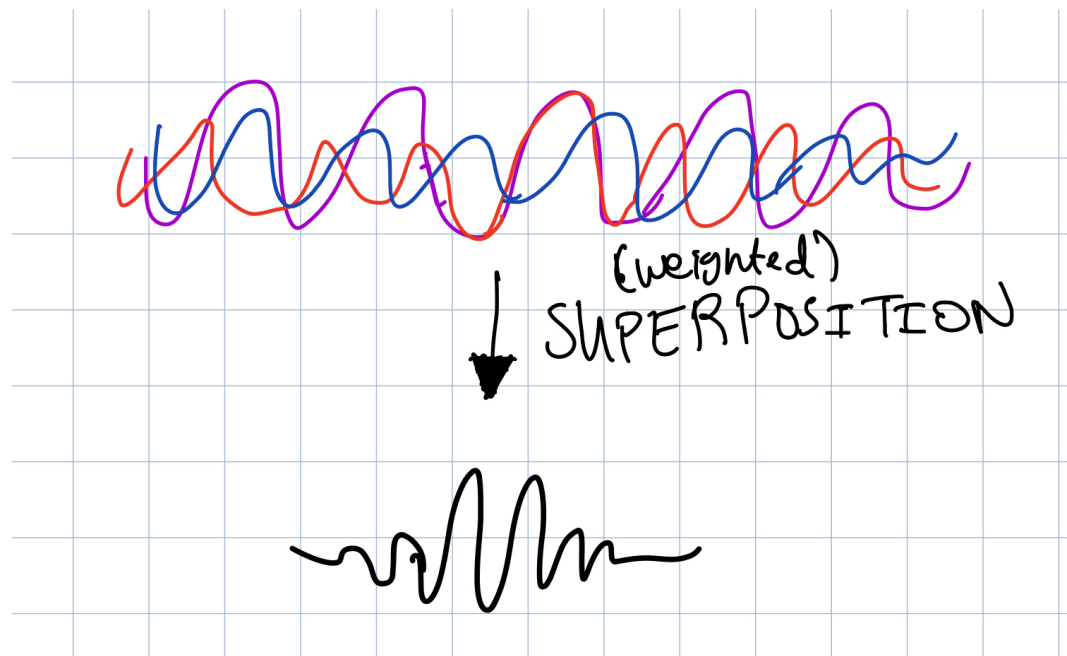For a 1-D wavepacket, the wave function is as follows (our index j has become continuous p_x).

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

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

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

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

$$\frac{\mathrm{d}\beta(p_x)}{\mathrm{d}p_x}\bigg|_{p_x = p_0} = 0$$

So, doing this yields:

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

$$\frac{x}{t} = \frac{\mathrm{d}E(p_x)}{\mathrm{d}p_x}$$

where this quantity is defined as the group velocity v_g. This is how fast the highest amplitude part of the wave packet moves:
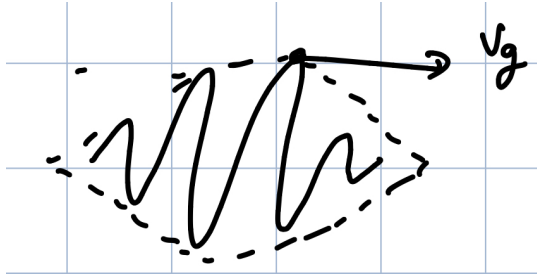
We can also find the phase velocity, the velocity of each component. Each component is:

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

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

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

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:

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

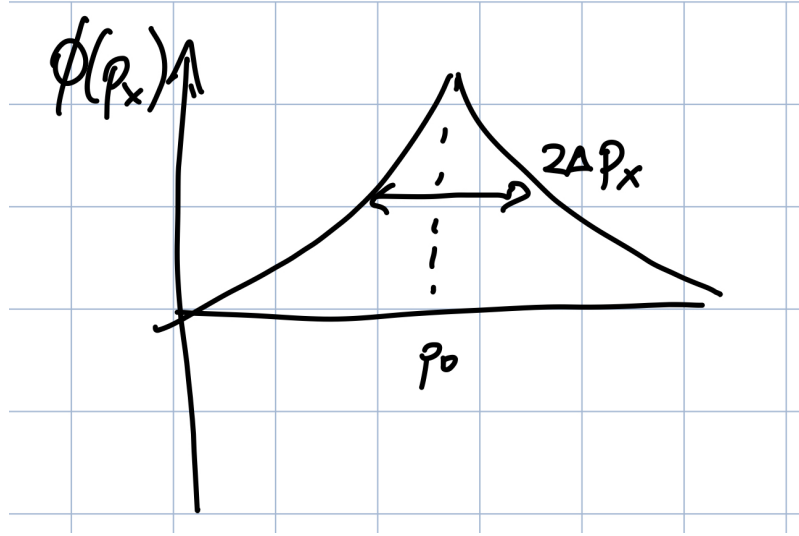Then since v_g is $\frac{\partial E}{\partial p}$, the energy can be integrated to be $E = \frac{p_x^2}{2m}$ and we recover the kinetic energy!

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:

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

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

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

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

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

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 $\Psi(x) = \Psi(x,0)$:

$$\begin{aligned}
\Psi(x) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{ip_x x/\hbar}\phi(p_x)\,dp_x \\
&= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{ip_x x/\hbar} \cdot ce^{-(p_x - p_0)^2 2(\Delta p_x)^2}\,dp_x \\
&= \frac{\pi^{-\frac{1}{4}}\sqrt{\Delta p_x}}{\sqrt{\hbar}} e^{ip_0 x/\hbar} e^{-(\Delta p_x)^2 x^2/2\hbar^2}
\end{aligned}$$

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:

$$p_\gamma = \frac{h}{\lambda_\gamma}$$

$$\Delta p_{e^{-1}} \sim \frac{h}{\lambda_\gamma}$$

$$\Delta p_{e^{-1}} \sim \frac{h}{\lambda_\gamma} \geq \frac{h}{d}$$

$$d\Delta p_{e^{-1}} \geq h$$

$$\Delta\theta = \frac{\Delta p_{e^{-1}}}{p_{e^{-1}}} = L\Delta\theta$$

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

In the quantum theory of an atom, electrons have defined energy levels.
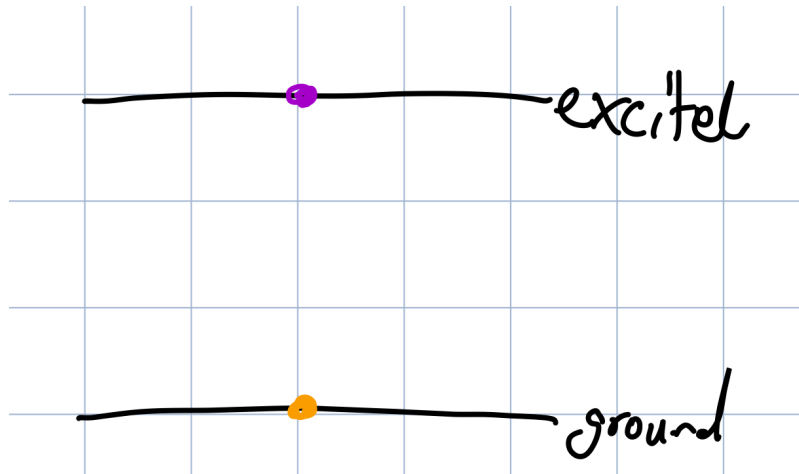
Consider an electron in the ground state–it can stay there for basically an infinite amount of time. When an electron is in the excited state, then it will drop down at some indeterminate time. If you average this together, you get a half life decay like this:
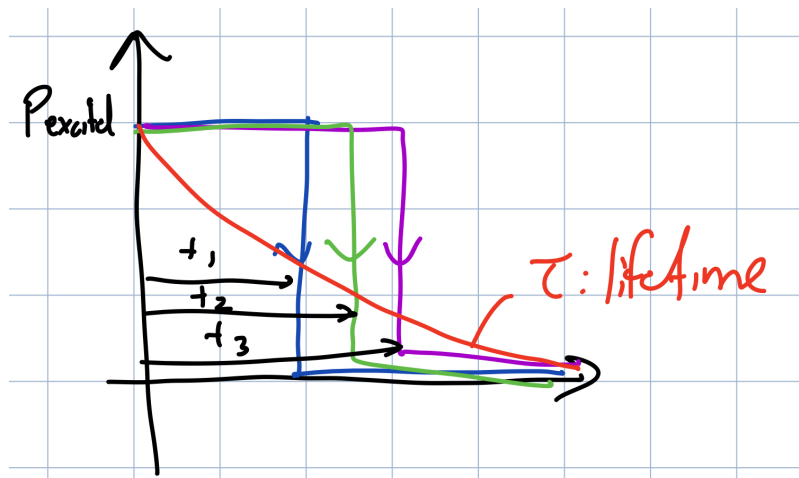
Because this is really a probability distribution, you actually see a small band of frequencies. The uncertainty is:

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

The diagram now more accurately looks like this:
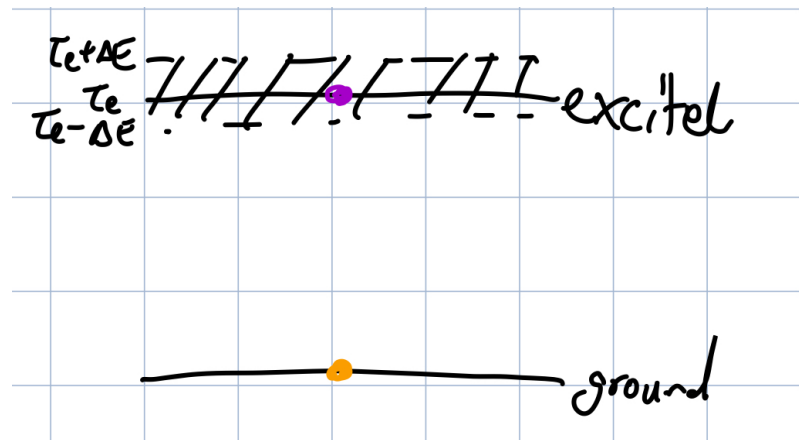
and the photon emission spectrum looks like this.

Imagine now a flourescent 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 get 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:

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

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:

$$\frac{\partial \Psi(x,t)}{\partial t} = A(-i\omega)e^{i(kx-\omega t)}$$

$$= -i\omega\Psi = \frac{-i}{\hbar}E\Psi$$

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = -k^2 Ae^{i(kx-\omega t)}$$

$$= \frac{-p_x^2}{\hbar^2}\Psi$$

$$= \frac{-2Em}{\hbar^2}\Psi$$

Setting the Es 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:

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

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

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:

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

So we can write down the full Schrodinger equation:

Theorem 6.2 (Time-Independent Schrodinger Equation)
We have for a wave function Ψ:

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

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.

$$\int |\Psi(\mathbf{r},t)|^2 \, \mathrm{d}r = 1$$

$$\frac{\partial}{\partial t}\int \Psi(\mathbf{r},t)^*\Psi(\mathbf{r},t)\, \mathrm{d}r = 0$$

$$= \int \Psi(\mathbf{r},t)^*\frac{\partial\Psi(\mathbf{r},t)}{\partial t} + \frac{\partial\Psi(\mathbf{r},t)^*}{\partial t}\Psi(\mathbf{r},t)\, \mathrm{d}r$$

$$= \int \frac{1}{i\hbar}\left[\Psi^*(\hat{H}\Psi) - (\hat{H}\Psi)^*\Psi\right]\mathrm{d}r$$

which means:

$$\int \Psi^*(\hat{H}\Psi)\, \mathrm{d}r = \int (\hat{H}\Psi)^*\Psi\, \mathrm{d}r$$

$$\int \Psi^*\hat{H}\Psi\, \mathrm{d}r = \int \Psi^*\hat{H}^*\Psi\, \mathrm{d}r$$

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):

$$
\frac{\partial}{\partial t} \int |\Psi|^2 \, d\mathbf{r} = \int \frac{1}{i\hbar} \left[\Psi^* (\hat{H}\Psi) - (\hat{H}\Psi)^* \Psi \right] d\mathbf{r}
$$

$$
= \int \frac{i\hbar}{2m} \left[\Psi^* (\boldsymbol{\nabla}^2 \Psi) - (\boldsymbol{\nabla}^2 \Psi)^* \Psi \right] d\mathbf{r}
$$

$$
= - \int \frac{i\hbar}{2m} \int \boldsymbol{\nabla} \cdot \left[\Psi^* \boldsymbol{\nabla} \Psi - (\boldsymbol{\nabla}\Psi^*) \Psi \right] d\mathbf{r}
$$

$$
= - \int \boldsymbol{\nabla} \cdot \mathbf{j} \, d\mathbf{r}
$$

Where we define:

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

the "probability current." Using Stokes' theorem:

$$
\frac{\partial}{\partial t} \int |\Psi|^2 \, d\mathbf{r} = - \int \mathbf{j} \cdot d\mathbf{s}
$$

$$
\frac{\partial P(\mathbf{r}, t)}{\partial t} + \boldsymbol{\nabla} \cdot \mathbf{j}(\mathbf{r}, t) = 0
$$

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:

$$
\langle \hat{p} = \int \Psi^* \hat{p} \Psi \, d\mathbf{r}
$$

$$
= -i\hbar \int \Psi^* \boldsymbol{\nabla} \Psi \, d\mathbf{r}
$$

Note that $\hat{p}$ is Hermitian but $\hat{p} = -i\hbar\boldsymbol{\nabla}$ 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 comes 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:

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

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

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

$$i\hbar\frac{\mathrm{d}f}{\mathrm{d}t} = Ef$$

$$f(t) = Ce^{-iEt/\hbar}$$

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

$$\langle\hat{H}\rangle_{\Psi_E} = \int \Psi^*(\hat{H})\Psi\,\mathrm{d}\mathbf{r}$$

$$= \int \Psi^* E\Psi\,\mathrm{d}\mathbf{r}$$

$$= E$$

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

$$P(\mathbf{r}, t) = \Psi_E^*(\mathbf{r}, t)\Psi_E(\mathbf{r}, t)$$

$$= \Psi_E^*(\mathbf{r})f^*(t)f(t)\Psi_E(\mathbf{r})$$

$$= \Psi_E^*(\mathbf{r})\Psi_E(\mathbf{r})$$

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:

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

We will work through the marked cases on the diagram.

1. Doing a simple subtraction:

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

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

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

2. We detail some possibilities considering curvature:

   However, Ψ and $\frac{\mathrm{d}\Psi}{\mathrm{d}x}$ 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.

3. 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:

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

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

$$\frac{\mathrm{d}^2\Psi(x)}{\mathrm{d}x^2} + k^2\Psi(x) = 0$$
$$\Psi(x) = Ae^{ikx} + Be^{-ikx}$$

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:

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

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

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

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

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