8.04 Notes

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Contents

1 February 06, 2019

1.1 Logistics

The course is heavily based off of 8.03[1]. Going to recitation is recommended but not mandatory. PSets are due Thursdays at 5PM, once per week, and at some point in the middle of the course it will change to Fridays at 5PM. This class is known for lengthy PSets because of the computational nature of the class, so start them early. There will be two midterms and a final. Grades are weighted as follows:

- Problem Sets: 20%
- Midterm 1: 20%
- Midterm 2: 25%
- Final: 35%

There are no textbooks required for this course, but there are a few recommended texts.

Lectures will be on the blackboard, no slides. The advantage to this is that the lecture will be so slow that students can follow along. As per MIT-time, we will typically start lectures at 14:35 and end at 15:55.

Also, if you're reading these notes, and want to skip the experimental motivation, you can skip to this part where we start doing things rigorously.

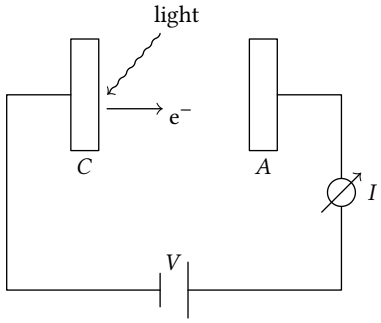
1.2 Introduction/Motivation

Quantum mechanics was discovered because people started to realize that classical physics was not a sufficient description of our universe. We will discuss some of the experiments that display this to motivate quantum mechanics.

1.2.1 Photoelectric Effect

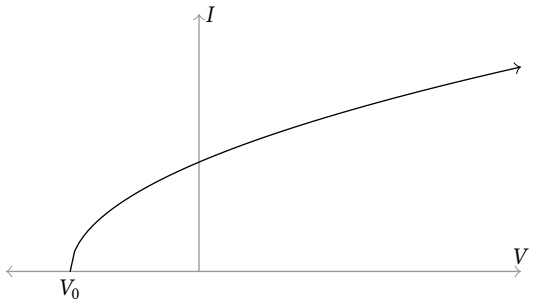
Consider the experiment where we shine light on a metallic surface. Then, it turns out that this surface emits elections, called **photoelectrons**. This was discovered by Hertz in 1887. The energies of the photoelectrons range from 0 to some maximum.

In 1916, Millikan performed an experiment with the following setup:



It was discovered that if $V > 0$, then the electrons e^- were attracted to A, and if $V < 0$, they were repelled. If the stopping potential is $V = V_0$, and we plot the stopping potential with respect to the current measured, we get something like this:

[1] oops



We know that the energy of the electron is

$$\begin{aligned} K_{\max} &= eV_0 \\ &= \frac{1}{2} m_e V_{\max}^2 \end{aligned}$$

It was found that if we changed the intensity of the light, the stopping potential does not change with it, which is not what classical mechanics predicts. Other observations include:

- $K_{\max}$ is independent of intensity of the light.
- $K_{\max}$ increases with frequency ν.
- There is a minimum frequency ν_0 below which no e^- are detected.

In 1905, Einstein realized the following:

- Light comes in photons with energy $E = h\nu$, where h is Planck's constant.
- Electrons are bound to metal with some binding energy $W \geq W_0$.
- Each photoelectron is ejected by one photon.
- The energy of the ejected electron is $K = h\nu - W$, and therefore $K_{\max} = h\nu - W_0$.

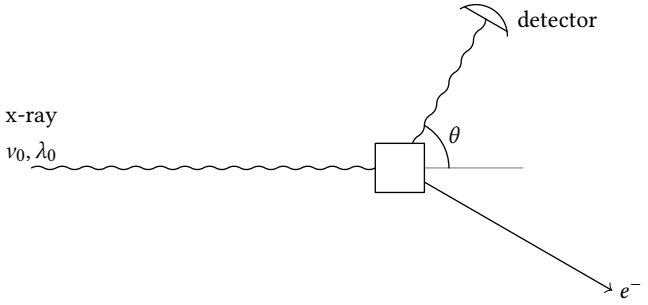
Overall, this experiment shows that:

- Increasing the intensity of the light only increases the number of photoelectrons.
- The minimum frequency ν_0 satisfies

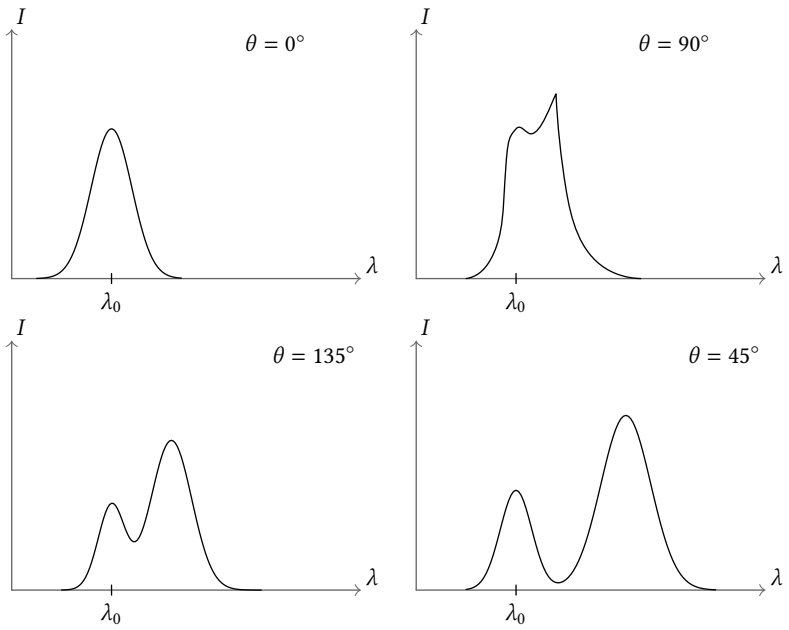
$$K_{\max} = h\nu - W_0 = h(\nu - \nu_0) \implies \nu_0 = \frac{W_0}{h}.$$

1.2.2 Compton Effect

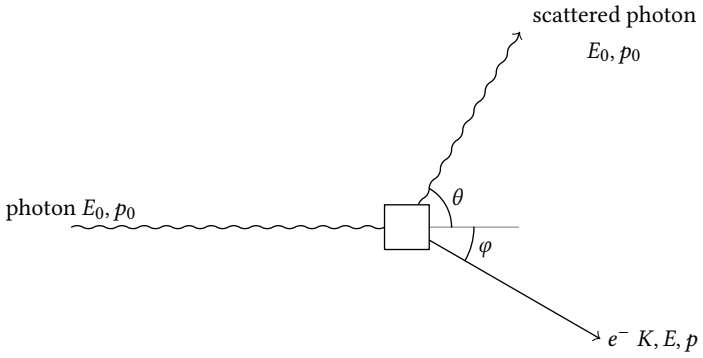
Consider the experiment where we shine an x-ray into a graphite object. It is known that an electron is emitted, and the x-rays are scattered at many angles. We will place a detector that detects photons at a fixed angle θ for now.



Classically, we expect all of the detected photons to have wavelength the same as the original photons. However, if (for a specific θ) we measure the distribution of photons with each wavelength, we get the following:



It is not clear how we get the second peak! Let's look at a more idealized version of the experiment. Let the incoming photon have energy E_0 and momentum p_0, the emitted electron have total energy E, kinetic energy K, and momentum p, and the scattered photon have energy E_1 and momentum p_1.



By conservation of momentum, we have

$$p_0 = p_1 \cos\theta + p\cos\varphi$$
$$p_1 \sin\theta = p\sin\varphi.$$

Subtracting $p_1\cos\theta$ in the first equation, squaring the equations and adding, we have

$$p_0^2 + p_1^2 - 2p_0p_1\cos\theta = p^2. \tag{A}$$

Now by conservation of energy, we have

$$E_0 + m_ec^2 = E_1 + \underbrace{K + m_ec^2}_{E} \implies E - m_ec^2 = E_0 - E_1. \tag{B}$$

From special relativity, we have that

$$E^2 = (pc)^2 + (mc^2)^2,$$

and that for a photon, $p = E/c = h/\lambda$.

Multiplying eq. (A) by c^2, we have

$$E_0^2 + E_1^2 - 2E_0E_1\cos\theta = (pc)^2 = E^2 - (m_ec^2)^2.$$

Squaring eq. (B), we have

$$E^2 + (m_e c^2)^2 - 2E(m_e c^2) = E_0^2 + E_1^2 - 2E_0 E_1.$$

Subtracting these two equations, we have

$$2E_0 E_1(1 - \cos\theta) = 2E(m_e c^2) - 2(m_e c^2)^2.$$

Since $E = K + m_e c^2 = (E_0 - E_1) + m_e c^2$, this simplifies to

$$E_0 E_1(1 - \cos\theta) = (E_0 - E_1)(m_e c^2).$$

Therefore,

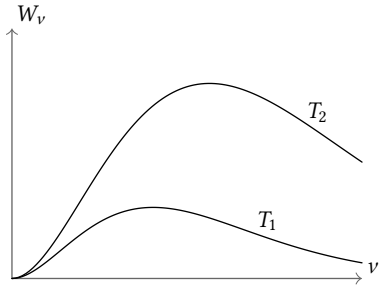
$$E_0 - E_1 = \frac{hc}{\lambda_0} - \frac{hc}{\lambda_1} = \frac{E_0 E_1}{m_e c^2}(1 - \cos\theta) = \frac{h^2 c^2}{\lambda_0 \lambda_1 m_e c^2}(1 - \cos\theta) \implies \lambda_0 - \lambda_1 = \Delta\lambda = \frac{h}{m_e c^2}(1 - \cos\theta).$$

2 February 11, 2019

2.1 More Experiments

2.1.1 Blackbody Spectrum

We know that matter radiates electromagnetic radiation at different frequencies ν depending on its temperature T. In particular, if we plot the spectral energy density with respect to frequency, we get



We have that the maximum ν value is linear with T and the integral with respect to the curve is proportional to T^4.

Let's try to explain this with classical physics. Consider a metal cube with sidelength L and temperature T. We will decompose the radiation field into a collection of standing waves. In particular, we will calculate the energy per mode and the number of modes, and use this to calculate the total energy.

Suppose that the electrons that generate the waves can be described as a harmonic oscillator with frequency ν and energy E. By statistical physics, we have that Boltzmann distribution describes the probability distribution of the energy as

$$P(E) = \frac{e^{-E/k_B T}}{k_B T},$$

where k_B is the Boltzmann constant. To get the average energy, we compute

$$\langle E \rangle = \int_0^\infty E \cdot P(E)\, dE = k_B T.$$

Note that we we omitted the division because the integral of $P(E)$ is just 1 since it is a probability distribution. Therefore, the average energy per mode is $k_B T$.

To calculate the number of modes in k space, we have

$$k = \frac{2\pi}{\lambda} = \frac{2\pi\nu}{c}.$$

Consider a cube lattice of points separated with distance π/L. The number of modes with wavenumber at most k is

$$M = \left(\frac{1}{8} \cdot \frac{4\pi}{3} \cdot R^3\right) \Big/ \left(\frac{\pi}{L}\right)^3 = \frac{4\pi L^3 \nu^3}{3c^2},$$

where we used $k = \frac{2\pi\nu}{c}$ in the second step. This gives the node density (after multiplying by 2 to account for polarization)

$$N(\nu) = 2\frac{dM}{d\nu} = \frac{8\pi L^3 \nu^2}{c^3}.$$

More generally, we can replace L^3 with the volume V.

Multiplying the number of modes by the average energy per mode and then dividing by volume for density, we get

$$W_\nu(\nu) = \frac{8\pi k_B T \nu^2}{c^3}.$$

This is the classical result. But we know this is wrong because if we take the total energy,

$$W(T) = \int_0^\infty W_\nu(T)\, d\nu = \infty,$$

which contradicts the Stefan-Boltzmann law.

The problem is that we assumed that the electrons that generate the waves could be described as harmonic oscillators. In particular, we assumed that the electrons' energy are described by the Boltzmann distribution, which is continuous. However, electrons only have discrete energies $E_m = h \cdot \nu \cdot m$. Then we have

$$\langle E \rangle = \left[\sum_{m=0}^\infty E_m \cdot P(E_m)\right] \Big/ \left[\sum_{m=0}^\infty P(E_m)\right] = \left[\sum_{m=0}^\infty mh\nu \exp(-\beta mh\nu)\right] \Big/ \left[\sum_{m=0}^\infty \exp(-\beta mh\nu)\right] = \frac{h\nu}{\exp(h\nu/k_B T) - 1}.$$

This gives

$$W_\nu = \frac{8\pi\nu^2}{c^3} \cdot \frac{h\nu}{\exp(h\nu/k_B T) - 1},$$

which fits our data.

3 February 13, 2018

3.1 Last Few Experiments

Recall that the energy of a photon is given by $E = h\nu$ and the momentum is given by $p = E/c = h/\lambda$. In 1924, de Broglie rewrote the momentum equation as $\lambda = h/p$. For all particles, we call this value the **de Broglie wavelength** of the particle.

In the Bohr model of the atom, we have a nucleus with electrons orbiting it in circular orbits bound by Coulombic attraction from the protons. Moreover, to explain the discrete values of energy that the atom omits, we say that the bound electrons are on discrete orbits.

Considering the orbital angular momentum $L = rp = rmv$. This is equal to $n\frac{h}{2\pi}$. Since the value $\frac{h}{2\pi}$ appears a lot in quantum mechanics, we will call this $\hbar = \frac{h}{2\pi}$. Using the de Broglie wavelength, we have

$$2\pi r = n \cdot \frac{h}{p} \implies L = rp = \frac{nh}{2\pi} = n\hbar.$$

Let's apply this to atoms that have one electron orbiting it. Suppose that there are Z protons in the nucleus. To find the radius r and energy E, we use Coulomb's law to get

$$-\frac{Ze^2}{r^2} = -\frac{mv^2}{r} \implies mv^2 r = Ze^2.$$

Since $L = rmv = n\hbar$, we have for the nth orbital radius that

$$v = \frac{n\hbar}{mr} \implies r_n = \frac{n^2}{Z}\left(\frac{\hbar^2}{m \cdot e^2}\right) = a_0 \frac{n^2}{Z},$$

where $a_0 = \frac{\hbar^2}{me^2}$ is the **Bohr radius**, approximately 0.5. Note that this tells us that the nth electron radius scales with $1/n^2$.

To find the energy, we have

$$E_n = K + V = \frac{1}{2}mv^2 - \frac{Ze^2}{r}.$$

Since $mv^2 r = Ze^2$, we have

$$E_n = -\frac{1}{2}\frac{Ze^2}{r} = -\frac{1}{n^2}\frac{Z^2e^2}{2a_0}.$$

We can also write this as

$$E_n = -\frac{1}{2}\left(\frac{e^2}{\hbar c}\right)^2 mc^2(Z^2)n^2.$$

The constant $\frac{e^2}{\hbar c}$ is called the **Fine structure constant**, and is approximately $\frac{1}{137}$.

For a hydrogen atom, $Z = 1$ and $E_n = -13.6\text{eV} \cdot \frac{1}{n^2}$. This agrees with the measurements we make.

3.2 Double-slit Experiment

Suppose we have a plane with two slits that will let large particles (like bullets) through. Behind the plane is a detector, which will detect at which points the particles hit the detector. We get that if one slit is open, then the distribution of particles will be Gaussian. If both slits are open, then we can just take the sum of the two distributions.

If we do the same experiment with light instead of large particles, then there is an interference pattern when we have both slits open. A similar thing happens when we send electrons through the slits. Even if we send the electrons through one by one, there is an interference pattern. The only explanation for this is that the electrons must act like a wave.

4 February 19, 2019

Suppose that we were to perform a variation of the double-slit experiment with electrons, but we put light detectors (emit photons and see which ones reflect) on each of the slits in attempts to see which slit the electrons go through. It turns out that the distribution returns to the sum of the two distributions, and there is no interference.

If we reduce the intensity of the light, the interference pattern slowly comes back. However, in this case, we do not have enough photons to detect all of the electrons, and it turns out that the electrons that are missed are the ones that form the interference pattern.

If we increase the wavelength in attempt to minimize the impact the photons have on the electrons, we will see the interference pattern come back, but when the wavelength is close to the distance between the slits, we lose the information about which slit it goes through.

In particular, if Δp is small then we get a large Δx, and if Δp is large then we get a small Δx. This is called **Heisenberg's Uncertainty Principle**, which states that

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2}.$$

4.1 Let's Actually Do Things Rigorously

4.1.1 Wavefunctions

Recall that we can describe particles by considering them to be waves. We do this by assigning a wavefunction ψ to every system. In contrast to classical mechanics, where the configuration of a system is fully given by $\vec{x}$ and $\vec{p}$, the configuration of a system is fully given by $\psi(\vec{x}, t)$. Moreover, in quantum mechanics the state evolves through Schrödinger's equation, as opposed to Newton's laws. One last difference is that quantum mechanics is probabilistic, as opposed to deterministic in classical mechanics.

1 **Definition**

A **wavefunction** is a complex function ψ that describes the state of a quantum system.

For now let's consider one dimensional wavefunctions for a single particle, i.e. ones of the form $\psi(x,t)$. We can relate the wavefunction to a probability density by taking the norm of the wavefunction squared:

$$P(x,t) = |\psi(x,t)|^2.$$

Since the probability density must integrate to 1 over all points, we can find the units of the wavefunction to be

$$1 = \int_{\mathbb{R}} |\psi(x)|^2 \, dx \implies [\psi] = \frac{1}{[\mathsf{L}]}.$$

2 **Example**

Let $k = \frac{2\pi}{\lambda}$ for some fixed λ. Consider the plane wave described by

$$\psi(x,t) = e^{ikx}.$$

By de Broglie, we have $\lambda = \frac{h}{p}$ and $p = \hbar k$. This means $\Delta p = 0$, and by uncertainty we have that Δx is unbounded. Alternatively, note that $|\psi(x,t)| = 1$ for all x. This means that ψ is not normalizable. We typically fix this by saying that ψ goes to 0 outside of a certain region.

5 February 20, 2019

The set of wavefunctions form a Hilbert space, i.e. a vector space that can be viewed as a complete metric space with respect to the inner product, which we will define in section 6.3.

5.1 Interference and Fourier Transforms

Suppose that we have a wavefunction that is the linear combination of two other wavefunctions:

$$\psi(x) = \alpha\psi_1(x) + \beta\psi_2(x).$$

Then consider the probability distribution of ψ. We get

$$\begin{aligned} P(x) = |\psi(x)|^2 &= \psi(x) \cdot \psi(x)^* \\ &= |\alpha|^2 P_1(x) + |\beta|^2 P_2(x) + \alpha^*\beta\psi_1(x)^*\psi_2(x) + \alpha\beta^*\psi_1(x)\psi_2(x)^*. \end{aligned}$$

We often call the last two terms the **interference terms**.

3 **Example**

Let's consider the linear combination of the wavefunctions $\psi_1(x) = e^{ik_1x}$ and $\psi_2(x) = e^{ik_2x}$. For $\psi = \alpha\psi_1(x) + \beta\psi_2(x)$, we have

$$P(x) = |\alpha|^2 + |\beta|^2 = 2|\alpha\beta| \cos((k_1 - k_2)x + \varphi).$$

Note that there is positive information about $P(x)$ with respect to x, so Δx is finite, and therefore $\Delta p > 0$.

To generalize, let's consider all possible linear combinations of plane waves e^{ikx}. Since k is a continuous variable, we can do this with an integral. Let

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{\psi}(k) e^{ikx} \, dk.$$

This is just the Fourier transform! Note that we also have

$$\tilde{\psi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(k) e^{-ikx}\, dx.$$

The interpretation of $|\tilde{\psi}(k)|^2$ is then the momentum probability density.

4 **Example**

Consider the plane wave $\psi(x) = e^{ik_0 x}$. It is not hard to guess that $\tilde{\psi}$ is some multiple of $\delta(k - k_0)$. In particular, letting $\tilde{\psi}(k) = \sqrt{2\pi}\delta(k - k_0)$, we get

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \delta(k - k_0) e^{ikx}\, dk = e^{ik_0 x},$$

as desired.

In momentum space, we have $p = \hbar k$. Therefore, we can rewrite the two equations as

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

5.2 Statistical Interpretation

The wavefunctions $\psi(x)$ and $\tilde{\psi}(p)$ have no direct physical meaning, i.e. it cannot be measured. It only gives us the probability densities $P(x) = |\psi(x)|^2$ and $P(p) = |\tilde{\psi}(p)|^2$. We can define the **average** of x to be

$$\langle x \rangle = \int_{-\infty}^{\infty} x P(x)\, dx,$$

the **variance** of x to be

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

and the **standard deviation** of x to be

$$\Delta x = \sqrt{\langle (x - \langle x \rangle)^2 \rangle}.$$

We can similarly define these for k and p.

Suppose that we have $\psi(x)$ and we wish to find $\langle p \rangle$. One way to do this is to use the Fourier transform to compute $\tilde{\psi}(p)$, and then using this to get $P(p)$ and $\langle p \rangle$. However, there is another way to do this. Trying to compute $\langle p \rangle$, we get

$$\begin{aligned} \langle p \rangle &= \int_{-\infty}^{\infty} p \cdot P(x)\, dx \\ &= \int_{-\infty}^{\infty} \psi^*(x) \cdot p \cdot \psi(x)\, dx. \end{aligned}$$

Note that $-i\hbar \frac{\partial}{\partial x} e^{ipx/\hbar} = p e^{ipx/\hbar} \implies -i\hbar \frac{\partial}{\partial x} \psi(x) = p\psi(x)$ by linearity (every wavefunction is just the superposition of plane waves). We call $\hat{p} = -i\hbar \frac{\partial}{\partial x}$ the **momentum operator**. Therefore, we can write the integral as

$$= \int_{-\infty}^{\infty} \psi^*(x) \hat{p} \psi(x)\, dx.$$

We can similarly write

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{x} \psi(x)\, dx,$$

which gives the **position operator** $\hat{x} = x$, which is just a multiplication by x.

An important thing to keep in mind is that these operators don't always commute with other terms, because they have derivative operators. Also, note that we have written the operators down in position-space. If we change our basis so that we are in

momentum-space, we get the operators

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

6 February 25, 2019

6.1 Summary

Here's what we have so far:

Given a wavefunction $\psi(x)$ of position, we can determine the probability density $P(x) = |\psi(x)|^2$ of the position. Then, we have the expected position

$$\langle x \rangle = \int_{-\infty}^{\infty} xP(x)\,dx.$$

We also have two spaces that are related through a Fourier transform. In position space, we have the wavefunction $\psi(x)$, and the operators

$$\hat{x} = x, \qquad \hat{p} = -i\hbar\,\partial_x.$$

In momentum space, we have the wavefunction $\tilde{\psi}(p)$ and the operators

$$\hat{x} = i\hbar\,\partial_p, \qquad \hat{p} = p.$$

6.2 Gaussian Wavepackets

Consider the wavefunction

$$\psi(x) = N \exp\left[i\frac{p_0}{\hbar} - \frac{x^2}{2\sigma_0^2} \right],$$

where N is a normalization constant and $p_0 \in \mathbb{R}$. To find the normalization constant, we take the integral and get

$$1 = \int_{-\infty}^{\infty} |\psi(x)|^2\,dx = |N|^2 \int_{-\infty}^{\infty} \exp\left[-\frac{x^2}{\sigma_0^2} \right] dx \implies |N| = (\pi\sigma_0^2)^{-1/4}.$$

Assuming $N \in \mathbb{R}$ gives us $N = (\pi\sigma_0^2)^{-1/4}$.

Now let's find the corresponding wavefunction in momentum space. Taking the Fourier transform of ψ, we have

$$\begin{aligned}
\tilde{\psi}(p) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x) e^{-ipx/\hbar}\,dx \\
&= (\pi\sigma_0^2)^{-1/4} \cdot \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \exp\left[-\frac{x^2}{2\sigma_0^2} - \frac{i(p-p_0)}{\hbar} x \right] dx \\
&= \left(\frac{\sigma_0}{\hbar\sqrt{\pi}} \right)^{1/2} \exp\left[-\sigma_0^2 \frac{(p-p_0)^2}{2\hbar^2} \right].
\end{aligned}$$

Finding the normalization constant, we have

$$\int_{-\infty}^{\infty} |\tilde{\psi}(p)|^2\,dp = \frac{\sigma_0}{\hbar\sqrt{\pi}} \int_{-\infty}^{\infty} \exp\left[-\frac{\sigma_0^2 (p-p_0)^2}{\hbar^2} \right] dp = \frac{\sigma_0}{\hbar\sqrt{\pi}} \sqrt{\frac{\pi}{\sigma_0^2/\hbar^2}} = 1.$$

so it is already normalized.

> **Note**
>
> It turns out that by Parseval's Theorem, the Fourier transform of a normalized wavefunction is already normalized.

Now we can try to find the uncertainties of position and momentum. We have

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}.$$

Computing each component,

$$\begin{aligned}\langle x\rangle &= \int_{-\infty}^{\infty} x|\psi(x)|^2\,dx \\ &= N^2\int_{-\infty}^{\infty} x\exp\left[-\frac{x^2}{\sigma_0^2}\right]dx \\ &= 0\end{aligned}$$

$$\begin{aligned}\langle x^2\rangle &= N^2\int_{-\infty}^{\infty} x^2\exp\left[-\frac{x^2}{\sigma_0^2}\right]dx \\ &= \frac{\sigma_0^2}{2}.\end{aligned}$$

Therefore,

$$\Delta x = \frac{\sigma_0}{\sqrt{2}}.$$

Similarly, we can calculate that $\langle p\rangle = p_0$ and

$$\langle p^2\rangle = N^2\int_{-\infty}^{\infty} p^2\exp\left[\frac{\sigma_0^2(p-p_0)^2}{\hbar^2}\right]dp = p_0^2 + \frac{\hbar^2}{2\sigma_0^2}.$$

Therefore, $\Delta p = \frac{\hbar}{\sigma_0\sqrt{2}}$. Note that this satisfies Heisenberg's Uncertainty principle, because

$$\Delta x\cdot\Delta p = \frac{\sigma_0}{\sqrt{2}}\cdot\frac{\hbar}{\sigma_0\sqrt{2}} = \frac{\hbar}{2} \geq \frac{\hbar}{2}.$$

Note that since the product of the uncertainties is equal to exactly $\frac{\hbar}{2}$, we say that this wavefunction has minimum uncertainty.

6.3 Operators

For a given system, things which can be measured (position, momentum, angular momentum, energy) are called **observables**. These are represented by linear Hermitian operators. Then, the values that can be measured for an observable are the eigenvalues of the corresponding operator. We will define everything more formally:

We will work over the complex vector space of square-integrable function, i.e. functions f that satisfy

$$\int_{-\infty}^{\infty}|f(x)|^2\,dx < \infty.$$

We call this our **state space**.

We define the inner product of two functions ϕ and ψ in our vector space to be

$$\langle\varphi,\psi\rangle = \int \varphi(x)^*\psi(x)\,dx.$$

This inner product gives us a Hilbert space.

6 **Definition**

An **operator** is a map from the state space to itself. We say that an operator $\hat{O}$ is **linear** if

$$\hat{O}(\alpha f+\beta g) = \alpha\hat{O}f + \beta\hat{O}g,$$

for all $\alpha,\beta\in\mathbb{C}$ and f,g in the function space.

7 **Example**

All of the following are operators:

$$\hat{\varnothing}: f \mapsto 0 \qquad \hat{1}: f \mapsto f \qquad \hat{x}: f \mapsto x \cdot f$$
$$\hat{S}: f \mapsto f^2 \qquad \hat{A}_3: f \mapsto f + 3 \qquad \hat{D}_x: f \mapsto \frac{\partial}{\partial x} \cdot f,$$

and the ones that are linear are $\hat{\varnothing}$, $\hat{1}$, $\hat{x}$, and $\hat{D}_x$.

8 **Definition**

For an operator $\hat{A}$, an **eigenfunction** is a function f_a such that

$$\hat{A} f_a = a \cdot f_a$$

for some $a \in \mathbb{C}$. We call a the **eigenvalue** corresponding to f_a.

9 **Example**

For the operator $\hat{D}_x$, we have the eigenfunction $e^{\alpha x}$ and the corresponding eigenvalue α, because

$$\hat{D}_x e^{\alpha x} = \alpha e^{\alpha x}.$$

It's important to note that operators do not commute! For example,

$$\hat{D}_x \hat{x} e^{\alpha x} = \hat{D}_x (x e^{\alpha x}) = (1 + \alpha x) e^{\alpha x}$$
$$\hat{x} \hat{D}_x e^{\alpha x} = \hat{x} (\hat{D}_x e^{\alpha x}) = \alpha x e^{\alpha x},$$

which are not equal. Therefore, $\hat{D}_x \hat{x} \neq \hat{x} \hat{D}_x$. Since they do not commute, we have the following definition:

10 **Definition**

Given operators $\hat{A}$ and $\hat{B}$, the **commutator** of $\hat{A}$ and $\hat{B}$ is the operator

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

Note that if two operators $\hat{A}$ and $\hat{B}$ commute, then we have $[\hat{A}, \hat{B}] = \hat{0}$.

11 **Example**

$$[\hat{x}, \hat{D}_x] = -1$$
$$[\hat{x}, \hat{p}] = i\hbar$$

6.4 Observables

If an operator $\hat{A}$ corresponds to an observable, then $\langle A \rangle$ is real. Then we can write the expected value of A as

$$\langle A \rangle = \int \psi(x)^* \hat{A} \psi(x) = \langle \psi, \hat{A} \psi \rangle.$$

12 **Definition**

Let the **adjoint** of $\hat{A}$ be the operator $\hat{A}^\dagger$ that satisfies

$$\langle \hat{A}^\dagger \varphi, \psi \rangle = \langle \varphi, \hat{A}\psi \rangle.$$

We say that an operator $\hat{A}$ is **Hermitian** (in physics, math has a stricter definition) if $\hat{A}^\dagger = \hat{A}$, i.e. it is self-adjoint.

If we have a Hermitian operator $\hat{A}$, then

$$\langle A \rangle = \langle \psi, \hat{A}\psi \rangle = \langle \hat{A}\psi, \psi \rangle = \int \psi (\hat{A}\psi)^* = \left[\int \psi^* (\hat{A}\psi) \right]^* = \langle A \rangle^*.$$

Therefore, $\langle A \rangle$ is real, which is what we expect for observables.

7 February 27, 2019

7.1 Measurement and Wavefunction Collapse

13 **Proposition** (Spectral Theorem)

Given a Hermitian operator $\hat{A}$, we have the following:

- The eigenvalues are real.
- The eigenfunctions are orthogonal, i.e. $\langle \psi_n, \psi_m \rangle = \delta_{n,m}$ for eigenfunctions ψ_n, ψ_m.
- The eigenfunctions form a complete basis, i.e. for all $f(x)$, there exists a function $c(n)$ such that

$$f(x) = \int c(n)\psi_{A,n}(x)\, dn.$$

When we measure an observable, it causes the wavefunction to collapse to one of its eigenfunctions. The value of $|c(n)|^2$ gives the corresponding probability of which eigenvalue we will measure if we collapse the wavefunction.

14 **Example**

Consider the momentum operator $\hat{p}$. Recall that the eigenfunctions of $\hat{p}$ are $f : x \mapsto e^{ikx}$ for $k \in \mathbb{R}$. Then we have that these functions form a complete basis of the vector space of wavefunctions, i.e.

$$\psi(x) = \int c(k) e^{ikx}\, dk.$$

To compute the $c(n)$, note that we can take the inner product of the wavefunction with the corresponding eigenfunction. This works because of both orthogonality and the wavefunctions form a complete basis:

$$\langle \psi_{A,n}(x), \psi(x) \rangle = \left\langle \psi_{A,n}(x), \int c(m)\psi_{A,m}(x)\, dm \right\rangle$$

Since the inner product is linear,

$$\begin{aligned} &= \int c(m) \left\langle \psi_{A,n}(x), \psi_{A,m}(x) \right\rangle dm \\ &= \int c(m)\delta_{n,m}\, dm \\ &= c(n). \end{aligned}$$

7.2 Dirac Notation

Note that $\psi(x), \tilde{\psi}(k), \tilde{\psi}(p)$ are just different representations of the same wavefunction in different bases. We will consider the basis independent notation, where we write the wavefunction as $|\psi\rangle$, called a **ket vector**. Similarly, for ψ^*, we will represent this as $\langle\psi|$, called a **bra vector** in the dual space. If we put these two together, then we get the scalar product

$$\langle\varphi|\psi\rangle = \langle\varphi(x), \psi(x)\rangle.$$

Similarly, we can rewrite the relations

- $\langle A\rangle = \langle\psi(x), \hat{A}\psi(x)\rangle = \langle\psi|\hat{A}|\psi\rangle$
- $\hat{A}^\dagger = \hat{A} \implies \langle\hat{A}\varphi|\psi\rangle = \langle\varphi|\hat{A}|\psi\rangle$
- $\langle\varphi|a\psi\rangle = a\langle\varphi|\psi\rangle$
- $\langle a\varphi|\psi\rangle = a^*\langle\varphi|\psi\rangle$

7.3 Time Evolution and Schrödinger Equation

There is no rigorous derivation to get Schrödinger equation from classical mechanics, otherwise classical physics will already be a quantum theory. However, we can give motivation for it.

7.3.1 Motivation

Recall the plane wave

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

(We write ψ_p because it is an eigenfunction of $\hat{p}$.) The photoelectric effect tells us that there is a relationship between the frequency and the energy. Therefore, we assume that $E = h\nu = \frac{h}{2\pi}\omega = \hbar\omega$. We want to get this value with the momentum operator somehow. We get

$$i\hbar\frac{d}{dt}\psi_p(x,t) = \hbar\omega\psi_p(x,t) = E\psi_p(x,t).$$

But from classical physics, we have $E = \frac{p^2}{2m} + V$, where V is the potential energy. This is often called the Hamiltonian of the system. If we define the **Hamiltonian operator** to be

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

we have **Schrödinger equation**

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

If we expand this out in position space, we get

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

Here the $\hat{V}$ in position space happens to be just multiplication by the potential V.

7.4 Time-independent Schrödinger Equation

Schrödinger equation seems pretty hard to solve, so we will simplify it by assuming that V is time independent, i.e. $V = V(x)$. Let's try to find a solution of the form

$$\Psi(x,t) = \psi(x)\cdot f(t).$$

This seems like a significant restriction at first, but it turns out that we can construct the general solution with the subset of solutions that we get this way. We compute the derivatives as

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2\psi}{dx^2} f, \qquad \frac{\partial \Psi}{\partial t} = \psi \frac{df}{dt}.$$

Substituting this into Schrödinger Equation, we get

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} f(t) + V\psi(x) f(t) = i\hbar\psi(x)\frac{df(t)}{dt}.$$

Dividing by $\psi(x)f(t)$,

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x) = i\hbar\frac{1}{f(t)}\frac{df(t)}{dt}.$$

Note that the left only depends on x and the right only depends on t. Therefore, both sides are constant. Let this constant be E.

For the right side, we get

$$i\hbar\frac{1}{f(t)}\frac{df(t)}{dt} = E \implies f(t) = ce^{-iEt/\hbar} = ce^{-i\omega t}$$

for some constant c and where $\omega = E/\hbar$.

For the left side, we get

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x) = E$$

multiplying by $\psi(x)$, we have

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

which is just the equation $\hat{H}\psi = E\psi$. Therefore, solving the time-independent Schrödinger equation is reduced to finding the eigenfunction of $\hat{H}$.

8 March 04, 2019

8.1 On the Separable Solutions

Consider the solutions to $\hat{H}$ in the time independent Schrödinger equation. They are **stationary states**, i.e. the observables are all independent of time for these states. In particular, we have the probability

$$P(x) = |\Psi(x,t)^2| = |\psi(x)\cdot ce^{-iEt/\hbar}|^2 = |\psi(x)c|^2.$$

Similarly, the expected value of some observable $\hat{A}$ is

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

Moreover, these states have a definite energy, i.e. $\Delta E = 0$. We can indeed compute

$$\langle H\rangle = \int \psi^*(x)\hat{H}\psi(x)\,dx = E$$
$$\langle H^2\rangle = \int \psi^*(x)\hat{H}^2\psi(x)\,dx = E^2,$$

since $\hat{H}\psi = E\psi$. Therefore, we have $\Delta E = \langle H^2\rangle - \langle H\rangle^2 = 0$.

15 **Proposition** (Separable Solutions to the Schrödinger Equation)
The most important thing about the separable solutions is that a general solution is a linear combination of the separable solutions. This is because we found all of the eigenfunctions $\psi_n(x)$ of a Hermitian operator $\hat{H}$, which we know form a basis

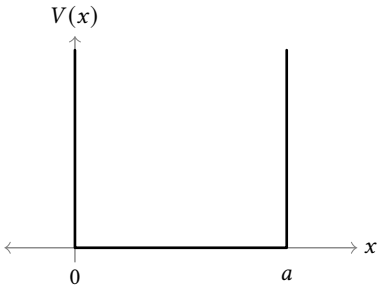
for the entire space. Therefore, once we find the eigenfunctions $\psi_n(x)$, a general solution can be written as

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar}.$$

8.2 Infinite Square Well

Consider a particle with the potential

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



This represents a particle that is completely free except at the two ends at $x = 0$ and $x = a$. Let the system start at $\Psi(x,0) = \psi_0(x)$. Then if we have the eigenstates $\phi_n(x)$ defined by $\hat{H}\phi_n = E_n\phi_n$, we have the general solution

$$\Psi(x,t) = \sum_n c_n \phi_n(x) e^{-iE_n t/\hbar},$$

where we find c_n by taking the dot product at $t = 0$:

$$\begin{aligned} c_n &= \langle \phi_n | \psi_0 \rangle \\ &= \int \phi_n^*(x)\phi_0(x)\,dx. \end{aligned}$$

We will now find the eigenstates. We have the equation

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

Outside of the interval $[0,a]$, we have $V = \infty$, so in order for E to be finite, $\psi(x) = 0$.

Inside the interval, we have something more interesting. In particular, we have

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

If we let $k = \sqrt{2mE}/\hbar$, then we have the general solution

$$\psi(x) = A\sin kx + B\cos kx.$$

To find A and B, we can use the fact that the wavefunctions are normalized, and they are continuous, i.e. $\psi(0) = \psi(a) = 0$. In particular,

$$\psi(0) = A\sin 0 + B\cos 0 = 0 \implies B = 0.$$

Moreover,

$$\psi(a) = A\sin ka = 0 \implies \sin ka = 0,$$

because otherwise $A = 0$ would give us the zero wavefunction. This means $ka = n\pi$ for some $n \in \mathbb{Z}$. Then we have the solutions $k = k_n = \frac{n\pi}{a}$ for $n \in \mathbb{Z}$. Note that $n = 0$ is bad because we get the zero wavefunction, and $n < 0$ give us repeated solutions, so we will

just take $n \in \mathbb{N}$. Surprisingly, this does not give a restriction on A, but rather a restriction on E. In particular, we get the possible values of E are

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

This means that the particle can only have specific energies! We say that the particle is **quantized**.

Finishing up, we normalize to get $|A|^2 = \frac{2}{a}$, and for simplicity we will choose the real value $A = \sqrt{\frac{2}{a}}$. This gives us the eigenstates

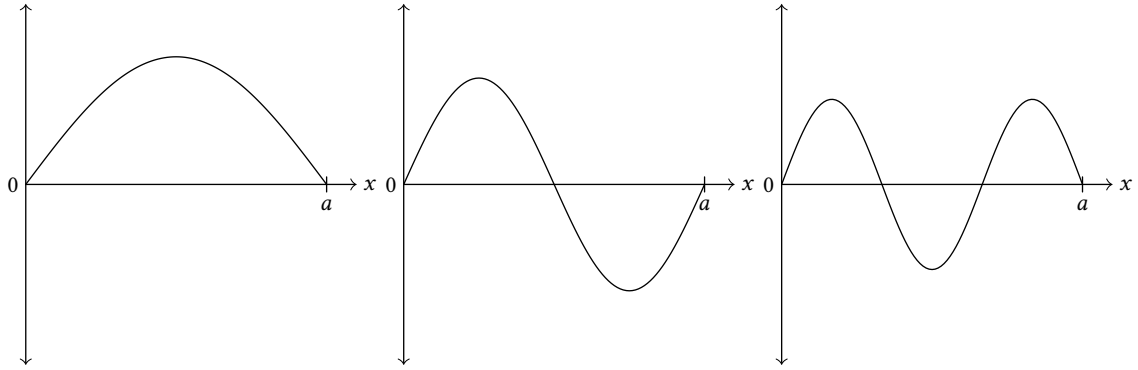
$$\phi_n(x) = \sqrt{\frac{2}{a}} \sin(k_n x),$$

where $k_n = \frac{n\pi}{a}$ for $n \in \mathbb{N}$, yielding $E_n = \frac{\hbar^2 k_n^2}{2m}$. Note that $E_n > 0$. This makes sense because we have a range that x is in, meaning that Δx is finite. This means Δp is nonzero, which means E is nonzero, because otherwise p will have a certain value.

9 March 06, 2019

9.1 More on the Solutions for the Infinite Square Well

If we plot the eigenstates, we get



Recall that, we know that $\int \phi_m^*(x)\phi_n(x)\,dx = \delta_{mn}$, because they are the eigenstates of a Hermitian operator. Moreover, the ϕ_m form a complete basis of Hilbert space.

Moreover, all of the eigenfunctions are odd. To see why this is true, consider the **parity operator** $\hat{\pi}\psi(x) = \psi(-x)$. The eigenvalues of $\hat{\pi}$ are 1 and -1, corresponding to even and odd functions respectively. Hence, we know that every wavefunction can be written as an even and an odd function. This makes sense because if we have some function $\psi(x)$, we can consider

$$\psi_+(x) = \frac{1}{2}(\psi(x) + \psi(-x))$$
$$\psi_-(x) = \frac{1}{2}(\psi(x) - \psi(-x)),$$

which are the even and odd functions respectively.

16 **Proposition**

For the shifted infinite square well potential $V(x) = \begin{cases} 0 & x \in [-a/2, a/2] \\ \infty & \text{otherwise,} \end{cases}$

$$[\hat{H}, \hat{\pi}] = 0.$$

Proof. We have $\hat{H} = \frac{\hat{p}^2}{2m} + V(x)$. It suffices to show that $[\hat{p}^2, \hat{\pi}] = 0$ and $[V(x), \hat{\pi}] = 0$. The first statement is true because $\hat{\pi}$ commutes with the derivative operator, and the second statement is true because $V(x)$ is even. □

9.2 General Properties of the Wavefunction

We have the following properties of $\psi(x)$:

- $\psi(x)$ is finite, because $P(x) = |\psi(x)|^2$.
- $\psi(x)$ is continuous
- $\psi'(x)$ is continuous if $V(x)$ is continuous.

If we know something about $V(x)$, then we can determine more properties of $\psi(x)$. We can write the Schrödinger equation as

$$\psi''(x) + k^2(x)\psi(x) = 0,$$

where $k^2(x) = \frac{2m}{\hbar^2}(E - V(x))$. Note that if $V(x) < E$, then we have ψ''' and ψ have opposite signs. Hence, in this case ψ is concave at x. Conversely, if $V(x) > E$, then ψ is convex at x.

In particular, if we have $V(x) = V_0 < E$, then we have

$$\psi(x) = c_+ e^{i\kappa_0 x} + c_- e^{-i\kappa_0 x}, \qquad \text{where} \qquad \kappa_0 = \left(\frac{2m}{\hbar^2}(E - V_0)\right)^{1/2}.$$

In the other case, if $V(x) = V_0 > E$, we have

$$\psi(x) = c_+ e^{\kappa_0 x} + c_- e^{-\kappa_0 x},$$

where κ_0 is the same value as before. Note that this is classically forbidden. However, in quantum mechanics, this is allowed, and gives us quantum tunneling.

10 March 11, 2019

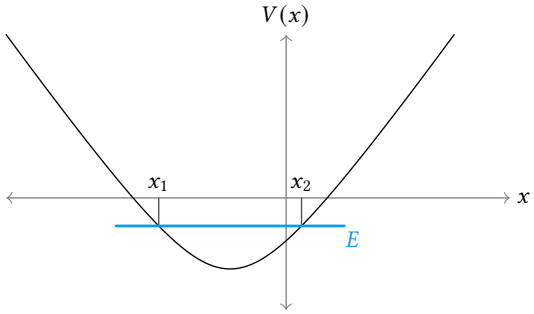
10.1 More properties about the Wavefunction

More generally, if we let $k(x) = \frac{\sqrt{2m(E-V(x))}}{\hbar}$, then we have that a particular x is **classically allowed** if $k(x)$ is real, i.e. if $V(x) < E$, and x is **classically forbidden** if $k(x)$ is imaginary, i.e. if $V(x) > E$. These correspond to sinusoidal and exponential wavefunctions respectively.

10.2 General Properties of the Spectrum of Eigenvalues

Consider what happens to the wavefunction for different possible eigenvalues E. First, note that if we have $E < \min V(x)$, then $\psi = 0$.

Let's consider the case where $V(x) \to \infty$ for $x \to \pm\infty$. Suppose we wish to check whether some E can be in the spectrum. Suppose $V(x) = E$ for $x = x_1$ and $x = x_2$.



We can try to graphically find a wavefunction for this just based on the concavity and convexity. For a given TODO: behaves exponentially

For the case where $V(x) \to V_{\pm\infty}$ as $x \to \pm\infty$, we will assume without loss of generality that $V_{+\infty} < V_{-\infty}$. Then we have that:

- If $E < V_{+\infty}$, $E < V_{-\infty}$, then there is a discrete energy spectrum, and ψ oscillates within the points where $V(x) = E$ while behaving exponentially beyond these points.
- If $V_{+\infty} < E < V_{-\infty}$ or $E > V_{-\infty}$, then there is a continuous energy spectrum, and ψ oscillates and behaves exponentially in their respective intervals.

We call the states first case the **bounded states** and the second case the **scattered states**.

10.3 Summary of What We Know

We have that the wavefunction ψ is a complete description of the state of a physical system, and $|\psi|^2$ is the probability density of a particular state. These wavefunctions form a vector space called Hilbert space. Physical observables A correspond to Hermitian operators, whose possible measurements are eigenvalues of the operator. Moreover, measuring the observable collapses the wavefunction to one of the eigenfunctions, and yields the respective eigenvalue. In particular,

$$P(\text{we observe the eigenvalue } a_n \text{ of } \psi_n) = |\langle \psi | \psi_n \rangle|.$$

We can then determine how the system will evolve throughout time with the Schrödinger equation

$$\hat{H}\psi = i\hbar \frac{d}{dt}\psi,$$

where $\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}$ is the Hamiltonian operator.

11 March 18, 2019

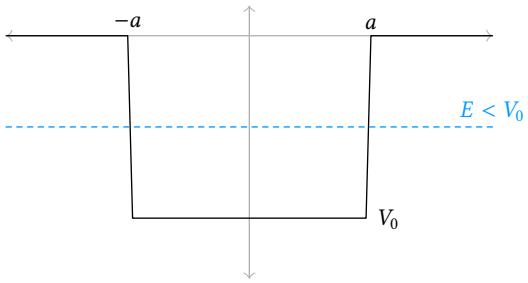
11.1 One-dimensional Systems

11.1.1 Finite Square Well

Consider the finite square well potential:

$$V(x) = \begin{cases} -V_0 & x \in [-a, a] \\ 0 & \text{otherwise,} \end{cases}$$

where V_0 is some positive constant.



To solve this system, suppose we have a constant potential $V(x) = V_0$ in some region. Then the time independent Schrödinger equation is

$$\psi''(x) = \frac{2m}{\hbar^2}(V_0 - E)\psi(x).$$

Let's gain some intuition about the solution first.

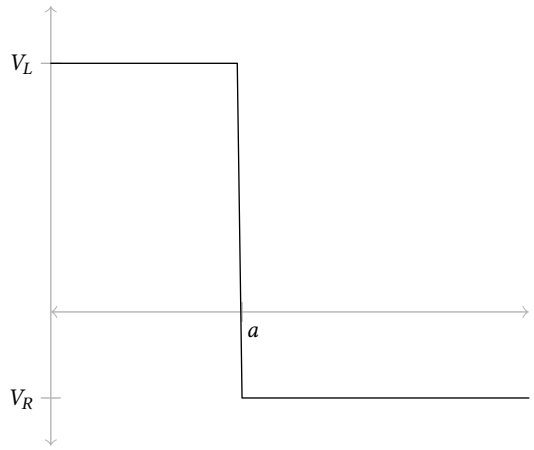
If $E > V_0$, then this is classically allowed, and we have the solutions $\sin kx$ and $\cos kx$, where $k = \frac{\sqrt{2m(E-V_0)}}{\hbar}$. If $E - V_0$ is large, then k is large, and $\lambda = 2\pi/k$ is small. Similarly, if $E - V_0$ is small, then λ is large.

If $E < V_0$, then this is classically forbidden, and we have the solutions $e^{\alpha x}$ and $e^{-\alpha x}$, where $\alpha = \frac{\sqrt{2m(E-V_0)}}{\hbar}$. Then, like before, if $E - V_0$ is large, then we have α is large, yielding a quick exponential function. Similarly, if $E - V_0$ is small, then we have a slowly changing exponential function.

To actually solve this, let's consider a simpler case V that we can use to form a solution to the finite square well problem. Consider the potential

$$V(x) = \begin{cases} V_L & x < a \\ V_r & x > a, \end{cases}$$

where $a \in \mathbb{R}$.



Consider the solutions $\psi(x)$ of this potential. We know that $\psi(x)$ is continuous. We will show that $V(x)$ is continuous if $V(x)$ is finite.

$$\lim_{\Delta \to 0} [\psi'(a+\Delta) - \psi'(a-\Delta)] = \lim_{\Delta \to 0} \int_{a-\Delta}^{a+\Delta} \frac{d}{dx}\psi'(x)\,dx$$

By the Schrödinger equation,

$$= \lim_{\Delta \to 0} \int_{a-\Delta}^{a+\Delta} \frac{2m}{\hbar^2}(V(x) - E)\psi(x)\,dx.$$

If $V(x)$ is finite, then we have that $\frac{2m}{\hbar^2}[V(x) - E]\psi(x)$. Then, we can write

$$\left| \int_{a-\Delta}^{a+\Delta} \frac{2m}{\hbar^2}[V(x) - E]\psi(x)\,dx \right| < c \cdot 2\Delta$$

for some constant c and for all Δ, so we have

$$\lim_{\Delta \to 0} [\psi'(a+\Delta) - \psi'(a-\Delta)] = 0,$$

and ψ' is continuous for finite $V(x)$.

Now suppose that $V(x)$ is infinite. If we have a hard wall $V_L = \infty$, then we have that

$$\lim_{\Delta \to 0} \int_{a-\Delta}^{a+\Delta} \frac{2m}{\hbar^2}(V(x) - E)\psi(x)\,dx \neq 0,$$

and therefore ψ' is discontinuous. If we have a delta function $\psi(x) = V_0\delta(x-a)$, then

$$\lim_{\Delta \to 0} \int_{a-\Delta}^{a+\Delta} \frac{2m}{\hbar^2}(V(x) - E)\psi(x)\,dx = \lim_{\Delta \to 0} \left[\int_{a-\Delta}^{a+\Delta} \frac{2m}{\hbar^2} V_0 \delta(x-a)\psi(x)\,dx - \int_{a-\Delta}^{a+\Delta} \frac{2m}{\hbar^2} E\psi(x)\,dx \right]$$

Note that the second term goes to 0, so this equals

$$= \lim_{\Delta \to 0} \frac{2m}{\hbar^2} V_0 \int_{a-\Delta}^{a+\Delta} \delta(x-a)\delta(x)\,dx = \frac{2m}{\hbar^2} V_0 \psi(a).$$

Therefore, ψ' is discontinuous, and moreover there is a difference of $\frac{2m}{\hbar^2}V_0\psi(a)$ at the point a.

12 March 20, 2019

Consider the finite square well with potential $V(x) = \begin{cases} -V_0 & |x| < a \\ 0 & \text{otherwise} \end{cases}$. Suppose we have an energy $-V_0 < E < 0$.

Consider the region where $x < -a$. By the Schrödinger equation,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \implies \psi'' = \alpha^2\psi, \qquad \text{where } \alpha = \frac{\sqrt{-2mE}}{\hbar}.$$

Then, the general solution in this region is

$$\psi(x) = Ae^{-\alpha x} + Be^{\alpha x}.$$

Since ψ must be normalizable, we must have $A = 0$, and $\boxed{\psi(x) = Be^{\alpha x}}$. For the region where $a < x$, the situation is similar to when $x < -a$, and we have the general solution

$$\boxed{\psi(x) = Fe^{-\alpha x}}.$$

In the region where $-a < x < a$, we have

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} - V_0\psi(x) = E\psi(x) \implies \psi'' = -k^2\psi, \qquad \text{where } k = \frac{\sqrt{2m(E+V_0)}}{\hbar}.$$

The general solution for this is

$$\boxed{\psi(x) = C\sin kx + D\cos kx}.$$

Now we have to patch these solutions together. To do this, we will use the fact that ψ and ψ' are continuous, and also the fact that $[\hat{H}, \hat{\pi}] = 0$. We will look for the even solutions. We have

$$\psi_{\text{even}}(x) = \begin{cases} Fe^{\alpha x} & x < -a \\ D\cos kx & -a < x < a \\ Fe^{-\alpha x} & x > a. \end{cases}$$

Now we check the boundary. At $x = a$, we have

$$\psi(a) = Fe^{-\alpha a} = D\cos ka$$
$$\psi'(a) = -\alpha Fe^{-\alpha a} = -kD\sin ka.$$

Dividing, we have

$$\alpha = k\tan ka.$$

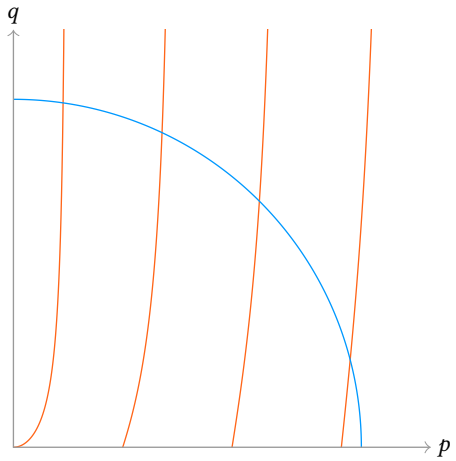
Letting $p = ka$ and $q = \alpha a$, we can rewrite the equation as

$$q = p\tan p.$$

We also know that

$$p^2 + q^2 = a^2 \cdot \frac{2mV_0}{\hbar^2} =: R_0^2.$$

If we plot these two equations, we get something like the following:



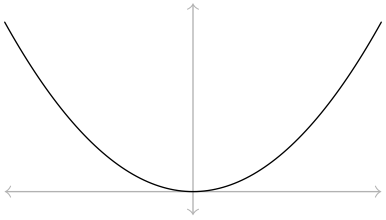
The blue curve is the equation $p^2 + q^2 = R_0^2$, and the orange curves are the equation $q = p \tan p$. We take the intersection points to be the solutions.

13 April 01, 2019

13.1 Harmonic Oscillator

We will now analyze the harmonic oscillator, where the potential is

$$V(x) = \frac{1}{2}kx^2.$$



This is interesting because this is the first order Taylor expansion of any small oscillation. We can derive this potential from the harmonic oscillator by considering Hooke's Law under classical mechanics.

Using this potential in Schrödinger's equation, we get

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi,$$

where we define $\omega = \sqrt{\frac{k}{m}}$.

There are two approaches to solving this. We can either use a power series, called the Sommerfeld method, or we can use ladder operators. We will first use a power series.

13.1.1 Algebraic Approach

Let's introduce the change of variables so that we are working with dimensionless variables:

$$y = \sqrt{\frac{m\omega}{\hbar}}x, \qquad \mathcal{E} = \frac{2E}{\hbar\omega} = \frac{E}{\frac{1}{2}\hbar\omega}.$$

Then we have the equation

$$\frac{d^2\psi(y)}{dy^2} = (y^2 - \mathcal{E})\psi(y).$$

Let's consider the asymptotic behavior where $y \gg \mathcal{E}$ for motivation. We have $\frac{d^2\psi}{dy^2} = y^2\psi$, which has general solution

$$\psi(y) = Ae^{-y^2/2} + Be^{y^2/2} \implies \psi(y) = Ae^{-y^2/2},$$

where we let $B = 0$ in order for the wavefunction to be normalizable. Now, let's suppose the solution is of the form $\psi(y) = h(y)e^{-y^2/2}$. Substituting this into the Schrödinger equation, we have

$$\frac{d^2h}{dy^2} - 2y\frac{dh}{dy} + (\mathcal{E} - 1)h = 0.$$

We now assume $h(y) = a_0 + a_1y + a_2y^2 + \cdots = \sum_{j=0}^{\infty} a_jy^j$. We have

$$\frac{dh}{dy} = \sum_{j=1}^{\infty} ja_jy^{j-1} = \sum_{j=0}^{\infty} ja_jy^{j-1}$$
$$\frac{d^2h}{dy^2} = \sum_{j=2}^{\infty} j(j-1)a_jy^{j-2} = \sum_{j=0}^{\infty}(j+2)(j+1)a_{j+2}y^j$$

This gives

$$\sum_{j=0}^{\infty}[(j+2)(j+1)a_{j+2}y^j - 2ja_jy^j + (\mathcal{E} - 1)a_jy^j] = 0.$$

Since y is arbitrary, we have that

$$(j+2)(j+1)a_{j+2} - 2ja_j + (\mathcal{E} - 1)a_j = 0 \iff a_{j+2} = \frac{2j + 1 - \mathcal{E}}{(j+1)(j+2)}a_j.$$

for all j. Therefore, we have that h is defined by a_0 and a_1. Moreover, since V is even, we have that $[\hat{H}, \hat{\pi}] = 0$ and the solutions are generated of even and odd solutions. However, we also know that the even and odd solutions are just the ones where $a_1 = 0$ and $a_0 = 0$ respectively. Therefore, it suffices to analyze the cases where $a_1 = 0$ and $a_0 = 0$.

However, we have a problem. In particular, sometimes for large $|y|$, $h(y)$ is unbounded. Note that for large $|y|$, the terms that dominate $h(y)$ are the ones that have large j. For large j, we have

$$a_{j+2} \approx \left(\frac{2}{j}\right)a_j \implies \frac{a_{j+2}}{a_j} \approx \frac{2}{j}.$$

Moreover, note that we can write

$$\exp(y^2) = \sum_{j=0}^{\infty}\frac{1}{j!}y^{2j} = \sum_{j=0,2,4,\ldots} B_jx^j,$$

where $B_j = \frac{1}{(j/2)!}$. Then for large j, we have $B_{j+2}/B_j \approx \frac{2}{j}$. Therefore, since the asymptotic behaviors are the same, we have $h(y) \sim \exp(y^2)$. This further gives $\psi(y) \sim \exp(y^2)\exp(-y^2/2) \sim \exp(y^2/2)$, which is bad.

To fix this, we will require the series to terminate, i.e. $a_{n+2} = 0$ for some n. Equivalently,

$$0 = a_{n+2} = \frac{2n + 1 - \mathcal{E}}{(n+1)(n+2)}a_n \implies \mathcal{E} = 2n + 1.$$

This gives the quantized energies $E_n = \frac{1}{2}(2n + 1)\hbar\omega$, where $n \in \{0, 2, 4, 6, \ldots\}$. In general, we have:

17 **Proposition** (Harmonic Oscillator Wavefunctions)

If we have the potential $V(x) = \frac{1}{2}kx^2$, then we have the wavefunctions

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

corresponding to the energies $E_n = \frac{1}{2}(2n + 1)\hbar\omega$, for $n \in \{0, 2, 4, 6, \ldots\}$. Here $\omega = \sqrt{\frac{k}{m}}$ and H_n are the **Hermite polynomials**,

defined by[a]

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2} = \left(2x - \frac{d}{dx}\right)^n \cdot 1.$$

[a] https://en.wikipedia.org/wiki/Hermite_polynomials

14 April 03, 2019

14.1 More on the Harmonic Oscillator

14.1.1 Ladder Operators

Recall that we have the Schrödinger Equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi = E\psi.$$

Rewriting,

$$\frac{1}{2m}\left[\hat{p}^2 + (m\omega\hat{x})^2\right]\psi = E\psi.$$

Let's try to use difference of squares to rewrite the left side. We guess that

$$\frac{1}{2m}\left[\hat{p}^2 + (m\omega\hat{x})^2\right]\psi = \frac{1}{2m}(\hat{p} + im\omega\hat{x})(\hat{p} - im\omega\hat{x}).$$

However, note that operators do not always commute! Let's see what happens when we try to apply this to ψ and expand it.

$$\begin{aligned}\frac{1}{2m}(\hat{p} + im\omega\hat{x})(\hat{p} - im\omega\hat{x})\psi &= \frac{1}{2m}\left(\frac{\hbar}{i}\frac{d}{dx} - im\omega x\right)\left(\frac{\hbar}{i}\frac{d}{dx} + im\omega x\right)\psi \\ &= \frac{1}{2m}\left(-\hbar^2\frac{d^2\psi}{dx^2} + \hbar m\omega\frac{d}{dx}(x\psi) - \hbar m\omega x\frac{d\psi}{dx} + (m\omega x)^2\psi\right)\end{aligned}$$

By the product rule,

$$\begin{aligned}&= \frac{1}{2m}\left(-\hbar^2\frac{d^2\psi}{dx^2} + \hbar m\omega\psi + \hbar m\omega x\frac{d\psi}{dx} - \hbar m\omega x\frac{d\psi}{dx} + (m\omega x)^2\psi\right) \\ &= \frac{1}{2m}\left(-\hbar^2\frac{d^2\psi}{dx^2} + \hbar m\omega\psi + (m\omega x)^2\psi\right)\end{aligned}$$

Rearranging more,

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

18 **Definition**

We will call these operators **ladder operators**, defined by

$$\hat{a}_+ = \frac{1}{\sqrt{2m}}\left(\frac{\hbar}{i}\frac{d}{dx} + im\omega x\right) = \frac{1}{\sqrt{2m}}(\hat{p} + im\omega\hat{x})$$

$$\hat{a}_- = \frac{1}{\sqrt{2m}}\left(\frac{\hbar}{i}\frac{d}{dx} - im\omega x\right) = \frac{1}{\sqrt{2m}}(\hat{p} - im\omega\hat{x}).$$

Sometimes, we call these the **creation** and **annihilation** operators, or the **raising** and **lowering** operators.

Then, we have the relations

$$\hat{a}_-^\dagger = \hat{a}_+, \qquad \hat{H} = \hat{a}_-\hat{a}_+ - \frac{1}{2}\hbar\omega, \qquad \hat{H} = \hat{a}_+\hat{a}_- + \frac{1}{2}\hbar\omega, \qquad [\hat{a}_-, \hat{a}_+] = \hbar\omega.$$

19 **Proposition**

If ψ is an eigenfunction of $\hat{H}$ with eigenvalue E, then

- $\hat{a}_+\psi$ is also an eigenfunction of $\hat{H}$ with energy $E + \hbar\omega$, and
- $\hat{a}_-\psi$ is also an eigenfunction of $\hat{H}$ with energy $E - \hbar\omega$.

Proof. Let ψ be an eigenfunction of $\hat{H}$ with eigenvalue E. Then

$$\begin{aligned}
\hat{H}(\hat{a}_+\psi) &= \left(\hat{a}_+\hat{a}_- + \frac{1}{2}\hbar\omega\right)(\hat{a}_+\psi) \\
&= \left(\hat{a}_+\hat{a}_-\hat{a}_+ + \frac{1}{2}\hbar\omega\hat{a}_+\right)\psi \\
&= \hat{a}_+\left(\hat{a}_-\hat{a}_+ + \frac{1}{2}\hbar\omega\right)\psi \\
&= \hat{a}_+\left(\hat{a}_-\hat{a}_+ - \frac{1}{2}\hbar\omega + \hbar\omega\right)\psi \\
&= \hat{a}_+\left(\hat{H} + \hbar\omega\right)\psi \\
&= \hat{a}_+(E + \hbar\omega)\psi \\
&= (E + \hbar\omega)(\hat{a}_+\psi).
\end{aligned}$$

$$\begin{aligned}
\hat{H}(\hat{a}_-\psi) &= \left(\hat{a}_-\hat{a}_+ - \frac{1}{2}\hbar\omega\right)(\hat{a}_-\psi) \\
&= \left(\hat{a}_-\hat{a}_+\hat{a}_- - \frac{1}{2}\hbar\omega\hat{a}_-\right)\psi \\
&= \hat{a}_-\left(\hat{a}_+\hat{a}_- - \frac{1}{2}\hbar\omega\right)\psi \\
&= \hat{a}_-\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\hbar\omega - \hbar\omega\right)\psi \\
&= \hat{a}_-\left(\hat{H} - \hbar\omega\right)\psi \\
&= \hat{a}_-(E - \hbar\omega)\psi \\
&= (E - \hbar\omega)(\hat{a}_-\psi).
\end{aligned}$$

□

Now, we know that if we have one solution then we can get all the solutions, but we need to find a solution first. We will find the ground state ψ_0. Since this is the lowest state, it turns out that we have $a_-\psi_0 = 0$. In particular, we get

$$a_-\psi_0 = \frac{1}{\sqrt{2m}}\left(\frac{\hbar}{i}\frac{d}{dx} - im\omega x\right)\psi_0 = 0 \implies \frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar}x\psi_0.$$

Solving this differential equation gives us $\psi_0 = A_0 e^{-(m\omega/2\hbar)x^2}$. We also have that

$$\hat{H}\psi_0 = \left(\hat{a}_+\hat{a}_- + \frac{1}{2}\hbar\omega\right)\psi_0 = \frac{1}{2}\hbar\omega\psi_0 \implies E_0 = \frac{1}{2}\hbar\omega.$$

Then, we get the general solution as follows.

20 **Proposition** (Harmonic Oscillator Wavefunctions)

If we have the potential $V(x) = \frac{1}{2}kx^2$, then we have the general wavefunction

$$\psi_n(x) = A_0(\hat{a}_+)^n e^{-(m\omega/2\hbar)x^2},$$

with the corresponding energy $E_n = (n + 1/2)\hbar\omega$.

15 April 08, 2019

15.1 Delta Function Potential

Recall that we have the delta function $\delta(x) = \begin{cases} 0 & x \neq 0 \\ \infty & x = 0, \end{cases}$ where $\int_{-\infty}^{\infty} \delta(x)f(x)\,dx = f(0)$. Then consider the potential function

$$V(x) = -W\delta(x),$$

where W is positive.

As usual, we will find the general solution for $x < 0$ and $x > 0$, and then use the boundary conditions to patch them together. Let's first consider the boundary conditions at $x = 0$. We have by the Schrödinger Equation that

$$\lim_{\varepsilon \to 0} \int_{-\varepsilon}^{\varepsilon} \left[-\frac{\hbar^2}{2m} \psi'' - W\delta(x)\psi \right] dx = \lim_{\varepsilon \to 0} \int_{-\varepsilon}^{\varepsilon} E\psi \, dx.$$

Simplifying both sides gives

$$-\frac{\hbar^2}{2m}[\psi'(0^+) - \psi'(0^-)] - W\psi(0) = 0,$$

where 0^+ means we take the limit as the argument goes to 0 from the positive side. This gives

$$\psi'(0^+) - \psi(0^-) = -\frac{2mW}{\hbar^2}\psi(0).$$

We know that the general wavefunction for this potential for the regions $x < 0$ and $x > 0$ are

$$\psi_1 = Ae^{\alpha x} \implies \psi_1' = \alpha A e^{\alpha x}, \qquad \psi_2 = Be^{-\alpha x} \implies \psi_1' = -\alpha B e^{-\alpha x},$$

where $\alpha = \sqrt{-\frac{2mE}{\hbar^2}}$. From the boundary conditions we have

$$\psi(0^+) = \psi(0^-) \implies A = B$$
$$\psi(0^+) - \psi(0^-) = -\frac{2mW}{\hbar^2}\psi(0) = -\frac{2mW}{\hbar^2}A \implies \alpha = \frac{mW}{\hbar^2}.$$

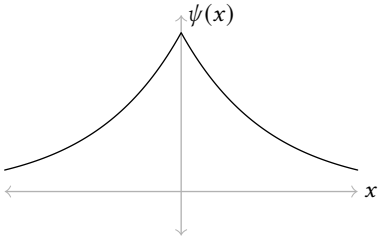
This gives

$$\sqrt{-\frac{2mE}{\hbar^2}} = \frac{mW}{\hbar^2} \implies E = \frac{mW^2}{2\hbar^2}.$$

This means that there is only one eigenvalue! The resulting wavefunction turns out to be

$$\psi(x) = \frac{\sqrt{mW}}{\hbar} \exp(-mW|x|/\hbar^2),$$

and it looks like this



15.2 Scattered States

15.2.1 Free Particle

Let $V = 0$. Then we have the Schödinger equation

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

We then get the solution

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

where $k = \frac{\sqrt{2mE}}{\hbar}$, and the time evolution of it is

$$\psi(x,t) = Ae^{i(kx - E/\hbar t)} + Be^{-i(kx + E/\hbar t)}.$$

This is just a plane wave, where if $k > 0$, then the plane wave travels to the right, and if $k < 0$ then it travels to the left. This is not normalizable, so this wavefunction does not exist. However, we can use this with the Fourier Transform to find how any

wavefunction evolves over time. In particular, if we have the initial wavefunction $\psi(x,0)$, then we compute

$$\tilde{\psi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x,0) e^{-ikx}\, dx,$$

and then we have

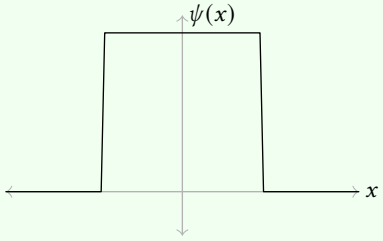
$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{\psi}(k) e^{i(kx-\omega(k)t)}\, dk,$$

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

21 **Example**

Suppose we have a wavefunction that looks like a square:

$$\psi(x,0) = \begin{cases} \frac{1}{\sqrt{2a}} & -a < x < a \\ 0 & \text{else.} \end{cases}$$



Let's find the evolution of this wavefunction. We have

$$\begin{aligned} \tilde{\psi}(k) &= \frac{1}{\sqrt{2\pi}} \int_{-a}^{a} \frac{1}{\sqrt{2a}} e^{-ikx}\, dx \\ &= \frac{1}{k\sqrt{4\pi a}} (e^{-ika} - e^{ika}) \\ &= \frac{\sin ka}{k\sqrt{\pi a}}. \end{aligned}$$

Then, we have

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\sin ka}{k\sqrt{\pi a}} e^{i(kx-\omega(k)t)}\, dk.$$

16 April 10, 2019

16.1 Quantum Tunneling

Consider the step potential

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

There are two cases depending on how large the energy is in relation to V_0. First, suppose that we have an energy $E = \frac{\hbar^2 k_1^2}{2m} > V_0$. Let $E - V = \frac{\hbar^2 k_2^2}{2m}$. Suppose that we have a wave with amplitude A_0 moving to the left. Then in the two regions $x \le 0$ and $x > 0$, we have

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \implies \psi(x) = A_0 e^{ik_1 x} + Ae^{-ik_1 x} \\ -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V_0\psi = E\psi \implies \psi(x) = Be^{ik_2 x}, \end{aligned}$$

where A is the amplitude of reflected wave and B is the amplitude of transmitted wave. Applying the boundary conditions, we have

$$A_0 + A = B, \qquad k_1 A_0 - k_1 A = k_2 B.$$

Solving this, we have

$$A = \left(\frac{k_1 - k_2}{k_1 + k_2}\right) A_0, \qquad B = \left(\frac{2k_1}{k_1 + k_2}\right) A_0.$$

Let the **reflection coefficient** R and the **transmission coefficient** T of the system be the fraction of incident particles that are reflected and transmitted respectively. We have

$$R = \frac{\text{probability current of reflected wave}}{\text{probability current of incident wave}}$$
$$T = \frac{\text{probability current of transmitted wave}}{\text{probability current of incident wave}}.$$

Recall that the probability current J is the product of the probability density and the group velocity. This means that for a plane wave $\psi = A_0 e^{ik_1 x} \implies |\psi|^2 = |A_0|^2$, we have its velocity $\frac{\hbar k_1}{m}$, so

$$J = \frac{\hbar k_1}{m} |A_0|^2.$$

Alternatively, we could have used the formula that we proved on a problem set:

$$J = \frac{\hbar}{2m}\left[\psi^* \frac{d\psi}{dx} - \psi \frac{d\psi^*}{dx}\right].$$

This gives the reflection and transmission coefficients

$$R = \frac{v_1 |A|^2}{v_1 |A_0|^2} = \frac{|A|^2}{|A_0|^2}$$
$$T = \frac{v_2 |B|^2}{v_1 |A_0|^2} = \frac{|B|^2}{|A_0|^2},$$

where

$$v_1 = \frac{\hbar k_1}{m}, \qquad v_2 = \frac{\hbar k_2}{m}.$$

Expanding this out, we have

$$R = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2, \qquad T = \frac{4k_1 k_2}{(k_1 + k_2)^2}.$$

17 April 17, 2019

Now consider the step potential

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

again, with $E < V_0$. Let $E = \frac{\hbar^2 k_1^2}{2m}$ and $V_0 - E = \frac{k^2 \alpha^2}{2m}$. For the two regions $x \le 0$ and $x > 0$, we have the general solutions

$$\psi(x) = A_0 e^{ik_1 x} + A e^{-ik_1 x}$$
$$\psi(x) = B_0 e^{-\alpha x}.$$

This gives

$$A = \left(\frac{ik + \alpha}{ik - \alpha}\right) A_0$$
$$B = \left(\frac{2ik}{ik - \alpha}\right) A_0.$$

Something interesting to note is that in order to establish that the particle is actually in the forbidden region, we must have

resolving power $\Delta x < \frac{1}{2}$. By Heisenberg Uncertainty, we have

$$\Delta p \geq \frac{\hbar}{\Delta x} \geq \hbar\alpha.$$

Therefore, we are given the particle an energy of

$$\frac{|\Delta p|^2}{2m} \geq \frac{\hbar^2\alpha^2}{2m} = V_0 - E.$$

17.1 Potential Barrier

Consider the potential

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

18 April 24, 2019

18.1 Three-dimensional Systems

We will first generalize the Schrödinger equation to three dimensions. To do this, we have

$$\hat{H} = \left(\frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m}\right) + V(x,y,z,t) = \frac{\hat{p}^2}{2m} + V(x,y,z,t),$$

where $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$, $\hat{p}_y = -i\hbar\frac{\partial}{\partial y}$, $\hat{p}_z = -i\hbar\frac{\partial}{\partial z}$, and we define $\hat{p} = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2$. Then, the Schrödinger equation is

$$\hat{H}\psi = i\hbar\frac{\partial}{\partial t}\psi.$$

Sometimes, we will write

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

We will similarly assert that

$$P(x,y,z,t) = |\psi(\vec{r},t)|^2$$
$$1 = \int |\psi(x,t)|^2\, d^3r.$$

As in the one-dimensional case, we have the time independent Schrödinger equation $\hat{H}\psi(\vec{r}) = E\psi(\vec{r})$, and the general solution

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

where $\hat{H}\psi_n = E_n\psi_n$ describes the eigenvectors.

18.1.1 Free Particle

Let $V(\vec{r}) = 0$. Then we have

$$\hat{H} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right),$$

and we wish to solve

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(\vec{r}) = E\psi(\vec{r}).$$

Let's guess a solution of the form $\psi(x,y,z) = \psi_x(x)\psi_y(y)\psi_z(z)$. Then we wish to solve

$$E\psi_x\psi_y\psi_z = -\frac{\hbar^2}{2m}(\psi_y\psi_z\partial_x^2\psi_x + \psi_z\psi_x\partial_y^2\psi_y + \psi_x\psi_y\partial_z^2\psi_z).$$

Dividing by $\psi_x\psi_y\psi_z$, we have

$$E = -\frac{\hbar^2}{2m}\left(\frac{\partial_x^2\psi_x}{\psi_x} + \frac{\partial_y^2\psi_y}{\psi_y} + \frac{\partial_z^2\psi_z}{\psi_z}\right).$$

Reducing, we get

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_x = E_x\psi_x \qquad -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\psi_y = E_y\psi_y \qquad -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}\psi_z = E_z\psi_z.$$

This is just the equation that describes a one-dimensional free particle! This means that we have

$$\psi_x(x) = e^{ik_x x} \qquad \psi_y(y) = e^{ik_y y} \qquad \psi_z(z) = e^{ik_z z},$$

where

$$k_x^2 = \frac{2m}{\hbar^2}E_x \qquad k_y^2 = \frac{2m}{\hbar^2}E_y \qquad k_z^2 = \frac{2m}{\hbar^2}E_z.$$

Combining, we get

$$E = E_x + E_y + E_z = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m}\vec{k}^2,$$

where $\vec{k} = (k_x, k_y, k_z)$. Then, we have the full solution

$$\psi(\vec{r}) = e^{i(\vec{k}\cdot\vec{r})} \implies \psi(\vec{r}, t) = e^{i\vec{k}\cdot\vec{r} - \omega t},$$

where $\omega = E/\hbar$.

18.1.2 Infinite Cube Well

Let $V(\vec{r}) = \begin{cases} 0 & 0 < x, y, z < a \\ \infty & \text{else} \end{cases}$. We will again use separation of variables. Recall that in one dimension, we have the eigenstates

$$\phi_n(x) = \sqrt{\frac{2}{a}}\sin(k_n x), \qquad E_n = \frac{\hbar^2}{2m}k_n^2, \qquad k_n = \frac{(n+1)\pi}{a},$$

where $n = 0, 1, 2, \ldots$. Then, in three-dimensions, we have the eigenstates

$$\phi_n(\vec{r}) = \left[\sqrt{\frac{2}{a}}\right]^3 \sin(k_{n_x}x)\sin(k_{n_y}y)\sin(k_{n_z}z),$$

where

$$k_{n_x} = \frac{(n_x+1)\pi}{a}, \qquad k_{n_y} = \frac{(n_y+1)\pi}{a}, \qquad k_{n_z} = \frac{(n_z+1)\pi}{a},$$

and $n_x, n_y, x_z = 0, 1, 2, \ldots$. Then we have

$$E_n = \frac{\hbar^2}{2m}\vec{k}^2 = \frac{\hbar^2\pi}{2m}[(n_x+1)^2 + (n_y+1)^2 + (n_z+1)^2].$$

However, note that this system is degenerate (in the sense that a particular energy does not correspond to a unique wavefunction). This can be seen easily by rearranging the dimensions.

18.1.3 Harmonic Oscillator

Let $V(\vec{r}) = \frac{1}{2}m\omega^2(x^2 + y^2 + z^2) = \frac{1}{2}m\omega^2\vec{r}^2$. Let's again guess the solution $\phi(x, y, z) = \phi_x(x)\phi_y(y)\phi_z(z)$. Recalling that in one dimension we have

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

we have the solution in three-dimensions

$$E_{n_x,n_y,n_z} = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right).$$

This again yields degeneracies. This is called the **isotropic harmonic oscillator**. To remedy some of this, we will modify the potential to be

$$V(\vec{r}) = \frac{1}{2}m(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2).$$

18.1.4 Radial Potentials

Sometimes our potential will be a function of the distance from the origin, i.e. we can write $V(\vec{r}) = V(|\vec{r}|) = V(r)$. In this case it makes sense to use spherical coordinates. (Recall that we use (r, φ) for the xy-plane and θ for angle between $\vec{r}$ and the z-axis). We have the Laplacian

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

which we will use in the Schrödinger equation.

19 April 29, 2019

From the Laplacian in polar coordinates, we get the time independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right] + V\psi = E\psi.$$

We assume that we have a solution of the form $\psi(r,\theta,\varphi) = R(r)\cdot Y(\theta,\varphi)$, where R is called the radial part and Y is called the angular part. Substituting this in and simplifying, we get

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] = \ell(\ell+1)$$

$$\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right] = -\ell(\ell+1)$$

for the radial and angular part of the wavefunction respectively, and where $\ell(\ell+1)$ is just some constant (motivation provided later). Note that the second equation has no dependence on $V(r)$, so when we solve this, we can use the solutions for all $V(r)$.

For the radial equation, if we make the substitution $u(r) = rR(r)$, then we get the equation

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu.$$

If we are looking for spherically symmetric solutions, then the second equation gives us $\ell = 0$. Simplifying this is nontrivial, so we will stop here.

22 **Example** (Infinite spherical well)

Suppose we want the spherically symmetric solutions $\psi(r)$ of the infinite spherical well

$$V(r) = \begin{cases} 0 & r \le a \\ \infty & r > a \end{cases}.$$

On the outside of the well, we have $u(r) = 0$, and on the inside, we have

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} = Eu.$$

This has the general solution

$$u(r) = A\sin kr + B\cos kr,$$

where $k = \frac{\sqrt{2mE}}{E}$. In order for $\psi = u/r$ to be finite at $r = 0$, we must have $B = 0$. Therefore, we have

$$u(r) = A \sin kr, \qquad \psi(r) = \frac{u(r)}{r}.$$

Considering the boundary condition at $r = a$, we have

$$\sin ka = 0 \implies k_n a = n\pi \implies k_n = \frac{n\pi}{a},$$

and we can compute the normalization constant $A = \frac{1}{\sqrt{2\pi a}}$.

23 **Example** (Hydrogen Atom)

Let's find the spherically symmetric solutions to the hydrogen atom potential

$$V(r) = -\frac{Ze^2}{r},$$

where Z is the atomic number and e is the elementary charge. Here we use **Gaussian units**, i.e. $4\pi\varepsilon_0 = 1$. Let $r = \sqrt{-\frac{\hbar^2}{8mE}}\rho$ and $\lambda = \frac{Ze^2}{\hbar}\sqrt{-\frac{m}{2E}}$. This gives the equation

$$\frac{d^2u}{d\rho^2} + \lambda\frac{u}{\rho} - \frac{u}{4} = 0.$$

First, note that as $\rho \to \infty$, we get $u(\rho) \sim e^{-\rho/2}$. Assume that

$$u(\rho) = h(\rho)e^{-\rho/2}.$$

Substituting this into the ODE, we get

$$\frac{d^2h}{d\rho^2} - \frac{dh}{d\rho} + \frac{\lambda}{\rho}h = 0.$$

Let $h(\rho) = \sum_{j=1}^{\infty} b_i\rho^j$, and then we get the recurrence relation

$$b_{j+1} = -\frac{\lambda - j}{j(j+1)}b_j.$$

This means that as $\rho \to \infty$, we have $b_{j+1} \sim \frac{b_j}{j+1}$, which implies that $h(\rho)$ grows exponentially. However, there is a solution if $\lambda - j = 0$ at some point, i.e. if $\lambda \in \mathbb{Z}_+$.

Let $\lambda = n$ be an integer. This is called the **principal quantum number**. Then, we have that

$$n = \lambda = \frac{Ze^2}{\hbar}\sqrt{-\frac{m}{2E}} \implies E_n = -\frac{Z^2me^4}{2\hbar}\frac{1}{n^2} = -\frac{1}{2}\frac{Z^2e^2}{a_0}\frac{1}{n^2} = \frac{E_1}{n^2},$$

where $a_0 = \frac{\hbar^2}{me^2}$.

The eigenfunctions are hard to explicitly write, but the ground state is

$$\psi_1(r) = \frac{1}{\sqrt{\pi}}\left(\frac{a_0}{Z}\right)^{-3/2}e^{-Zr/a_0}.$$

This gives us all spherically symmetric solutions, which correspond to 1s, 2s, 3s, ... orbitals.

20 May 06, 2019

20.1 Angular Momentum

Recall that in classical mechanics, we have

$$\vec{L} = \vec{r} \times \vec{p},$$

i.e.

$$L_x = yp_z - zp_y, \qquad L_y = zp_x - xp_z, \qquad L_z = xp_y - yp_x.$$

We will define the corresponding quantum operators by letting

$$\hat{L}_x = y\hat{p}_z - z\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right),$$
$$\hat{L}_y = z\hat{p}_x - x\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right),$$
$$\hat{L}_z = x\hat{p}_y - y\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).$$

Note that by symmetry, $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ have the same eigenvalues. We consider $\hat{L}_z$ in spherical coordinates:

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}.$$

Then we wish to solve

$$\hat{L}_z\psi(r,\theta,\varphi) = L_z\phi(r,\theta,\varphi) \implies -i\hbar\frac{\partial\psi}{\partial\varphi} = L_z\phi,$$

which has the solution

$$\psi(r,\theta,\varphi) = f(r,\theta)\exp(iL_z\varphi/\hbar).$$

Moreover, note that we must have $\psi(r,\theta,\varphi) = \psi(r,\theta,\varphi+2\pi)$. This implies $\exp(2\pi iL_z/\hbar) = 1 \implies L_z = m\hbar$ for some $m \in \mathbb{Z}$. This gives the eigenvalues for $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$.

Recall that

$$[\hat{L}_x, \hat{L}_y] = i\hbar L_z,$$
$$[\hat{L}_y, \hat{L}_z] = i\hbar L_x,$$
$$[\hat{L}_z, \hat{L}_x] = i\hbar L_y,$$

are nonzero, so there are no simultaneous eigenfunctions for these operators. However, if we consider

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

then we have

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_x] = 0.$$

Therefore, there might be a simultaneous eigenfunction ψ with

$$\hat{L}^2\psi = a\psi, \qquad \hat{L}_z\psi = b\psi.$$

Let us define $\hat{L}_+ = \hat{L}_x + i\hat{L}_y$ and $\hat{L}_- = \hat{L}_x - i\hat{L}_y$. Then we get

$$[\hat{L}_z, \hat{L}_\pm] = \pm\hbar\hat{L}_\pm, \qquad [\hat{L}^2, \hat{L}_\pm] = 0.$$

24 **Proposition**

If ψ is an eigenfunction of $\hat{L}^2$ and $\hat{L}_z$, then $\hat{L}_\pm\psi$ is also an eigenfunction of $\hat{L}^2$ and $\hat{L}_z$.

Proof. Let $\hat{L}^2\psi = a\psi$ and $\hat{L}_z\psi = b\psi$. Then

$$\hat{L}^2(\hat{L}_\pm\psi) = \hat{L}_\pm(\hat{L}^2\psi) = \hat{a}L_\pm\psi,$$

where we used the commutativity in the first step and the fact that ψ is an eigenfunction in the second step.

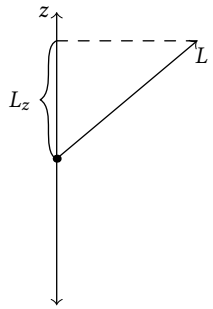
Similarly, we have

$$\hat{L}_z(\hat{L}_\pm\psi) = ([\hat{L}_z, \hat{L}_\pm] + \hat{L}_\pm\hat{L}_z)\psi = (\pm\hbar\hat{L}_\pm + b\hat{L}_\pm)\psi = (b \pm \hbar)\hat{L}_\pm\psi.$$ □

Note that in the first case, we get the same eigenvalue, but in the second case, we get a different eigenvalue. We call $\hat{L}_+$ and $\hat{L}_-$

raising and lowering operators, because they increase and decrease the eigenvalues for $\hat{L}_z$.

We can think of L_z as an L vector that is projected onto the L_z axis.



We have that $\hat{L}_+$ increases the value of L_z, but does not change the length of L. Therefore, there will be some point in which when we apply $\hat{L}_+$, we will get 0.

We can use this to help us find the value of a where $\hat{L}^2\psi_{\text{top}} = a\psi_{\text{top}}$. Suppose that $\hat{L}_+\psi_{\text{top}} = 1$. Then let $\hat{L}^2\psi_{\text{top}} = \hbar\ell\psi_{\text{top}}$. We also have

$$\hat{L}^2 = \hat{L}_\pm\hat{L}_\mp + \hat{L}_z^2 \pm \hbar\hat{L}_z.$$

Hence,

$$\begin{aligned}\hat{L}^2\psi_{\text{top}} &= (\hat{L}_-\hat{L}_+ + \hat{L}_z^2 + \hbar\hat{L}_z)\psi_{\text{top}} \\ &= (0 + \hbar^2\ell^2 + \hbar^2\ell)\psi_{\text{top}} \\ &= \hbar^2\ell(\ell+1)\psi_{\text{top}},\end{aligned}$$

and $a = \hbar^2\ell(\ell+1)$.

Similarly, we can say that there exists a state ψ_{bot} such that $\hat{L}_-\psi_{\text{bot}} = 0$. Let $\hat{L}_z\psi_{\text{bot}} = \hbar\overline{\ell}\psi_{\text{bot}}$. Then by a similar process as above, we get

$$\hat{L}^2\psi_{\text{bot}} = \hbar^2\overline{\ell}(\overline{\ell}-1)\psi_{\text{bot}}.$$

Therefore, we have the equation

$$\ell(\ell+1) = \overline{\ell}(\overline{\ell}-1),$$

which has the solutions $\overline{\ell} = \ell+1$ or $\overline{\ell} = -\ell$. The first one is not possible because $\overline{\ell}$ must be less than ℓ, so we have $\overline{\ell} = -\ell$.

Therefore, the eigenvalues of $\hat{L}_z$ are $m\hbar$, where m foes from $-\ell$ to ℓ in N steps. Therefore $\ell = N/2$, and we have the general solution:

$$\begin{aligned}\ell &= 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots \\ m &= -\ell, -\ell+1, \dots, \ell-1, \ell\end{aligned}$$

21 May 08, 2019

21.1 Angular Part of Schrödinger Equation

Recall that when we had the time independent Schrödinger equation, we let $\psi(r,\theta,\varphi) = R(r)\cdot Y(\theta,\varphi)$, and this yields

$$\begin{aligned}\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r)-E] &= \ell(\ell+1) \\ \frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right] &= -\ell(\ell+1).\end{aligned}$$

We solved this for $\ell = 0$, i.e. for spherically symmetric solutions. Now suppose that ℓ is any nonnegative integer. Let

$$Y(\theta, \varphi) = \Theta(\theta)\Phi(\varphi).$$

We then get

$$\frac{1}{\Theta}\left[\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \ell(\ell+1)\sin^2\theta\right] + \frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = 0.$$

The first term only depends on θ, and the second term only depends on φ, so both must be a constant. Let the constant be m^2. We get

$$\frac{1}{\Theta}\left[\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \ell(\ell+1)\sin^2\theta\right] = m^2$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = -m^2.$$

The second equation gives us $\Phi(\varphi) = \exp(im\varphi)$, implying that $m = 0, 1, 2, \ldots$ since Φ has period 2π.

The first equation is hard to solve. We know (from math) that the solution is

$$\Theta(\theta) = AP_{\ell m}(\cos\theta),$$

where $P_{\ell m}$ are the **associated Legendre function**, defined by

$$P_{\ell m}(x) = (1-x^2)^{|m|/2}\frac{d^{|m|}}{dx^{|m|}}P_\ell(x),$$

where P_ℓ is the ℓth **Legendre polynomial**, defined by

$$P_\ell(x) = \frac{1}{2^\ell \ell!}\frac{d^\ell}{dx^\ell}(x^2-1)^\ell.$$

Overall, this gives the **spherical harmonics** $Y_{\ell m}(\theta, \varphi) = A\exp(im\varphi)P_{\ell m}(\cos\theta)$. Here are some values of $P_{\ell m}$ for small ℓ and m.

$$P_{1,1}(\cos\theta) = \sin\theta \qquad P_{1,0}(\cos\theta) = \cos\theta$$

$$P_{2,2}(\cos\theta) = 3\sin^2\theta \qquad P_{2,1}(\cos\theta) = 3\sin\theta\cos\theta \qquad P_{2,0}(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1).$$

21.1.1 Relationship between $Y_{\ell m}$ and $\hat{L}^2$, $\hat{L}_z$

Writing $\hat{L}^2$ in spherical coordinates, we have

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right].$$

We know that $\psi_{\ell m}$ is an eigenvalue for $\hat{L}^2$, so we have

$$\hat{L}^2\psi_{\ell m} = \hbar^2\ell(\ell+1)\psi_{\ell m}$$

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi_{\ell m}}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi_{\ell m}}{\partial\varphi^2}\right] = \hbar^2\ell(\ell+1)\psi_{\ell m}$$

$$\frac{1}{Y_{\ell m}}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi_{\ell m}}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi_{\ell m}}{\partial\varphi^2}\right] = -\ell(\ell+1).$$

This is precisely the equation for the angular momentum, so the eigenvalues are $\psi_{\ell m} = Y_{\ell m}$.

21.2 Radial Part of Schrödinger Equation

Recall that we let $u(r) = r \cdot R(r)$. Then we have

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu.$$

We call $V_{\text{eff}} = V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$ the **effective potential**, where the second term of the effective potential is called the **centrifugal term**. The centrifugal term is nonzero for $\ell > 0$.

We can rewrite our equation as

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + V_{\text{eff}}u = Eu,$$

but it is difficult to solve without knowing a specific V_{eff}.

22 May 13, 2019

22.1 General solution for Hydrogen Atom

Note: The notes from this day were adapted from a combination of the handwritten lecture notes, Yoshihiro Saito's notes, and Griffiths, as I was not at lecture.

Let's find the complete solution for the wavefunctions of the hydrogen atom. Recall that we have the potential

$$V(r) = -\frac{e^2}{r},$$

where we are using Gaussian units again. We can again split the solution as $\psi(r,\theta,\varphi) = u(r)\cdot Y(\theta,\varphi)$, where $u(r) = rR(r)$.

Since this potential is spherically symmetric, we already know that the set of solutions for Y are the $Y_{\ell m}$ that we have computed already.

For the radial part, recall that we have

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu.$$

We have already solved this for $\ell = 0$, i.e. the spherically symmetric solutions. Now consider $\ell > 0$. Since we are looking for bound states, we have $E < 0$, so let us divide by E. This gives

$$-\frac{\hbar^2}{2mE}\frac{d^2u}{dr^2} = \left[1 + \frac{e}{rE} - \frac{\hbar^2}{2mE}\frac{\ell(\ell+1)}{r^2}\right]u.$$

For convenience, let

$$\alpha = \frac{\sqrt{-2mE}}{\hbar}, \qquad \rho = \alpha r, \text{ and} \qquad \rho_0 = \frac{2me^2}{\hbar^2\alpha}.$$

Then the equation can be rewritten as

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u.$$

To solve this, let's analyze the asymptotics as $\rho \to \infty$. The equation gives

$$\frac{d^2u}{d\rho^2} = u,$$

so we know that $u \sim A\exp(-\rho)$ for large ρ, where we discard the part with positive exponent because we want the wavefunction to be normalizable.

Similarly, we have

$$\rho \to 0^+ \implies \frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2}u \implies u = B\rho^{\ell+1} + C\rho^{-\ell} \implies u \sim B\rho^{\ell+1}$$

for small ρ.

Therefore, we will try to find a solution of the form $u(\rho) = \rho^{\ell+1}\exp(-\rho)v(\rho)$. We can compute the first few derivatives:

$$\frac{du}{d\rho} = \rho^{\ell}\exp(-\rho)\left[(\ell+1-\rho)v + \rho\frac{dv}{d\rho}\right]$$
$$\frac{d^2u}{d\rho^2} = \rho^{\ell}\exp(-\rho)\left[\left(-2\ell - 2 + \rho + \frac{\ell(\ell+1)}{\rho}\right)v + 2(\ell+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right]$$

Substituting this into the equation, we have

$$\rho\frac{d^2v}{d\rho^2}+2(\ell+1-\rho)\frac{dv}{d\rho}+[\rho_0-2(\ell+1)]v=0.$$

To find $v(\rho)$, suppose that we have the Taylor expansion $v(\rho)=\sum_{j=0}^{\infty}a_j\rho^j$. We have

$$\frac{dv}{d\rho}=\sum_{j=0}^{\infty}ja_j\rho^{j-1}=\sum_{j=0}^{\infty}(j+1)a_{j+1}\rho^j$$
$$\frac{d^2v}{d\rho^2}=\sum_{j=0}^{\infty}j(j+1)a_{j+1}\rho^{j-1}.$$

Substituting this into the equation, get get a recursion for the coefficients a_j:

$$\sum_{j=0}^{\infty}j(j+1)a_{j+1}\rho^j+2(\ell+1)\sum_{j=0}^{\infty}(j+1)a_{j+1}\rho^j-2\sum_{j=0}^{\infty}ja_j\rho^j+[\rho_0-2(\ell+1)]\sum_{j=0}^{\infty}a_j\rho^j=0$$
$$j(j+1)a_{j+1}+2(\ell+1)(j+1)a_{j+1}-2ja_j+[\rho_0-2(\ell+1)]a_j=0$$
$$a_{j+1}=\left[\frac{2(j+\ell+1)-\rho_0}{(j+1)(j+2\ell+2)}\right]a_j$$

Now let's check whether or not this is a valid solution. For large j, we have that the larger terms dominate for large ρ. Then, we have

$$a_{j+1}\approx\frac{2j}{j(j+1)}a_j=\frac{2}{j+1}a_j\implies a_j\approx\frac{2^j}{j!}a_0.$$

This implies that $v(\rho)\approx\exp(2\rho)$, which is bad because it implies that $u(\rho)=a_0\rho^{\ell+1}\exp(\rho)$. Therefore, the series must become zero at some point. In particular, there exists some $j_{\max}$ such that

$$a_{j_{\max}+1}=0\iff\left[\frac{2(j_{\max}+\ell+1)-\rho_0}{(j_{\max}+1)(j_{\max}+2\ell+2)}\right]=0\iff 2(j_{\max}+\ell+1)=\rho_0.$$

Let $j_{\max}+\ell+1=n$ be the **principal quantum number**. Since $\rho_0=\frac{2me^2}{\hbar^2\alpha}$ and $\rho_0=2n$, equating these give $n=\frac{me^2}{\hbar^2\alpha}$. Letting $a_0=\frac{\hbar^2}{me^2}\approx 5.29\times10^{-11}\text{m}$ be the **Bohr radius**, we have $\alpha=\frac{1}{a_0n}\implies\rho=\alpha r=\frac{r}{a_0n}$.

Since n is an integer, this gives the energy quantization of

$$2n=\rho_0=\frac{2me^2}{\hbar^2\alpha}=\frac{2me^2}{\hbar^2\sqrt{-2mE}/\hbar}=\frac{2me^2}{\hbar\sqrt{-2mE}}.$$

Solving for E gives

$$E_n=-\frac{me^4}{2\hbar^2}\cdot\frac{1}{n^2}\approx\frac{-13.6\text{eV}}{n^2},$$

where m is the electron mass and e is the elementary charge. This gives us the **Laguerre polynomials**. In particular,

$$v(\rho)=L_{n-\ell-1}^{2\ell+1}(2\rho),$$

where

$$L_q^p(x)=(-1)^p\frac{d^p}{dx^p}L_{p+q}(x)$$

is an **associated Laguerre polynomial**, and

$$L_r(x)=e^x\frac{d^r}{dx^r}(e^{-x}x^r)$$

is the qth **Laguerre polynomial**. This concludes the search for the full solution.

To summarize:

25 **Proposition** (Eigenstates and eigenvalues of a Hydrogen Atom)

For the potential $V = -\frac{e^2}{r}$ (using Gaussian units), the energy eigenstates are

$$\phi_{n\ell m} = A_{n\ell m} R_{n\ell}(r) Y_{\ell m}(\theta, \varphi),$$

where

$$\begin{aligned} R_{n\ell}(r) &= \frac{u}{r} = \frac{1}{r}\rho^{\ell+1}\exp(-\rho)v(\rho) \\ &= \frac{r^\ell}{(a_0 n)^{\ell+1}} e^{-r/a_0 n} L^{2\ell+1}_{n-\ell-1}\left(\frac{2r}{a_0 n}\right), \\ Y_{\ell m}(\theta, \varphi) &= e^{im\varphi} P_{\ell m}(\cos\theta) \\ &= e^{im\varphi}(1-x^2)^{|m|/2}\frac{d^{|m|}}{dx^{|m|}}\left[\frac{1}{2^\ell \ell!}\frac{d^\ell}{dx^\ell}(x^2-1)^\ell\right], \end{aligned}$$

and where L_q^p is defined above. The values n, l, and m are the principal, angular, and magnetic quantum numbers respectively, and

$$n = 1, 2, 3, \ldots, \qquad \ell = 0, 1, 2, \ldots, n-1, \qquad m = -\ell, -\ell+1, \ldots, \ell-1, \ell.$$

The energy associated with $\phi_{n\ell m}$ is given by

$$E_n = -\frac{me^4}{2\hbar^2}\cdot\frac{1}{n^2}.$$

The normalization constant is

$$A_{n\ell m} = \sqrt{\left(\frac{2}{a_0 n}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}}.$$

26 **Note**

The angular quantum number ℓ corresponds to which orbital we have! In particular, we have the table

ℓ	0	1	2	3	4	5	$\cdots$
	s	p	d	f	g	h	$\cdots$

22.1.1 Degeneracies

Note that each energy E_n only depends on n. However, for each n, there are n possible values for ℓ, and for each ℓ, there are $2\ell+1$ values for m. This implies that E_n has degeneracy $\sum_{\ell=0}^{n-1}(2\ell+1) = n^2$.

22.1.2 Probability Density Function

Note that the probability does not depend on φ, because in the wavefunction, the only term containing it is $e^{im\varphi}$, and $|e^{im\varphi}| = 1$.

Therefore, we have the probability density function

$$P(\rho, \theta) \propto R_{n\ell}(\rho)^2 P_{\ell m}(\cos\theta)^2.$$

To find the radial density functions, we can integrate over all θ, i.e.

$$P_r(\rho) = \int_{-\pi/2}^{\pi/2} P(\rho, \theta)\, d\theta = 4\pi\rho^2 R_{n\ell}(\rho)^2.$$

23 May 15, 2019

23.1 Final Exam Review

There will be seven problems; two multiple choice problems (total 31 points), and five longer ones. The exam will be 180 minutes long.

For the multiple choice, some keywords are:

- Hermitian operator
- Time evolution of wavefunctions
- Uncertainty in $\hat{L}_x, \hat{L}_y, \hat{L}_z$
- General wavefunction properties with respect to the potential

Some details about the five longer problems:

23.1.1 Infinite Square Well (17 pts)

We know that the eigenfunctions of the infinite square well are

$$\phi_n(x) = \begin{cases} \sqrt{2/L}\sin(k_n x) & 0 \le x \le L \\ 0 & \text{otherwise.} \end{cases}$$
$$k_n = \frac{(n+1)\pi}{L}.$$

Consider what happens if we change the value of L at some time t. In particular, suppose that we are in the ground state of the initial system. At some point t, we double L. What's the probability that we will be in the ground state of the new system?

23.1.2 One-dimensional harmonic Oscillator

Given some wavefunction that is the sum of the eigenstates, how do we find $\langle p \rangle$? One way is to take the integral, but another way is to write $\hat{p}$ in terms of $\hat{a}$ and $\hat{a}^\dagger$. We will also look at the time evolution of states.

23.1.3 Isotropic Harmonic Oscillator

Look over how we derive the energy $E_{n_x n_y n_z} = \hbar\omega(n_x + n_y + n_z + 3/2)$ from the potential function. Also think about how to count the number of degeneracies.

23.1.4 Angular Momentum

Know about the eigenfunctions and eigenvalues of $\hat{L}^2$ and $\hat{L}_z$, as well as relations like $\langle Y_{\ell m} | Y_{\ell' m} \rangle = \delta_{\ell\ell'}\delta_{mm'}$. Also, look at problems where we use $\hat{L}_+$ and $\hat{L}_-$. In particular, think about how to calculate $\langle L_x \rangle$. A good way to do this is to write $\hat{L}_x$ as the linear combination of $\hat{L}_+$ and $\hat{L}_-$.

23.1.5 Hydrogen Atom

Look at PSet10 problem 5. In particular, the eigenstates $\phi_{n\ell m}$ are eigenstates of $\hat{H}$, $\hat{L}^2$, and $\hat{L}_z$. This is apparently the easiest problem.