

PHYS 52: Quantum Physics

Connor Neely, Spring 2024

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1 Wave Mechanics

1.1 Introduction

Our exploration of quantum mechanics began after a variety of experiments suggested that light behaves as both a wave and a particle. The massless particles that compose light are called photons. Each photon has energy $E = h\nu$, where ν is the photon's frequency and h is Planck's constant. The inherently probabilistic nature of the photon is described by complex numbers called probability amplitudes.

Using these probability amplitudes, we were able to describe the results of the double-slit experiment. Suppose light with wavenumber $k = 2\pi/\lambda$ passes through two infinitesimal slits spaced a distance d apart; the probability amplitude of detecting a photon at an angle θ above the slits is given by

$$z = re^{ikd_1} (1 + e^{ikd \sin \theta}),$$

where d_1 is the total distance traveled by light coming from the top slit and r is the probability amplitude for light diffracting in the correct direction. This gives the probability of detection

$$z^*z = 4r^2 \cos^2 \left(\frac{kd \sin \theta}{2} \right).$$

Using a similar line of reasoning (and some calculus), for a single slit of width a , the detection probability is

$$z^*z = r^2 \frac{\sin^2 \alpha}{\alpha^2},$$

where $\alpha = \frac{1}{2}ka \sin \theta$.

Shockingly, both of these results hold for massive particles! In order to describe the interference that leads to these equations, though, we need a wavelength. Taking inspiration from the fact that an individual photon has energy $E = h\nu = pc$ and thus wavelength $\lambda = h/p$, we can define a particle's de Broglie wavelength as

$$\lambda_{\text{dB}} = \frac{h}{p} = \frac{h}{mv}.$$

Mathematically, this wavelength correctly predicts the way in which matter behaves in the double-slit experiment and others. This suggests that the wave-particle duality is not just true for light, but also for matter.

An immediate application of this revelation comes in the form of crystal diffraction. In an ideal crystal, there are many very thin layers of atoms that are spaced a very small distance d apart. Each layer of atoms acts as a mirror that reflects some incident atoms and reflects others.

If a stream of, say, electrons is incident on a two-layer crystal at an angle θ above the horizontal, then some electrons are reflected off of the top layer and some off of the bottom layer. The bottom electrons travel an extra $2d \sin \theta$, so in order for the top and bottom electrons to leave the crystal in phase with each other, this number must be an integer number of wavelengths. Mathematically,

$$2d \sin \theta = n\lambda.$$

This is called the Bragg relation.

1.2 The Schrödinger Equation

We've seen that light (i.e., an electromagnetic field) obeys the wave equation

$$\frac{\partial^2 \mathcal{E}_z}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 \mathcal{E}_z}{\partial t^2},$$

where \mathcal{E}_z is the z -component of the electric field. Solutions to this equation include linear combinations of the oscillating functions $\cos(kx \pm \omega t)$ and $\sin(kx \pm \omega t)$, where $k = 2\pi/\lambda$ and $\omega = 2\pi/T$ are the light's spatial and temporal angular frequencies. We can't just pick any values of k and ω , however; specifically, the quantities must satisfy the equation

$$\omega = ck.$$

This is called the dispersion relation for the photon wave equation. If we can find such a relation for matter waves, it would be very useful in finding a matter wave equation.

Recall from quantum optics that, for light, $E = h\nu$ and $p = h/\lambda$. Taking inspiration from de Broglie (whose hypothesis we know to be sound), suppose that these relations also hold for massive particles. If we define the reduced Planck constant $\hbar = h/2\pi$, we can write

$$E = \hbar\omega \text{ and } p = \hbar k.$$

We relate the (kinetic) energy and momentum of the particle via the equation

$$E = \frac{mv^2}{2} = \frac{p^2}{2m};$$

substituting our de Broglie relations gives the dispersion relation

$$\omega = \frac{\hbar k^2}{2m}.$$

Any matter wave equation we construct must have oscillatory solutions that satisfy this equation. As it turns out, the correct equation is the Schrödinger equation,

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

where $V(x)$ is the particle's potential energy (not potential!). $\Psi(x, t)$ is called the wave function, and it encodes the wave property of the particle. For a free particle ($V = 0$),

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

Something like $\Psi(x, t) = \cos(kx - \omega t)$ doesn't quite work as a solution since it doesn't have any imaginary parts to it. There's no way it satisfies our dispersion relation. However, a complex exponential

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

works just fine! But this means solutions to the Schrödinger equation are irreducibly complex, so there's no immediate physical interpretation for them. So what do they represent?

1.3 Wave Functions

Recall that the behavior of photons is characterized by complex probability amplitudes. When we take the magnitude of an amplitude, we get real probabilities.

Wave functions are probability amplitude *density* functions. So $|\Psi(x, t)|^2$ is a probability density function, that is, a probability per unit length. Specifically, $|\Psi(x, t)|^2$ gives the probability of measuring a particle in $[x, x + dx]$. Mathematically, we have the Born rule,

$$dP(x, t) = |\Psi(x, t)|^2 dx.$$

It follows that the units of $\Psi(x, t)$ are $L^{-1/2}$.

So we can calculate the probability of finding a particle in an interval of space using the integral

$$P(a \leq x \leq b, t) = \int_a^b |\Psi(x, t)|^2 dx.$$

Also, we must find the particle *somewhere*, so

$$1 = \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx.$$

This means the wave function goes to zero in the infinite limits. These are not consequences of the Schrödinger equation, but rather the physical interpretation of the wave function. Given an arbitrary wave function that decays to zero, we can normalize it by determining the coefficient that makes its integral equal to one.

We can use the Schrödinger equation to show that probability is conserved both locally and globally. Let's start by finding the time derivative of probability density:

$$\frac{\partial |\Psi|^2}{\partial t} = \frac{\partial (\Psi^* \Psi)}{\partial t} = \Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t}.$$

From the Schrödinger equation we get

$$\begin{aligned} \frac{\partial \Psi}{\partial t} &= \frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x) \Psi \right), \\ \frac{\partial \Psi^*}{\partial t} &= \frac{-1}{i\hbar} \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + V(x) \Psi^* \right). \end{aligned}$$

Substituting gives

$$\begin{aligned} \frac{\partial |\Psi|^2}{\partial t} &= \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \Psi \frac{\partial^2 \Psi^*}{\partial x^2} \right) \\ &= \frac{\partial}{\partial x} \left[\frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right) \right]. \end{aligned}$$

When we rewrite this as

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

it becomes more clear that we've just written an equation describing a local conservation of probability! Recall the local conservation of charge equation, $d\rho/dt = -\nabla \cdot \mathbf{J}$, where ρ is charge density and \mathbf{J} is current density. In a similar fashion, we can define a probability current

$$j_x(x, t) = \frac{\hbar}{2mi} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right)$$

that describes the flow of probability throughout space. So any change in probability density at a point in space is matched with an inward or outward flow of probability.

We can use this to show that probability is conserved globally:

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = - \int_{-\infty}^{\infty} \frac{\partial j_x}{\partial x} dx = -j_x \Big|_{-\infty}^{\infty} = 0.$$

(The last step follows from the fact that $\Psi(x, t) \rightarrow 0$ as $x \rightarrow \pm\infty$.)

1.4 Physical Wave Solutions

We've seen that $\Psi(x, t) = Ae^{i(kx - \omega t)}$ is a solution to the Schrödinger equation. However, it's easy to show that this wave function cannot be normalized! So this solution doesn't align with our physical interpretation of Ψ very well.

We can exploit the fact that the Schrödinger equation is linear to write a solution of the form

$$\Psi(x, t) = \sum_n A_n \sin(k_n x - \omega t).$$

But this still doesn't work, because for any finite number of terms we'll still have some overall periodic behavior which does not converge. So instead, we need an infinite number of terms, which we can express using an integral (for now at a snapshot in time):

$$\Psi(x, 0) = \int_{-\infty}^{\infty} A(k) e^{i(kx-0)} dk.$$

This integral produces a wave packet, a localized “bump” of probability.

Example: Wave packets

Suppose we want to find $\Psi(x, 0)$ for

$$A(k) = \begin{cases} A & k_0 - \frac{\Delta k}{2} < k < k_0 + \frac{\Delta k}{2}, \\ 0 & \text{elsewhere.} \end{cases}$$

We simply integrate:

$$\begin{aligned} \Psi(x, 0) &= \int_{k_0 - \frac{\Delta k}{2}}^{k_0 + \frac{\Delta k}{2}} A e^{ikx} dk \\ &= \frac{A}{ix} \left(e^{i(k_0 + \frac{\Delta k}{2})x} - e^{i(k_0 - \frac{\Delta k}{2})x} \right) \\ &= \frac{2A e^{ik_0 x}}{x} \sin\left(\frac{\Delta k x}{2}\right) \end{aligned}$$

We can show that this results in a probability density function that converges:

$$|\Psi|^2 = \frac{4|A|^2}{x^2} \sin^2\left(\frac{\Delta k}{2}x\right).$$

Notice that there is an inverse relationship between the width Δx of the wave packet and the range Δk of wavenumbers we're integrating over. It can be shown that, in general, this relationship is

$$\Delta x \Delta k \geq \frac{1}{2}.$$

In quantum mechanics we have $p = \hbar k$, so we get the Heisenberg uncertainty principle

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}.$$

Here we can interpret Δx and Δp_x as uncertainties in a particle's position and momentum, respectively, when we take a measurement.

Let's allow time to move forward again. We'd like for the speed of $\Psi(x, t)$ to be the same as the speed of the particle it represents. We have two options: the velocity of the individual wavelengths (the phase velocity) and the velocity of the envelope enclosing them (the group velocity). These are given by

$$v_p = \frac{\omega}{k} \quad \text{and} \quad v_g = \lim_{\Delta \rightarrow 0} \frac{\Delta \omega}{\Delta k} = \frac{d\omega}{dk},$$

respectively. (Recall how, when we superpose two waves, the resulting envelope has wavenumber Δk and frequency $\Delta \omega$; to find the group velocity, we take the speed of the envelope enclosing the superposition two very closely-spaced wavelengths.) The phase velocity doesn't work because, applying the dispersion relation,

$$v_p = \frac{\omega}{k} = \frac{\hbar k}{2m} = \frac{p}{2m} = \frac{1}{2}v.$$

However, the group velocity gives

$$v_g = \frac{d\omega}{dk} = \frac{\hbar k}{m} = \frac{p}{m} = v,$$

so this is the velocity we seek!

1.5 Quantum Averages and the Classical Limit

Recall how, for discrete variables, we define the expectation value

$$\langle n \rangle = \sum_{n=0}^{\infty} n P(n)$$

and uncertainty (standard deviation)

$$(\Delta n)^2 = \sum_{n=0}^{\infty} (n - \langle n \rangle)^2 P(n).$$

We can do some simplification to make this a bit less unwieldy:

$$\begin{aligned} &= \sum_{n=0}^{\infty} P(n) n^2 - \sum_{n=0}^{\infty} P(n) 2n \langle n \rangle + \sum_{n=0}^{\infty} P(n) \langle n \rangle^2 \\ &= \langle n^2 \rangle - 2 \langle n \rangle^2 + \langle n \rangle^2 \\ (\Delta n)^2 &= \langle n^2 \rangle - \langle n \rangle^2. \end{aligned}$$

These definitions and results generalize nicely to the continuous case:

$$\langle x^\alpha \rangle = \int_{-\infty}^{\infty} x^\alpha |\Psi(x, t)|^2 dx, \quad (\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2.$$

We've seen how microscopic objects like photons and atoms obey the principles of quantum mechanics, but for this to be a truly accurate theory it must also apply to macroscopic objects in some limit. This is called the principle of correspondence.

For large systems, the average position and momentum should obey the classical relationship between momentum and velocity; that is, we expect to see that

$$\langle p_x \rangle = m \frac{d \langle x \rangle}{dt}.$$

This allows us to find an expression for average momentum! But first, we must differentiate to find $d \langle x \rangle / dt$.

$$\begin{aligned} \frac{d \langle x \rangle}{dt} &= \frac{d}{dt} \int_{-\infty}^{\infty} x |\Psi|^2 dx \\ &= \int_{-\infty}^{\infty} x \frac{\partial |\Psi|^2}{\partial t} dx \end{aligned}$$

By conservation of probability:

$$= - \int_{-\infty}^{\infty} x \frac{\partial j_x}{\partial x} dx$$

Proceeding with integration by parts:

$$= - \left(x j_x \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} j_x dx \right)$$

Since j_x goes to zero in the infinite limits, that first term disappears. Substituting the probability current gives

$$\begin{aligned} &= \frac{\hbar}{2mi} \int_{-\infty}^{\infty} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right) dx \\ &= \frac{\hbar}{2mi} \left(\int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx - \int_{-\infty}^{\infty} \Psi \frac{\partial \Psi^*}{\partial x} dx \right) \end{aligned}$$

Proceeding again with integration by parts on the second term::

$$\begin{aligned}
 &= \frac{\hbar}{2mi} \left[\int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx - \left(\Psi \Psi^* \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{\partial \Psi}{\partial x} \Psi^* dx \right) \right] \\
 &= \frac{\hbar}{mi} \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx
 \end{aligned}$$

Multiplying by m gives us an expression for $\langle p_x \rangle$! We could follow a similar line of reasoning for $\langle p_x^2 \rangle$, but doing it here is unproductive so we just state

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \Psi^* \frac{\hbar}{i} \frac{\partial \Psi}{\partial x} dx, \quad \langle p_x^2 \rangle = - \int_{-\infty}^{\infty} \Psi^* \hbar^2 \frac{\partial^2 \Psi}{\partial x^2} dx.$$

Finally, we can use the correspondence principle to motivate a quantum analog of Newton's second law:

$$\frac{dp_{x,\text{cl}}}{dt} = - \frac{\partial V}{\partial x_{\text{cl}}} \iff \frac{d\langle p_x \rangle}{dt} = - \left\langle \frac{\partial V}{\partial x} \right\rangle.$$

This is known as Ehrenfest's theorem. (Going through the derivation here is not productive.)

2 The Time-Independent Schrödinger Equation

2.1 Separation of Variables

With a solid foundation in wave mechanics, we can now move into actually producing solutions to the Schrödinger equation.

We begin with an ansatz, a guess as to what our solution might look like. Specifically, suppose a function of the form $\Psi(x, t) = f(t)\psi(x)$ solves the Schrödinger equation. (Not every solution is of this form, but it'll give us the building blocks we need to create other ones!)

What follows from this assumption? Substituting our ansatz into Schrödinger's equation gives

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

Obviously this holds when $f(t) = \psi(x) = 0$, but this is a pretty boring solution. To find some others, we can separate variables: dividing by $f(t)\psi(x)$ gives

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

an equation in which the left side is in x and the right side is in t . Now, the only way for these two sides to be equal for all x, t is for both of them to be constant; call this constant E . (As we'll see later, this is the energy in our system.) This generates two, entirely disjoint ordinary differential equations:

$$\begin{aligned} \frac{i\hbar}{f(t)} \frac{df}{dt} &= E & -\frac{1}{\psi(x)} \frac{\hbar^2}{2m} + V(x) &= E \\ \frac{df(t)}{dt} &= -\frac{iE}{\hbar} f(t) & -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) &= E\psi(x) \end{aligned}$$

The time equation is easy enough to solve. Clearly,

$$f(t) = f(0)e^{-\frac{iE}{\hbar}t} = f(0)e^{-i\omega t}, \quad \omega = \frac{E}{\hbar}.$$

(Usually we ignore the coefficient $f(0)$ because it'll probably change when we go to normalize the wave function anyway.) The bottom right equation, on the other hand, is much more difficult. It is known as the time-independent Schrödinger equation, and it requires a specific choice of $V(x)$ to solve. Once we have this, though, we may be able to solve for $\psi(x)$ to get the wave function

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

This function solves the Schrödinger equation! It is often referred to as a stationary state since its associated probability density is time-independent. $E = \hbar\omega$ is the energy of this state.

2.2 The Infinite Square Well

To begin our study of the time-independent Schrödinger equation, let's pick the most ideal potential energy function we can: the infinite square well (also known as the particle in a box). It is defined as follows:

$$V(x) = \begin{cases} 0 & 0 \leq x \leq L, \\ \infty & \text{elsewhere.} \end{cases}$$

We can imagine our particle being “trapped” in the region in which V is finite. Infinite energy and momentum is bad. Let’s solve the time-independent Schrödinger equation under these conditions!

Outside the bounds of the box we have $V(x) = \infty$, so here $\psi(x) = 0$. Inside the box, however, $V(x) = 0$, which gives the equation

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

Define $k^2 = 2mE/\hbar^2$, so this turns into

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

which has the general solution

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

Now, when we go to pick our boundary conditions, note that the function must be continuous for its second derivative to exist in the first place. So we must have $\psi(0) = 0$ and $\psi(L) = 0$. The former immediately gives $B = 0$; the latter,

$$0 = A \sin kL.$$

The only way we get interesting solutions from this is to take

$$kL = n\pi, \quad n = 1, 2, \dots$$

Negative values of n don’t lead to new (linearly independent) solutions, and $n = 0$ is just boring. The allowed values of k can be labeled based on what integers they use:

$$k_n = \frac{n\pi}{L}.$$

From how we defined k , though, this also means we only have certain allowed energies:

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

The wave functions corresponding to these energies are

$$\psi_n(x) = A_n \sin \frac{n\pi x}{L}, \quad 0 \leq x \leq L,$$

where $A = \sqrt{2/L}$ is found via normalization. So, in summary,

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} & 0 \leq x \leq L, \\ 0 & \text{elsewhere,} \end{cases} \quad n = 1, 2, \dots$$

Notice some things about this solution.

- The associated wave function

$$\Psi_n(x, t) = e^{-i\omega t} \psi_n(x),$$

appears to evolve in precisely the same way as, say, a guitar string would—all of the n sinusoidal extrema periodically wriggle up and down with a set amplitude.

- Each wave function Ψ_n is associated with a different amount of energy E_n ; since these wave functions are “discrete”, only supporting a half-integer number of wavelengths, their associated energy levels are also discrete!
- There is no $E = 0$ state. Even in the ground state $n = 1$, the wave function still needs to oscillate so that it’s connected to each wall of the well. (We don’t consider $n = 0$ because it isn’t normalizable.)

2.3 Time Evolution and Measurement Properties

In general, the time-independent Schrödinger equation gives a discrete set of solutions ψ_n , each of which is associated with a quantized energy level E_n and phase factor $e^{-iE_n t/\hbar}$. Though the wave functions $\Psi_n(x, t)$ are stationary states (i.e., $|\Psi_n(x, t)|^2$ is time-independent), we can combine them together to get solutions that do evolve in time.

Example

Suppose we construct a wave function using the linear combination

$$\begin{aligned}\Psi(x, t) &= \frac{1}{\sqrt{2}}\Psi_1(x, t) + \frac{1}{\sqrt{2}}\Psi_2(x, t) \\ &= \frac{1}{\sqrt{2}}e^{-iE_1t/\hbar}\psi_1(x) + \frac{1}{\sqrt{2}}e^{-iE_2t/\hbar}\psi_2(x) \\ &= \frac{1}{\sqrt{2}}e^{-iE_1t/\hbar} \left[\psi_1 + e^{-i(E_2-E_1)t/\hbar}\psi_2 \right].\end{aligned}$$

The corresponding probability density function described turns out to be

$$\begin{aligned}|\Psi(x, t)|^2 &= \frac{1}{2}|\psi_1|^2 + \frac{1}{2}|\psi_2|^2 + \frac{1}{2}\psi_2^*\psi_1e^{i(E_2-E_1)t/\hbar} + \frac{1}{2}\psi_1^*\psi_2e^{i(E_2-E_1)t/\hbar} \\ &= \frac{1}{2}\psi_1^2 + \frac{1}{2}\psi_2^2 + \psi_2\psi_1 \cos \frac{(E_2 - E_1)t}{\hbar},\end{aligned}$$

where the last step is valid because ψ_n are real-valued. Notice that this function is composed of two parts, one constant and one time-varying, and the time-varying portion has frequency $\omega = (E_2 - E_1)/\hbar$.

As it turns out, the wave functions produced by the time-independent Schrödinger equation form an orthonormal set! The vector space spanned by these functions is called a Hilbert space.

We can use this to our advantage to determine how initial wave functions evolve through time. First, we write the wave function as a linear combination of stationary states:

$$\Psi(x, 0) = \sum_{n=1}^{\infty} c_n(0)\psi_n(x).$$

To incorporate time-dependence, we simply multiply each stationary state by its phase factor; these factors vary the coefficients of the linear combination through time.

$$\begin{aligned}\Psi(x, t) &= \sum_{n=1}^{\infty} c_n(t)\psi_n(x) = \Psi(x, t) \\ &= \sum_{n=1}^{\infty} c_n(0)e^{-iE_nt/\hbar}\psi_n(x)\end{aligned}$$

Now, to determine the coefficients $c_n(0)$, we calculate the inner product

$$\langle \Psi(x, 0), \psi_n(x) \rangle = \int_{-\infty}^{\infty} \Psi^*(x, 0)\psi_n(x) dx$$

To see how this is useful, let's decompose Ψ into stationary states:

$$\begin{aligned}&= \int_{-\infty}^{\infty} (c_1(0)\psi_1^*(x) + c_2(0)\psi_2^*(x) + \cdots)\psi_n(x) dx \\ &= \int_{-\infty}^{\infty} c_1(0)\psi_1^*(x)\psi_n(x) dx + \int_{-\infty}^{\infty} c_2(0)\psi_2^*(x)\psi_n(x) dx + \cdots\end{aligned}$$

Notice that, by the orthogonality of stationary states, all but one of these integrals cancel:

$$= \int_{-\infty}^{\infty} c_n(0)\psi_n^*(x)\psi_n(x) dx = c_n(0)$$

As a side note, it will be useful to us to characterize cancellations like these using the Kronecker delta:

$$\delta_{mn} = \begin{cases} 1 & m = n, \\ 0 & m \neq n. \end{cases}$$

For example, if ψ_m and ψ_n are normalized, then we can write

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = \delta_{mn}.$$

Now, aside from being the coefficients in the linear combination for Ψ , c_n have another very important interpretation: they describe the probability of measuring a particle as having a certain energy! Specifically,

$$P(E_n) = |c_n|^2.$$

So we can write expectation values for energy:

$$\langle E \rangle = \sum_{n=1}^{\infty} |c_n(0)|^2 E_n \quad \langle E^2 \rangle = \sum_{n=1}^{\infty} |c_n(0)|^2 E_n^2$$

2.4 The Energy Operator

The expression for $\langle E \rangle$ above (via linear combination) is a good start, but it requires that we know *all* of the c_n ahead of time, which in general we won't. To fix this, let's take a look at the expressions for the other expectation values we know:

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} \Psi^*(x, t) x \Psi(x, t) dx & \langle p_x \rangle &= \int_{-\infty}^{\infty} \Psi^*(x, t) \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi(x, t) dx \\ \langle x^2 \rangle &= \int_{-\infty}^{\infty} \Psi^*(x, t) x^2 \Psi(x, t) dx & \langle p_x^2 \rangle &= \int_{-\infty}^{\infty} \Psi^*(x, t) \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right)^2 \Psi(x, t) dx \end{aligned}$$

This notation allows us to understand these integrals in a new light. We are not, in fact, just doing multiplications and derivatives in these integrals. Instead, we are applying the position and momentum operators

$$x_{\text{op}} = x \quad \text{and} \quad p_{\text{op}} = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

to Ψ , and then doing stuff with the result. So we expect that there is some energy operator E_{op} that we can use to determine $\langle E \rangle$. We call this operator the Hamiltonian H and, as we might expect, it is the sum of the kinetic and potential energy operators!

$$H = \frac{p_{\text{op}}^2}{2m} + V(x_{\text{op}}) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

So the important expectation values for E are

$$\langle E \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) H \Psi(x, t) dx \quad \text{and} \quad \langle E^2 \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) H^2 \Psi(x, t) dx.$$

Importantly, we can also write the time-independent Schrödinger equation as

$$H\psi(x) = E\psi(x).$$

So the eigenfunctions of H are the ψ_n found via separation of variables, and its eigenvalues are their corresponding energies E_n ! We'll often refer to ψ_n as energy eigenfunctions and E_n as energy eigenvalues.

In fact, every observable has an associated operator whose eigenvalues are precisely the possible outcomes of a measurement! Take the momentum operator, for example. A particle's momentum is determined by its wavenumber k ; applying p_{op} to a wave function with this wavenumber gives

$$p_{\text{op}} e^{ikx} = \frac{\hbar}{i} \frac{\partial}{\partial x} e^{ikx} = \hbar k e^{ikx}.$$

So e^{ikx} is an eigenfunction of p_{op} , and its corresponding eigenvalue is the momentum $\hbar k$. Since k can vary continuously, this tells us that momentum is continuous (unlike energy!).

3 One-Dimensional Potentials

3.1 The Finite Square Well

Now we'll look at a few different potentials $V(x)$ and determine what their corresponding wave functions look like. Let's start with the finite square well:

$$V(x) = \begin{cases} 0 & |x| < a/2, \\ V_0 & |x| > a/2. \end{cases}$$

We're interested in bound states, ones that satisfy $E < V_0$ (so that they're restricted to the well's interior).

The key difference between this arrangement and the infinite square well is that the particle *can* exist in a state of finite energy. It is now possible to detect the particle outside the bounds of our box, so our boundary conditions are going to change a bit. We'll still require that ψ be normalizable, so it must go to zero in its infinite limits. It should also be continuous, but now that we're dealing with a finite potential, we also want ψ to be smooth (so its first derivative is continuous).

We'll start by solving the Schrödinger equation as we did before. On the left we have the inside of the well, and on the right the outside.

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} &= E\psi & -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V_0\psi &= E\psi \\ \frac{d^2\psi}{dx^2} &= -\frac{2mE}{\hbar^2}\psi & \frac{d^2\psi}{dx^2} &= \frac{2m(V_0 - E)}{\hbar^2}\psi \\ \psi'' &= -k^2\psi & \psi'' &= \kappa^2\psi \end{aligned}$$

Here we've defined $k^2 \equiv 2mE/\hbar^2$ (as before) and $\kappa^2 \equiv 2m(V_0 - E)/\hbar^2$. We can see that the inside of our well has complex exponential (or oscillatory) solutions, and the outside has real exponential solutions. So we have the general solution

$$\psi(x) = \begin{cases} C_1 e^{\kappa x} + C_2 e^{-\kappa x} & x < -a/2 \\ A e^{ikx} + B e^{-ikx} & |x| < a/2 \\ D_1 e^{\kappa x} + D_2 e^{-\kappa x} & x > a/2 \end{cases}$$

But since ψ must be normalizable, we can kill off a couple of divergent terms.

$$\psi(x) = \begin{cases} C e^{\kappa x} & x < -a/2 \\ A e^{ikx} + B e^{-ikx} & |x| < a/2 \\ D e^{-\kappa x} & x > a/2 \end{cases} \implies \frac{d\psi}{dx} = \begin{cases} \kappa C e^{\kappa x} & x < -a/2 \\ ik A e^{ikx} - ik B e^{-ikx} & |x| < a/2 \\ -\kappa D e^{-\kappa x} & x > a/2 \end{cases}$$

Now, to stitch these pieces together, we must ensure the continuity of ψ and ψ' at $x = -a/2$ and $x = a/2$.

$$\begin{aligned} (1) \quad C e^{-\kappa a/2} &= A e^{-ika/2} + B e^{ika/2} & (3) \quad D e^{-\kappa a/2} &= A e^{ika/2} + B e^{-ika/2} \\ (2) \quad \kappa C e^{-\kappa a/2} &= ik A e^{-ika/2} - ik B e^{ika/2} & (4) \quad -\kappa D e^{-\kappa a/2} &= ik A e^{ika/2} - ik B e^{-ika/2} \end{aligned}$$

We can eliminate C from the equations by dividing (1)/(2), and we remove D by dividing (3)/(4). Solving each quotient for A/B gives

$$\frac{A}{B} = e^{ika} \left(\frac{\kappa + ik}{-\kappa + ik} \right) \quad \text{and} \quad \frac{A}{B} = e^{-ika} \left(\frac{-\kappa + ik}{\kappa + ik} \right).$$

Multiplying these equations gives, simply, $(A/B)^2 = 1$! So we have either $A = B$ and $A = -B$, in which cases (1) and (3) together show that $C = D$ or $C = -D$, respectively. This gives us two different types of solutions:

$$\psi(x) = \begin{cases} C e^{\kappa x} & x < -a/2 \\ 2A \cos kx & |x| < a/2 \\ C e^{-\kappa x} & x > a/2 \end{cases} \quad \text{and} \quad \psi(x) = \begin{cases} -C e^{\kappa x} & x < -a/2 \\ 2iA \sin kx & |x| < a/2 \\ C e^{-\kappa x} & x > a/2 \end{cases}$$

Notice that the ψ on the left is even while the ψ on the right is odd.

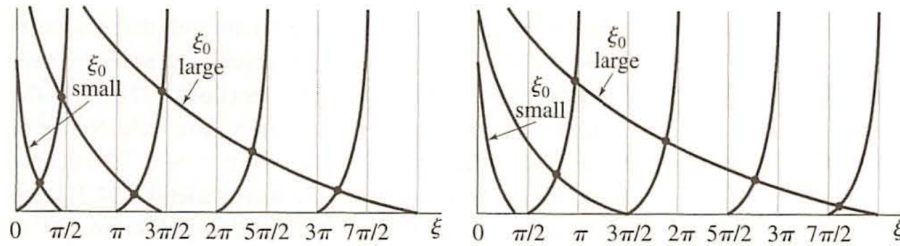
At this point we still haven't quantized anything. To change this, let's go back to dividing (1)/(2) and (3)/(4):

$$\begin{aligned} \frac{ik}{\kappa} &= \frac{e^{-ika/2} + e^{ika/2}}{e^{-ika/2} - e^{ika/2}} & -\frac{ik}{\kappa} &= \frac{e^{ika/2} - e^{-ika/2}}{e^{ika/2} + e^{-ika/2}} \\ &= \frac{\cos(ka/2)}{-i \sin(ka/2)} & &= \frac{i \sin(ka/2)}{\cos(ka/2)} \\ \tan(ka/2) &= \frac{\kappa a/2}{ka/2} & \cot(ka/2) &= -\frac{\kappa a/2}{ka/2} \\ \tan \xi &= \frac{\sqrt{\xi_0^2 - \xi^2}}{\xi} & -\cot \xi &= \frac{\sqrt{\xi_0^2 - \xi^2}}{\xi} \end{aligned}$$

Here we've defined the dimensionless variables

$$\xi \equiv ka/2 \quad \text{and} \quad \xi_0 \equiv \frac{a}{\hbar} \sqrt{mV_0/2}.$$

Both of these equations are transcendental—in order to solve them, we must do so numerically or graphically. Below we've provided a plot for each equation, in which the two sides of the equation are graphed against each other.



There are a few things to notice here. First, each intersection corresponds to a distinct allowed k and thus a distinct allowed energy, so our equations quantize the energy states of our wave functions! There is also a finite number of energies this time, with a higher ξ_0 corresponding to more allowed energies. This hopefully makes some intuitive sense: ξ_0 is a function of the well's size, and we'd expect that potential wells produce more bound states. Finally, when we take the limit $V_0 \rightarrow \infty$, we get an infinite number of allowed energies determined by $\xi = n\pi/2$ and we recover the infinite potential well energies, as we'd hope.

3.2 General Potential Wells

Before moving on to other particular potentials, let's determine some qualitative characteristics of wave functions subject to potential wells in general.

Again, we're mostly interested in bound states. For such a state there is a finite region for which $E > V$, which we'll call the classically bound region, and another for which $E < V$, which is classically forbidden. Taking inspiration from the finite square well, we can rewrite the time-independent Schrödinger equation in convenient ways—one for $E > V$ and another for $E < V$.

$$\begin{aligned} \frac{d^2\psi}{dx^2} &= -\frac{2m[E - V(x)]}{\hbar^2} \psi & \frac{d^2\psi}{dx^2} &= \frac{2m[V(x) - E]}{\hbar^2} \psi \\ \frac{d^2\psi}{dx^2} &= -k^2(x) \psi & \frac{d^2\psi}{dx^2} &= \kappa^2(x) \psi \end{aligned}$$

These differential equations have oscillatory and exponential solutions, respectively.

- In the $E > V$ region the wave function will oscillate, and the frequency of oscillation increases as $E - V$ increases (i.e., as the potential energy V decreases). If $E > V$ everywhere then we have a continuum of solutions that we can combine to create a normalizable wave packet, as we did before.
- In the $E < V$ region the wave function will be exponential, and the curve gets steeper as $V - E$ increases (as V increases). If $E < V$ everywhere there are no physical solutions because ψ will diverge and be non-normalizable.

If $E = V$ then $\psi''(x) = 0$ and we have an inflection point. These are where we can apply continuity and differentiability boundary conditions to stitch together the exponential and oscillatory solutions. This is also how energies get quantized—there are only so many energies that produce well-behaved, normalizable wave functions beyond these inflection points. Each energy corresponds to a different number of half-oscillations; the n th bound state has $n - 1$ nodes (zeroes).

At any particular point in the bound region, the wave function “instantaneously” looks like the sinusoid

$$\psi(x) = A \sin(kx + \phi),$$

whose derivative is

$$\frac{d\psi}{dx} = kA \cos(kx + \phi).$$

Suppose the potential V abruptly rises at this point, so k decreases; to maintain differentiability, the amplitude A of the wave function must increase. Thus there is an inverse relationship between k and A , meaning the wave function has larger amplitudes in places with higher V . This is perhaps counterintuitive from a classical standpoint since a higher potential energy corresponds to a lower kinetic energy and thus a lower amplitude, which goes to show how we can't lean so heavily on existing intuition here.

3.3 The Quantum Harmonic Oscillator

Recall, from Newtonian mechanics, that any smooth potential energy in the vicinity of a minimum looks like a harmonic oscillator and can be approximated by $V(x) \approx \frac{1}{2}kx^2$. We can do something similar in quantum mechanics by solving the quantum harmonic oscillator,

$$V(x) = \frac{1}{2}m\omega_0^2 x^2,$$

where $\omega_0^2 \equiv \frac{K}{m}$ and K can be interpreted as the oscillator's “effective spring constant”. Like the particle in a box, we can solve for the exact energy eigenvalues and eigenfunctions, though it'll probably be less satisfying.

Let's gain our bearings by making a prediction about what the ground state energy should be. For reasons that will soon become clear, let's call the ground-state eigenfunction ψ_0 . The expectation value of the corresponding energy is

$$\langle E \rangle = \frac{\langle p_x^2 \rangle}{2m} + \frac{1}{2}m\omega_0^2 \langle x^2 \rangle.$$

But since ψ_0 is a stationary state, the energy has a definite value E_0 . Also, since ψ_0 is an even, real function, $\langle x \rangle = \langle p_x \rangle = 0$. So we can write

$$E_0 = \frac{(\Delta p_x)^2}{2m} + \frac{1}{2}m\omega_0^2 (\Delta x)^2.$$

By the Heisenberg uncertainty principle,

$$E_0 \geq \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2}m\omega_0^2 (\Delta x)^2.$$

Nature wants to minimize the energy in the ground state, so we differentiate the right side and set it equal to zero to get $(\Delta x)^2 = \hbar/2m\omega_0$; substituting this back into our inequality,

$$E_0 \geq \frac{1}{4}\hbar\omega_0 = \frac{1}{4}\hbar\omega_0 = \frac{1}{2}\hbar\omega_0.$$

So the absolute smallest energy a particle can have under the influence of the harmonic oscillator is $\hbar\omega_0/2$. This is another profound departure from classical physics—our particle cannot just sit at rest at the bottom of our well because that would require knowing precisely both Δx and Δp_x , which is impossible!

Armed with this preliminary result, we must now solve the time-independent Schrödinger equation

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2} \left[E - \frac{1}{2}m\omega_0^2 x^2 \right] \psi.$$

This equation is nonlinear, which complicates things quite a bit. To simplify things slightly, we can take the asymptotic limit as $x \rightarrow \pm\infty$ to get

$$\frac{d^2\psi}{dx^2} \approx -\frac{m^2\omega_0^2 x^2}{\hbar^2} \psi.$$

One can verify that an approximate solution for large $|x|$ is

$$\psi_n(x) = x^n e^{-m\omega_0 x^2/2\hbar},$$

where n is a whole number. In fact, if $n = 0$, then this solution is exactly right for our original equation! We can substitute ψ_0 to get the corresponding energy eigenvalue:

$$\begin{aligned}\psi_0(x) &= A_0 e^{-m\omega_0 x^2/2\hbar} \\ H\psi_0(x) &= \frac{1}{2}\hbar\omega_0 \psi_0(x)\end{aligned}$$

Note, also, that ψ_0 must be the ground state since it has no nodes. (So our indexing in this section will be slightly different from previous sections.) We can normalize this function quite easily with a slick method using double integrals, shown below.

Example: Gaussian integral

Suppose we want to normalize the wave function $\psi_0(x) = A_0 e^{-m\omega_0 x^2/2\hbar}$. This requires solving the equation

$$\begin{aligned}1 &= \int_{-\infty}^{\infty} |A_0|^2 e^{-m\omega_0 x^2/\hbar} dx \\ \frac{1}{|A_0|^2} &= \int_{-\infty}^{\infty} e^{-bx^2} dx,\end{aligned}$$

where $b = m\omega_0/\hbar$. Let's call the integral \mathcal{I} , so we can write

$$\begin{aligned}\mathcal{I}^2 &= \int_{-\infty}^{\infty} e^{-bx^2} dx \int_{-\infty}^{\infty} e^{-by^2} dy \\ &= \iint_{\mathbb{R}^2} e^{-b(x^2+y^2)} dx dy.\end{aligned}$$

Rewriting in polar form,

$$\begin{aligned}&= \int_0^{2\pi} \int_0^{\infty} e^{-br^2} r dr d\theta \\ \mathcal{I}^2 &= \frac{\pi}{b}\end{aligned}$$

So the normalization constant satisfies $|A_0| = (b/\pi)^{1/4}$.

One could use power series to generate more solutions to our Schrödinger equation, but for brevity's sake we won't do that here. Instead we'll just quote the solution:

$$\psi_n(x) = A_n H_n \left(\sqrt{\frac{m\omega_0}{\hbar}} x \right) e^{-m\omega_0 x^2/2\hbar},$$

where H_n is the n th degree Hermite polynomial. Plotting these solutions shows that they have all the characteristics we'd expect from the previous section! They're oscillatory with increasing amplitude up to a point, after which they decay exponentially to zero. The corresponding energy eigenvalues are

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega_0.$$

Now, each ψ_n is a stationary state. Their magnitudes do not evolve in time. However, there *is* a linear combination of these states that exhibits the same kind of oscillatory behavior we'd expect from a classical standpoint, which is pretty cool!

3.4 Delta Function Potentials

We'll look at a new potential in this section, but first, let's talk about the Dirac delta function. Firstly, the word "function" is an incredible misnomer—the Dirac delta function is not a function at all, but rather a distribution that only has meaning when integrated over. If we define it as the limit of normalized Gaussians,

$$\delta(x) = \lim_{b \rightarrow \infty} \sqrt{\frac{b}{\pi}} e^{-bx^2} = \begin{cases} 0 & x \neq 0 \\ \infty & x = 0 \end{cases},$$

then the integral over a delta spike is one. Thus

$$\int_{-\infty}^{\infty} f(x) \delta(x) dx = f(0) \int_{-\infty}^{\infty} \delta(x) dx = f(0),$$

which we'll take advantage of plenty later. As a side note, notice that we can write

$$f(x) \delta(x - x_0) = f(x_0) \delta(x - x_0),$$

and that we can substitute $f(x) = x$ to get

$$x \delta(x - x_0) = x_0 \delta(x - x_0).$$

This is an eigenvalue equation for the position operator! So $\delta(x - x_0)$ is an eigenfunction and x_0 its eigenvalue.

Anyway, now we'll consider the point potential

$$V(x) = -\frac{\hbar^2 \alpha}{2ma} \delta(x),$$

where α is dimensionless and tells us about the strength of the potential, and a is some other constant with units of length. (The unitless space integral of δ implies that δ has units of inverse length.) In order for a state to be bound in this potential it must have $E < 0$, so on either side of the origin we have $E < V$. This gives the time-independent Schrödinger equation

$$\frac{d^2 \psi}{dx^2} = -\frac{2mE}{\hbar^2} \psi \implies \frac{d^2 \psi}{dx^2} = \kappa^2 \psi,$$

the solution of which is

$$\psi(x) = \begin{cases} Ae^{\kappa x} & x < 0, \\ Be^{-\kappa x} & x > 0, \end{cases}$$

as expected based on our qualitative understanding of wave functions. Now let's apply the boundary conditions. Since ψ is continuous, $A = B$. But since we have an infinity here, ψ need not be differentiable. We can still determine a relationship between the one-sided derivatives at $x = 0$. First, we have the time-independent Schrödinger equation

$$\begin{aligned} \frac{d^2 \psi}{dx^2} &= \frac{2m}{\hbar^2} (V(x) - E) \psi \\ \frac{d}{dx} \frac{d\psi}{dx} &= \frac{2m}{\hbar^2} \left(-\frac{\hbar^2 \alpha}{2ma} \delta(x) - E \right) \psi(x) \end{aligned}$$

We want to determine what happens to ψ' as we move across $x = 0$, so let's integrate over a small neighborhood of 0 and see what happens!

$$\begin{aligned} \int_{-\epsilon}^{\epsilon} \frac{d}{dx} \frac{d\psi}{dx} dx &= \int_{-\epsilon}^{\epsilon} \frac{2m}{\hbar^2} \left(-\frac{\hbar^2 \alpha}{2ma} \delta(x) - E \right) \psi(x) dx \\ \frac{d\psi}{dx} \Big|_{-\epsilon}^{\epsilon} &= -\frac{\alpha}{a} \int_{-\epsilon}^{\epsilon} \delta(x) \psi(x) dx - \frac{2mE}{\hbar^2} \int_{-\epsilon}^{\epsilon} \psi(x) dx \end{aligned}$$

Taking the limit as $\epsilon \rightarrow 0$:

$$\frac{d\psi}{dx} \Big|_{0-}^{0+} = -\frac{\alpha}{a} \psi(0)$$

This is our boundary condition for differentiability. To apply it, let's take the derivative of our wave function.

$$\psi(x) = \begin{cases} \kappa A e^{\kappa x} & x < 0, \\ -\kappa A e^{-\kappa x} & x > 0, \end{cases}$$

So we must have

$$\begin{aligned} -\kappa A e^{-\kappa \cdot 0} - \kappa A e^{\kappa \cdot 0} &= -\frac{\alpha}{a} \psi(0) \\ -\kappa \psi(0) - \kappa \psi(0) &= -\frac{\alpha}{a} \psi(0) \end{aligned}$$

So $\kappa = \frac{\alpha}{2a}$, which corresponds to $E = -(\hbar^2 \alpha^2)/(8ma^2)$. This is the only possible energy level!

Closely related to this is the double delta well. We'll skim over the details, but in general we have

$$V(x) = -\frac{\hbar^2 \alpha}{2ma} [\delta(x-a) + \delta(x+a)],$$

and by noting that the ground-state wave function is even we get

$$\psi_0(x) = \begin{cases} C e^{\kappa x} & x < -a, \\ A \cosh(\kappa x) & |x| < a, \\ C e^{-\kappa x} & x > a. \end{cases}$$

When we impose the continuity and differentiability boundary conditions we get

$$\tanh(\kappa a) = \frac{\alpha}{\kappa a} - 1.$$

This is another transcendental equation, but since $\tanh(\kappa a)$ we'll always have

$$\frac{\alpha}{\kappa a} - 1 < 1 \implies E < -\frac{\hbar^2 \alpha^2}{8ma^2}.$$

So this double well is more tightly bound than the single well! Interpreted as a crude model for diatomic molecules, this explains why molecules are more stable than individual atoms.

3.5 Quantum Scattering

Now we'll step into the world of unbound states, which have continuous energy eigenvalues and non-normalizable energy eigenfunctions. While we study the potentials of bound states using spectroscopy, we use scattering to study those of unbound states.

To simplify things, we'll just talk about the step potential:

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

Suppose a particle with $E > V_0$ travels to the right and is incident on the step. The corresponding wave function will have a reflected component and a transmitted component. To see the specifics of how this works, let's once again go through the process of solving the Schrödinger equation. In the left and right regions we have, respectively,

$$\begin{aligned} \psi'' &= -k^2 \psi, & \psi'' &= -k_0^2 \psi, \\ k^2 &= \frac{2mE}{\hbar^2}, & -k_0^2 &= \frac{2m(E - V_0)}{\hbar^2}. \end{aligned}$$

This yields the wave function

$$\psi(x) = \begin{cases} A e^{ikx} + B e^{-ikx} & x < 0 \\ C e^{ik_0 x} + D e^{-ik_0 x} & x > 0 \end{cases} \implies \psi'(x) = \begin{cases} ik(A e^{ikx} - B e^{-ikx}) & x < 0 \\ ik_0(C e^{ik_0 x} - D e^{-ik_0 x}) & x > 0 \end{cases}$$

The continuity of ψ and its derivative require that

$$\begin{aligned} A + B &= C + D \\ ik(A - B) &= ik_0(C - D) \end{aligned}$$

For any individual k we won't get a solution that's normalizable, so they can't give us any absolute probabilities. But we can appeal to the probability current to determine what fraction of the incident probability is reflected and transmitted! It's straightforward to show that

$$j_x = \begin{cases} \frac{\hbar k}{m} (|A|^2 - |B|^2) & x < 0, \\ \frac{\hbar k_0}{m} (|C|^2 - |D|^2) & x > 0. \end{cases}$$

Looking back at our wave function, we might interpret $|A|$ as describing the amount of probability on the left side of $x = 0$ that flows in the $+x$ direction (the incident probability) and $|B|$ as that in the $-x$ (the transmitted). So we can break the probability current into two parts:

$$j_L = j_{\text{inc}} - j_{\text{ref}}.$$

We can do a similar analysis in the right region. Notice, though, that we must set $D = 0$ because the particle enters the region from the left and can only travel rightward. We can use this to simplify our boundary conditions:

$$\begin{aligned} A + B &= C \\ k(A - B) &= k_0 C \end{aligned}$$

This leads us to $C = [2k/(k + k_0)]A$ and $B = [(k - k_0)/(k + k_0)]A$. So the reflection and transmission coefficients are

$$R = \frac{j_{\text{ref}}}{j_{\text{inc}}} = \frac{|B|^2}{|A|^2} = \left(\frac{k - k_0}{k + k_0} \right)^2, \quad T = \frac{j_{\text{trans}}}{j_{\text{inc}}} = \frac{k_0 |C|^2}{k |A|^2} = \frac{4kk_0}{(k + k_0)^2}.$$

Now, what if $E < V_0$? In this case the left region is the same as before, but on the right we have the time-independent Schrödinger equation

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

The solution of this equation is real-valued, meaning its probability current is zero. So there is no transmitted probability and the reflection coefficient is one! (Note that there is still a decaying probability of detection beyond the step—this probability just doesn't "propagate".)

3.6 Quantum Tunneling

Now consider the finite barrier

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

If a particle has energy $E > V_0$ then we'll still get reflection and transmission, it'll just happen locally at each "interface". What we're really interested in is the $E < V_0$ case!

In the left, center, and right regions we have the respective time-independent Schrödinger equations

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

where k^2 and κ^2 are defined in the familiar ways. This gives the wave function

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

where the decaying term in the third region is omitted because, as before, there is no probability coming in from the right here. Now we'll apply the continuity and differentiability boundary conditions:

$$\begin{aligned} A + B &= F + G & Fe^{\kappa a} + Ge^{-\kappa a} &= Ce^{ika} \\ ik(A - B) &= \kappa(F - G) & \kappa(Fe^{\kappa a} - Ge^{-\kappa a}) &= ikCe^{ika} \end{aligned}$$

From here we could show, with some nasty algebra, that the transmission coefficient through the barrier is

$$T = \frac{k_{\text{trans}}}{k_{\text{inc}}} \frac{|C|^2}{|A|^2} = \left[1 + \frac{(k^2 + \kappa^2)^2}{4k^2\kappa^2} \sinh^2(\kappa a) \right]^{-1}.$$

To make some sense of this expression, let's consider the limits as the barrier gets very thin ($\kappa a \ll 1$) or very thick ($\kappa a \gg 1$). In the thin limit $\sinh^2 \kappa a \approx \kappa^2 a^2$ is negligibly small, so

$$T_{\text{small}} \approx 1.$$

In the thick limit, though, $\sinh^2 \kappa a \approx e^{2\kappa a}/2$, which is much larger than the constant term. This gives

$$T_{\text{big}} \approx \left(\frac{4k\kappa}{k^2 + \kappa^2} \right)^2 e^{-2\kappa a}.$$

Both of these should, hopefully, make some intuitive sense! We'd expect most particles to tunnel through a very thin barrier, and based on our qualitative understanding of wave functions, the probability of tunneling should decay exponentially with thicker barriers.

We can easily extend our analysis to non-rectangular barriers by breaking it into a series of "thick" rectangular barriers, each with transmission coefficient

$$T_j = C_j(k) \exp[-2\kappa(x_j)\Delta x],$$

where $C_j(k)$ is some (constant) polynomial in k . If we use N pieces then the total transmission coefficient is approximately

$$T \approx \prod_{j=1}^N T_j \propto \exp \left[-2 \sum_{j=1}^N \kappa(x_j) \Delta x \right].$$

In the limit, this turns into

$$T \propto \exp \left[-2 \int_a^b \kappa(x) dx \right] = \exp \left[-\frac{2\sqrt{2m}}{\hbar} \int_a^b \sqrt{V(x) - E} dx \right],$$

where the constant of proportionality is some other polynomial in k .

4 Principles of Quantum Mechanics

4.1 Hermitian Operators

So far we've talked about position, momentum, and energy operators. We'll now add a fourth to our collection: the parity operator Π , defined by

$$\Pi\psi(x) = \psi(-x).$$

The eigenvalues $\lambda = \pm 1$ of Π are clearly real. The eigenfunctions corresponding to $\lambda = 1$ are the even functions, and those corresponding to $\lambda = -1$ are the odd functions. It follows that eigenfunctions corresponding to distinct eigenvalues are orthogonal. Also, the eigenfunctions are complete—that is, any function $\psi(x)$ can be written as a superposition of even and odd functions. For example, we might write

$$\psi(x) = \frac{1}{2} [\psi(x) + \psi(-x)] + \frac{1}{2} [\psi(x) - \psi(-x)].$$

All of these properties are characteristic of a general class of linear operators called Hermitian operators. Such an operator A is defined by the equation

$$\int_{-\infty}^{\infty} \Phi^* (A\Psi) dx = \int_{-\infty}^{\infty} (A\Phi)^* \Psi dx,$$

where Φ and Ψ are physical wave functions. This looks pretty abstract, but notice that in the special case $\Phi = \Psi$ it turns into

$$\begin{aligned} \int_{-\infty}^{\infty} \Psi^* (A\Psi) dx &= \int_{-\infty}^{\infty} (A\Psi)^* \Psi dx \\ \int_{-\infty}^{\infty} \Psi^* (A\Psi) dx &= \left(\int_{-\infty}^{\infty} \Psi^* (A\Psi) dx \right)^* \\ \langle A \rangle &= \langle A \rangle^* \end{aligned}$$

So a Hermitian operator is just one that yields real expectation values! In fact, every Hermitian operator corresponds to an observable (something we can measure), which we'd certainly hope to be real.

Consider the eigenvalue equation $A\psi_a = a\psi_a$, where ψ_a is a normalized eigenfunction of A with eigenvalue a . We can show that the expectation values of A are also its eigenvalues:

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi_a^* A\psi_a dx = \int_{-\infty}^{\infty} \psi_a^* a\psi_a dx = a.$$

Thus A has also real eigenvalues. If ψ_1 and ψ_2 are eigenfunctions corresponding to distinct eigenvalues a_1 and a_2 , respectively, then we have

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_2^* (A\psi_1) dx &= \int_{-\infty}^{\infty} (A\psi_2)^* \psi_1 dx \\ a_1 \int_{-\infty}^{\infty} \psi_2^* \psi_1 dx &= a_2 \int_{-\infty}^{\infty} \psi_2^* \psi_1 dx \end{aligned}$$

The only way for this equation to be true is for the integral to be zero. Thus eigenfunctions that correspond to different eigenvalues are orthogonal.

Proving the completeness of these eigenfunctions is difficult, but completeness is a very important part of quantum mechanics. Without it, we could not make the argument that

$$\Psi = \sum_{n=1}^{\infty} c_n \psi_n \implies 1 = \sum_{n=1}^{\infty} |c_n|^2,$$

and thus we would not identify $|c_n|^2$ as the probability of obtaining the eigenvalue a_n upon a measurement of A . Given an arbitrary wave function Ψ , we could find the coefficient c_n on the n th eigenfunction using

$$c_n = \int_{-\infty}^{\infty} \psi_n^* \Psi dx$$

and use these coefficients to compute the expectation values

$$\int_{-\infty}^{\infty} \Psi^* A \Psi = \sum_{n=1}^{\infty} |c_n|^2 a_n \quad \text{and} \quad \int_{-\infty}^{\infty} \Psi^* A^2 \Psi = \sum_{n=1}^{\infty} |c_n|^2 a_n^2.$$

4.2 Operator Commutation and Uncertainty

Suppose we have two Hermitian operators A and B . We define their commutator $[A, B] = AB - BA$ as a quantity that is equal to zero if and only if the two operators commute, that is, if $AB = BA$. As we'll see here, the commutativity of two operators is of utmost importance in quantum mechanics!

Let's start with the case in which $[A, B] = 0$. We know, from linear algebra, that the eigenspaces spanned by each operator's eigenfunctions are the same. But if all eigenvalues are nondegenerate—that is, if each corresponds to exactly one eigenfunction—then we can make an even stronger statement. In this case, the eigenvalues of A and B are precisely the same! One nice implication of this fact is that, because the parity operator commutes with even Hamiltonians, the eigenfunctions of such Hamiltonians must be even or odd.

If two operators commute, then we can simultaneously know both of their associated observables without uncertainty. Conversely, if two operators do not commute, it is not possible to have definitive values for both observable at the same time. This leads to uncertainty! For example, consider a particle in a box in its ground state; a measurement of its position causes the wave function to collapse into a non-eigenstate, so we are not guaranteed to get the ground-state energy upon a subsequent measurement.

This uncertainty is quantified by the value of the commutator. Specifically, if $[A, B] = iC$, then we have the generalized uncertainty principle

$$\Delta A \Delta B \geq \frac{|\langle C \rangle|}{2}.$$

Not only does this lead to the familiar Heisenberg uncertainty principle (via $[x, p_x] = i\hbar$), but it can also be used to derive many other important uncertainty relations. One very important one is

$$\Delta E \Delta t \geq \frac{\hbar}{2},$$

which might make sense given how the relativistic relationship between time and energy is analogous to that between position and momentum. But there's a problem here: there is no time operator, so Δt can't represent the uncertainty in an observable. So what is it?

The answer has something to do with the rate at which an operator's expectation value changes. Let A be a time-independent Hermitian operator; the derivative of its expectation value is

$$\begin{aligned} \frac{d\langle A \rangle}{dt} &= \frac{d}{dt} \int_{-\infty}^{\infty} \Psi^*(x, t) A \Psi(x, t) dx \\ &= \int_{-\infty}^{\infty} \left(\frac{\partial \Psi^*}{\partial t} A \Psi + \Psi^* A \frac{\partial \Psi}{\partial t} \right) dx \end{aligned}$$

By the time-independent Schrödinger equation, we can substitute $d\Psi/dt = (1/i\hbar)H\Psi$ and its conjugate.

$$\begin{aligned} &= \frac{i}{\hbar} \int_{-\infty}^{\infty} (H\Psi)^* A \Psi dx - \frac{i}{\hbar} \int_{-\infty}^{\infty} \Psi^* A H \Psi dx \\ &= \frac{i}{\hbar} \left(\int_{-\infty}^{\infty} \Psi^* H A \Psi dx - \int_{-\infty}^{\infty} \Psi^* A H \Psi dx \right) \\ \frac{d\langle A \rangle}{dt} &= \frac{i}{\hbar} \langle [H, A] \rangle \end{aligned}$$

So if A commutes with the Hamiltonian, then its expectation value is conserved! Otherwise, $[A, H] = iC$ and $\langle C \rangle = \langle [H, A] \rangle / i = \hbar(d\langle A \rangle / dt)$, so

$$\Delta A \Delta E \geq \frac{|\langle C \rangle|}{2} \implies \Delta A \Delta E \geq \frac{\hbar}{2} \left| \frac{d\langle A \rangle}{dt} \right|$$

One possible interpretation of this is that, in a stationary state, there is no energy uncertainty. But otherwise there is a distribution of possible energies and we can interpret $\Delta t = \Delta A / |d\langle A \rangle / dt|$ to get

$$\Delta t \Delta E \geq \frac{\hbar}{2}.$$

Here, Δt is the time it takes $\langle E \rangle$ to change by an amount equal to its uncertainty. Any smaller change is statistically insignificant.

4.3 Quantum Entanglement and Measurement

We're now in a position to address some of the fundamental “paradoxes” that come with quantum mechanics.

Consider a two-particle state involving particles A and B . If these particles have positions x_A and x_B , respectively, then the wave function describing their combined state is $\Psi(x_A, x_B)$. We say that such a state is entangled if this Ψ cannot be expressed as a product of independent wave functions for A and B ; in this case, the Born rule looks like $dP = |\Psi(x_A, x_B)|^2 dx_A dx_B$.

One source of entangled states is nuclear decay. Consider, for example, an unstable particle of mass m in the fifth energy state of the infinite square well. It decays into two particles with masses $m_A = m/5$ and $m_B = 4m/5$. We can show, by conservation of energy, that

$$5n_A^2 + \frac{5}{4}n_B^2 = 25.$$

This equation has two solutions: $(n_A, n_B) = (1, 4)$ and $(n_A, n_B) = (2, 2)$. Hence the two-particle system has the wave function

$$\Psi(x_A, x_B) = c_1 \psi_1(x_A) \psi_4(x_B) + c_2 \psi_2(x_A) \psi_2(x_B).$$

Suppose we measure the energy of A and get E_1 . Then the wave function for the multiparticle state collapses: without even observing it, we know by conservation of energy that the energy of B is E_4 .

The strange thing about this is that there's no limit to how far apart these entangled particles can be. No matter what, the wave functions collapse simultaneously. This troubled many physicists, including Einstein, who hypothesized that the energies of both particles at the moment we're produced—we just don't know what they are until we measure them. This is called the Realist view of quantum mechanics, which is contrary to the Orthodox view we've been learning.

Running with this view, Einstein and two of his colleagues devised the Einstein-Podolsky-Rosen (EPR) “paradox”. Consider, again, two particles A and B that interact for a short time and then never again. The positions and momenta of the particles are individually equal in magnitude and opposite in direction. So if we measure the position of A , then we also get the position of B ; this is consistent with the Realist view that these states were predetermined when the particles stopped interacting. Similarly, a measurement of the momentum of A allows us to determine that of B , which is again consistent with Realism.

But then the position and momentum of B were both determined when its interaction with A ceased meaning both quantities can be known precisely, a clear violation of the Heisenberg uncertainty principle. So we are left with two possibilities:

- Quantum mechanics is complete. The measurement of A 's properties affects the state of B , no matter how far apart they are.
- Quantum mechanics is incomplete. There are some “hidden variables” that encode the simultaneous values of position and momentum.

Subsequent experiments with other noncommutative properties like photon polarization have shown, to the extent of 250 standard deviations, that there are no such hidden variables.

We should be careful not to take this superposition interpretation too far, though. Suppose a cat is confined to a chamber equipped with a mechanism to kill the cat if a particular quantum event occurs, say the decay of a radioactive atom. Within our current understanding of multiparticle systems the survival of the cat is entangled with the atomic decay, but this is clearly ridiculous because that would mean the cat is in a superposition of “survival states”, not definitely alive or dead!

Our best guess for why this superposition breaks down for macroscopic objects is that environmental interactions cause wave functions to lose the relative phase information that is essential to quantum phenomena like interference. Perhaps this so-called decoherence somehow leads to the collapse of the system into one of the states comprising the initial superposition. But this seems inconsistent with the Schrödinger equation which, as a linear differential equation, should conserve superpositions over time. This question of what, exactly, happens when a wave function collapses (if anything) is the crux of the measurement problem.

5 Quantum Mechanics in 3D

5.1 Particle in a 3D Box

To begin our foray into three dimensions, let's return to the particle in a box model:

$$V(x, y, z) = \begin{cases} 0 & 0 < x, y, z < L, \\ \infty & \text{elsewhere.} \end{cases}$$

The Hamiltonian for this potential is

$$\begin{aligned} H &= \frac{|\mathbf{p}|^2}{2m} + V(x, y, z) \\ &= -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z), \end{aligned}$$

and the Schrödinger equation is, as usual,

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

where Ψ is a function of time and the three spatial variables. As before, separation of variables gives the temporal solution $f(t) = e^{-iEt/\hbar}$ and the time-independent Schrödinger equation

$$H\psi = E\psi,$$

where ψ is a function of the three spatial variables. For our choice of potential, this becomes

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

Let's do separation of variables again, this time assuming a solution of the form $\psi(x, y, z) = X(x)Y(y)Z(z)$. Substituting and dividing by ψ gives

$$-\frac{\hbar^2}{2m} \left(\frac{1}{X} \frac{d^2 X}{dx^2} + \frac{1}{Y} \frac{d^2 Y}{dy^2} + \frac{1}{Z} \frac{d^2 Z}{dz^2} \right) = E_x + E_y + E_z,$$

where we've split the energy into three parts, one for each dimension. For each dimension we have an equation that looks like For each variable we have an equation that looks like

$$-\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} = E_x X,$$

whose solution we know is

$$X(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n_x \pi x}{L}\right), \quad E_x = \frac{n_x^2 \hbar^2 \pi^2}{2mL^2}, \quad n_x \in \mathbb{N}.$$

So, in all, for the three-dimensional state we have

$$\begin{aligned} \psi_{n_x, n_y, n_z}(x, y, z) &= \left(\frac{2}{L}\right)^{\frac{3}{2}} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \\ E &= (n_x^2 + n_y^2 + n_z^2) \frac{\hbar^2 \pi^2}{2mL^2} \end{aligned}$$

The general solution, with time dependence, involves multiplying each stationary state by a phase factor corresponding to the state's "total energy" $E_n = E_x + E_y + E_z$.

As an application, let's talk about Fermi energy. Consider a macroscopic conducting cube, which we can model as a sea of valence electrons. These electrons are “cold”, meaning they occupy the lowest energy states they can.

Imagine a three-dimensional grid of states, each corresponding to (n_x, n_y, n_z) . By the Pauli exclusion principle, each state houses up to two electrons, and the states fill from the origin outward in an eighth-spherical fashion. If we have N electrons, then the maximum radius in this n -space is given by

$$N = 2 \cdot \frac{1}{8} \cdot \frac{4}{3} \pi r_{\max}^3 \implies r_{\max} = \left(\frac{3N}{\pi} \right)^{\frac{1}{3}},$$

and the highest energy state is

$$E_{\max} = \left(\frac{3N}{\pi} \right)^{\frac{2}{3}} \frac{\hbar^2 \pi^2}{2mL^2}.$$

This is called the Fermi energy, and it's usually written as

$$E_F = \frac{\hbar^2}{2m} (3\pi^2)^{\frac{2}{3}} \left(\frac{N}{L^3} \right)^{\frac{2}{3}}.$$

Notice that the Fermi energy is only a function of the number density of electrons in the solid.

5.2 Orbital Angular Momentum

In three dimensions we have many more choices for the geometry of our potentials. One especially important class of potentials are the central potentials, which depend only on the distance r from some source. Spherical coordinates will come in handy here—we'll define θ to be the polar angle (from the z -axis) and ϕ to be the planar angle.

The time-independent Schrödinger equation for a central potential is clearly not separable in rectangular coordinates, since the potential is of the form $V(\sqrt{x^2 + y^2 + z^2})$. But if we rewrite the equation using the Laplacian to get

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

then one could show that in spherical coordinates,

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

This equation might look much more complex, but it turns out to be separable! As a first step, we'll separate the radial and angular components.

Our hint is that \hbar has units of angular momentum. Taking inspiration from Newtonian mechanics, we can get angular momentum operators in each of the three Cartesian directions:

$$\begin{aligned} \hat{L}_x &= y\hat{p}_z - z\hat{p}_y \\ \hat{L}_y &= z\hat{p}_x - x\hat{p}_z \\ \hat{L}_z &= x\hat{p}_y - y\hat{p}_x \end{aligned}$$

Converting from rectangular to spherical coordinates,

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

This naturally leads to another operator,

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

But this is precisely what we see in the spherical time-independent Schrödinger equation! So we can write

$$\left[-\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{\mathbf{L}}^2}{2mr^2} + V(r) \right] \psi = E\psi.$$

We can see that H and $\hat{\mathbf{L}}^2$ commute, so they have a common set of eigenfunctions. The eigenfunctions of $\hat{\mathbf{L}}^2$ are of the form $Y(\theta, \phi)$ and the Hamiltonian only adds a radial component, so the combined eigenfunctions have the form $\psi_E(r, \theta, \phi) = R(r)Y(\theta, \phi)$.

We'll focus on the angular stuff for now. The eigenvalue equation for $\hat{\mathbf{L}}^2$ is

$$-\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = L^2 Y(\theta, \phi),$$

but notice that we can immediately substitute \hat{L}_z to get

$$\left[-\frac{\hbar^2}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{\hat{L}_z^2}{\sin^2 \theta} \right] Y(\theta, \phi) = L^2 Y(\theta, \phi).$$

Let's take another step down the ladder. $\hat{\mathbf{L}}^2$ commutes with \hat{L}_z , and \hat{L}_z depends only on ϕ , so their shared eigenfunctions can be found by employing separation of variables again. In particular, the eigenfunctions of $\hat{\mathbf{L}}^2$ are $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$, where Φ is an eigenfunction of \hat{L}_z . So we have the eigenvalue equation

$$\begin{aligned}\hat{L}_z \Phi(\phi) &= L_z \Phi(\phi) \\ \left(\frac{\hbar}{i} \frac{\partial}{\partial \phi} \right) \Phi(\phi) &= L_z \Phi(\phi) \\ \frac{d}{d\phi} \Phi(\phi) &= \frac{iL_z}{\hbar} \Phi(\phi)\end{aligned}$$

Now we can see that this equation has the normalized solution

$$\Phi(\phi) = N e^{iL_z \phi / \hbar}, \quad N = 1/\sqrt{2\pi}.$$

Since each point in space must have a unique value of $\psi(r, \theta, \phi)$ associated with it, Φ must be periodic with period 2π . So

$$\begin{aligned}N e^{iL_z(\phi+2\pi)/\hbar} &= N e^{iL_z \phi / \hbar} \\ e^{iL_z 2\pi / \hbar} &= 1\end{aligned}$$

Thus $L_z = m_l \hbar$, where m_l is an integer. So the z -component of orbital angular momentum is quantized with eigenfunctions

$$\Phi_{m_l}(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l \phi}.$$

Note that these eigenfunctions are orthonormal and comprise a complete basis, as we'd expect. Also note that there's nothing that makes the z -direction special—we could've done the same thing for the x - and y -directions and gotten the same result! So angular momentum is quantized in all three directions, and $\lambda \hbar^2$ is an eigenvalue for $\hat{\mathbf{L}}^2$.

To add in θ -dependence and find $Y(\theta, \phi)$, we use the eigenvalue equation $\hat{\mathbf{L}}^2 Y(\theta, \phi) = \lambda \hbar^2 Y(\theta, \phi)$ and our definition of Y to get

$$-\hbar^2 \left[\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) - \frac{m_l^2}{\sin^2 \theta} \Theta \right] = \lambda \hbar^2 \Theta.$$

We could use power series to show that Θ is a satisfactory wave function only if $\lambda = l(l+1)$ for whole l (including $l=0$), so $L^2 = l(l+1)\hbar^2$ is quantized! The associated eigenfunctions are derived from a set of polynomials called the Legendre polynomials. In particular,

$$\Theta_{l,m_l}(\theta) = N_{l,m_l}(\sin \theta)^{|m_l|} \frac{d^{|m_l|} P_l(\cos \theta)}{d(\cos \theta)^{|m_l|}}, \quad P_l(u) = \frac{1}{2^l l!} \frac{d^l}{du^l} (u^2 - 1)^l.$$

Note that we must index Θ using both l and m_l , and since P_l has at most l nonzero derivatives, we have the additional restriction that $m_l = 0, \pm 1, \dots, \pm l$.

So in all we have the angular eigenfunctions

$$Y_{l,m_l}(\theta, \phi) = \Theta_{l,m_l}(\theta) e^{im_l \phi}.$$

These are called the spherical harmonics, and they satisfy the two equations

$$\begin{aligned} \hat{L}_z Y_{l,m_l}(\theta, \phi) &= m_l \hbar Y_{l,m_l}(\theta, \phi), \quad m_l = 0, \pm 1, \dots, \pm l \\ \hat{L}^2 Y_{l,m_l}(\theta, \phi) &= l(l+1) \hbar^2 Y_{l,m_l}(\theta, \phi), \quad l = 0, 1, \dots \end{aligned}$$

The spherical harmonics are complete and orthogonal under the inner product

$$\int_0^{2\pi} \int_0^\pi Y_{l,m_l}^* Y_{l',m_{l'}} \sin \theta \, d\theta \, d\phi = \delta_{l,l'} \delta_{m_l,m_{l'}},$$

and we normalize one by integrating over the entire unit sphere:

$$\int_0^{2\pi} \int_0^\pi |Y_{l,m_l}|^2 \sin \theta \, d\theta \, d\phi = 1.$$

The radial portion of ψ is customarily normalized separately.

Two final side notes. Since $L = \sqrt{L^2} = \sqrt{l(l+1)}\hbar$, and $L_z = m_l \hbar$, if $l m_l \neq 0$ we have $|L_z| < L$, as we might expect. We can also evaluate the commutator

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

to get the uncertainty relation

$$\Delta L_x \Delta L_y \geq \frac{\hbar}{2} |\langle L_z \rangle|.$$

We can write similar relations for the other two commutators. Two components will be on the left, and the third on the right. The point is, we have to give up our vector notion of angular momentum since it can't point in any particular direction!

5.3 Hydrogenic Atoms

We've found the angular component Y_{l,m_l} of our solution to the time-independent Schrödinger equation. Let's get into the radial component R ! For starters, we could use separation of variables to show that

$$-\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{l(l+1)\hbar^2}{2mr^2} R(r) + V(r)R(r) = ER(r).$$

This is true for any radial potential, but for now we'll focus on the Coulomb potential

$$V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r}$$

for an atom with Z protons and one electron, all with charge $\pm e$. We call such an atom a hydrogenic atom. Substituting gives

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{l(l+1)\hbar^2}{2mr^2} R - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r} R = ER.$$

We could do some product rule magic to turn this into

$$-\frac{\hbar^2}{2mr} \frac{d^2(rR)}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} R - \frac{Ze^2}{4\pi\epsilon_0 r} R = ER,$$

substituting $u(r) = rR(r)$ into which gives

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \right] u = Eu.$$

This looks a lot like a standard one-dimensional Hamiltonian! We can define the effective potential

$$V_{\text{eff}}(r) = \frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r}.$$

A sketch illustrating this potential is included at right; note that the first term is secretly a form of kinetic energy, but it serves as a “centrifugal barrier” that prevents the wave function from approaching zero.

Moving along, let’s rewrite our equation:

$$\frac{d^2 u}{dr^2} - \frac{l(l+1)u}{r^2} + 2 \frac{mZe^2}{4\pi\epsilon_0 \hbar^2} \frac{u}{r} = -\frac{2mE}{\hbar^2} u.$$

To simplify things, let’s define

$$a \equiv \frac{4\pi\epsilon_0 \hbar^2}{mZe^2} = \frac{a_0}{Z}, \quad -\frac{2mE}{\hbar^2} = \frac{1}{a^2 \lambda^2},$$

where a_0 is the Bohr radius (the “characteristic size” of an orbital) and λ is a dimensionless quantity. (Notice that $E = -\hbar^2/(2ma^2\lambda^2)$, which resembles the particle in a box energies!) All this gives

$$\frac{d^2 u}{dr^2} - \frac{l(l+1)u}{r^2} + \frac{2u}{ar} - \frac{u}{a^2 \lambda^2} = 0.$$

In the limits $r \rightarrow \infty$ and $r \rightarrow 0$, the solutions to this equation are $u(r) = Be^{-Zr/\lambda a_0}$ and $u(r) = Cr^{l+1}$, respectively, where we’ve ignored divergent terms. Put together, we get a reasonable guess

$$u(r) = Nr^{l+1}e^{-Zr/\lambda a_0}F(r),$$

where $F(r)$ is some power series. Going through the motions of determining this power series gives the energies and corresponding eigenfunctions

$$E_n = -\frac{Z^2 \hbar^2}{2ma_0^2} \frac{1}{n^2} = -\frac{Z^2 e^4 m}{2(4\pi\epsilon_0)^2 \hbar^2} \frac{1}{n^2}, \quad n = \lambda = l+1, l+2, \dots$$

$$R_{n,l}(r) = \frac{u(r)}{r} = N_{n,l} r^l F_{n-(l+1)}(r) e^{-Zr/na_0},$$

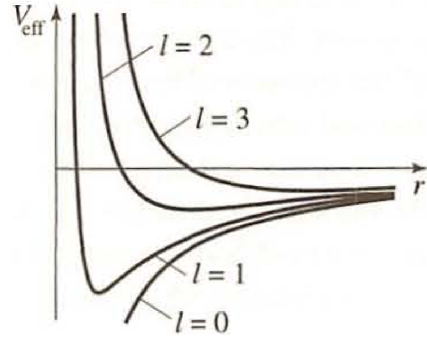
where $F_{n-(l+1)}$ is a Laguerre polynomial of $[n - (l+1)]$ th order. (In practice we think of n as fixing the possible values of l .)

In summary, we have the wave function

$$\psi_{n,l,m_l}(r, \theta, \phi) = R_{n,l} Y_{l,m_l}(\theta, \phi),$$

which is indexed by the quantum numbers

$$\begin{aligned} n &= 1, 2, 3, \dots \\ l &= 0, 1, \dots, n-1 \\ m_l &= 0, \pm 1, \dots, \pm l \end{aligned}$$



The wave function is normalized if the integral of $\psi^*\psi$ over all space is equal to one. In particular,

$$1 = \int_0^{2\pi} \int_0^\pi \int_0^\infty (R_{n,l}^* Y_{l,m_l}^*)(R_{n,l} Y_{l,m_l}) r^2 \sin \theta dr d\theta d\phi$$

$$1 = \left[\int_0^\infty R_{n,l}^* R_{n,l} r^2 dr \right] \left[\int_0^{2\pi} \int_0^\pi Y_{l,m_l}^* Y_{l,m_l} \sin \theta d\theta d\phi \right]$$

By convention, we normalize the radial and angular components individually. Note that the radial probability density is $|R_{n,l}|^2 r^2$ while the angular probability density is $|Y_{l,m}|^2$. (The probabilities get “thinner” as r changes, but not as θ or ϕ change.)

All of the qualitative characteristics we determined in one dimension still hold here! This includes node counting, but we must be careful to count the nodes in both the radial and angular components—any one individual component might not have the correct number of zeroes. Also note that for nonzero l (nonzero angular momentum), $R_{n,l}$ must go to zero at the origin.

What we’ve derived here is experimentally confirmed by the existence of atomic emission spectra. When a hydrogenic atom transitions from a state with principal quantum number n_i to one with n_f , a photon of frequency ν is emitted, where $h\nu = E_{n_i} - E_{n_f}$. The lowest four transitions in the visible spectrum are called the Balmer series, corresponding to transitions from $n_i > 2$ to $n_f = 2$.

The energy of the atom is fully described by its principal quantum number n , but there are multiple eigenstates corresponding to this energy. In particular, there is one eigenstate for each allowed l and m_l , so the degeneracy of each energy is given by the sum

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

Soon we’ll introduce a fourth quantum number that brings this number up to $2n^2$.

Note that these eigenfunctions are stationary states, so they don’t correspond to an electron classically “orbiting” a nucleus. But there is an associated probability current! In particular, we can show that

$$\mathbf{j} = \frac{\hbar}{2mi} (\psi^* \nabla \psi - \psi \nabla \psi^*)$$

$$= \frac{\hbar m_l}{mr \sin \theta} |\psi_{n,l,m_l}(r, \theta, \phi)|^2 \hat{\phi}$$

This is completely analogous to an electric current in a loop of wire—though the charge is moving, the amount of charge at any given point along the loop is constant over time.

5.4 The Zeeman Effect

Something interesting happens when we add a magnetic field to the scenario. Let’s first consider an analogous classical picture. A particle with charge q and mass m moves in a circular orbit of radius r with speed v . The current $I = qv/(2\pi r)$ associated with this particle corresponds to a magnetic dipole moment of magnitude

$$\mu = I \cdot \pi r^2 = \frac{qrv}{2}.$$

But $L = rmv$, so we can write this as $\mu = (q/2m)\mathbf{L}$. If this particle is in a magnetic field $\mathbf{B} = B\hat{z}$, then the energy of interaction is

$$-\mu \cdot \mathbf{B} = -\frac{q}{2m} \mathbf{L} \cdot \mathbf{B} = -\frac{qB}{2m} L_z.$$

This suggests that if we were to immerse a hydrogenic atom in an external magnetic field in the z -direction, then we will need to add an extra $(q_e B/2m)\hat{L}_z$ term to the Hamiltonian. So we have

$$\hat{H} = \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right) + \frac{q_e B}{2m} \hat{L}_z.$$

The eigenfunctions for the old Hamiltonian still hold here—they are eigenfunctions for \hat{L}_z , so the new term doesn’t change anything. The new eigenvalues are simply

$$E_{n,m_l} = E_n + \frac{q_e B}{2m} m_l \hbar = E_n + \mu_B m_l B,$$

where E_n are the energies without the magnetic field and $\mu_B = q_e \hbar / 2m$ is the very small “Bohr magneton” correction. This breaks the degeneracy of each energy level with respect to m_l , which can be observed in emission lines. A transition from $l = 1$ to $l = 0$, for example, would result in three very slightly different frequencies for emitted light.

If we look even more closely at the emission lines, though, an interesting phenomenon emerges. For example, if we were to fire a beam of $l = 0$ silver atoms through a magnetic field with a vertical magnitude gradient, we’d expect to see no Zeeman splitting since there’s only one allowed m_l . But the Stern-Gerlach experiment showed that the beam actually splits into two! This splitting cannot be explained using the quantum mechanics we’ve done so far, so we’re forced to introduce a new property of particles: spin.

5.5 Intrinsic Spin

Spin angular momentum \mathbf{S} is a completely new property of particles with no classical equivalent. For an electron, its associated magnetic moment is

$$\boldsymbol{\mu} = -g \frac{q_e}{2m} \mathbf{S},$$

where g is a “fudge factor” introduced to provide agreement with experiment. The total magnetic moment can be found by adding the individual moments from orbital and spin angular momentum.

We define spin in a very similar fashion to orbital angular momentum. For one, the same commutation relations hold:

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

We also have similar eigenvalue equations:

$$\begin{aligned} \hat{S}_z \chi &= m_s \hbar \chi, \quad m_s = 0, \pm \frac{1}{2}, \dots, \pm s \\ \hat{\mathbf{S}}^2 \chi &= s(s+1) \hbar^2 \chi, \quad s = 0, \frac{1}{2}, 1, \dots \end{aligned}$$

Unlike the orbital l -values, which depend on the physical state of the particle, the value of s is an intrinsic property of the particle that cannot be changed. Despite this, orbital and spin angular momentum are still both angular momentum and one type may be converted to another. Despite the fundamental difference between orbital and spin angular momentum, though, they are still both angular momentum and one type may be converted to another.

Observations indicate that $s = 1/2$ for all “matter particles” like electrons. Thus these particles only have two spin eigenstates, which we’ll call χ_+ (“spin up”) and χ_- (“spin down”). These eigenstates form a complete, orthonormal basis, so any spin state can be expressed as $\chi = c_+ \chi_+ + c_- \chi_-$. We may also write this in vector notation:

$$\chi_+ = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \chi_- = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \implies \chi = \begin{bmatrix} c_+ \\ c_- \end{bmatrix}.$$

In this formalism, operators are represented by matrices. We first write down a matrix for \hat{S}_z that yields the correct eigenvalue for each eigenstate—the easiest way to do this is to simply use the diagonal matrix

$$\hat{S}_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.$$

The other two matrix operators follow from the commutation relations:

$$\hat{S}_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \hat{S}_y = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}.$$

Finally, some algebra leads to

$$\hat{\mathbf{S}}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \frac{3\hbar^2}{4} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}.$$

We can immediately see that

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

just like with orbital angular momentum, so \hat{S}_z and \hat{S}^2 have simultaneous eigenstates!

Consider, now, a modified version of the Stern-Gerlach experiment. A beam of silver atoms is fired through a Stern-Gerlach device with a magnetic field in the x -direction; this splits the beam into two, one with $S_x = 1/2$ and another with $S_x = -1/2$. Effectively, the device performs a measurement of S_x , collapsing each particle's spin state into an eigenstate. Subsequent passes through x -directed magnetic fields will result in no beam splitting. But if we were to feed, say, the $S_x = 1/2$ beam into a z -directed field, 50/50 once again splitting occurs! We could have predicted this by simply computing the eigenvectors of the \hat{S}_x matrix to get

$$\chi_+^{(x)} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = \frac{1}{\sqrt{2}}\chi_+ \pm \frac{1}{\sqrt{2}}\chi_-.$$

We now have a complete description of the energy eigenfunctions for a hydrogen atom:

$$\psi_{n,l,m_l,m_s}(r, \theta, \phi) = R_{n,l}(r)Y_{l,m_l}(\theta, \phi)\chi_{\pm}.$$

The Zeeman eigenvalues we found earlier are also essentially correct, but there are some other subtle effects that change things slightly. Relative motion between the electron and nucleus generates an internal magnetic field in the atom, which in turn creates a “fine structure” for the energy levels—even without an external field, spin-up states have slightly higher energies than spin-down ones. The error in each from the mean looks like $E_{fs} = \boldsymbol{\mu}_S \cdot \mathbf{B}_{int} \propto \mathbf{S} \cdot \mathbf{L}$. To formalize this we may define the total angular momentum operator

$$\hat{\mathbf{J}}^2 = 2(\mathbf{L} \cdot \mathbf{S}) + \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2;$$

this operator is quantized and has eigenvalues $J^2 = j(j+1)\hbar^2$ with $j = l \pm s$ and $m_j = 0, \pm 1, \dots, \pm j$. The total fine-structure energy correction turns out to depend only on j .

6 Identical Particles

6.1 Multiparticle Systems

The Hamiltonian of a one-dimensional system of two distinguishable, non-interacting particles looks like

$$\hat{H} = -\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial x_1^2} + V(x_1) - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial x_2^2} + V(x_2).$$

As usual, we have the eigenvalue equation and Born rule

$$\hat{H}\Psi(x_1, x_2) = E\Psi(x_1, x_2), \quad dP = |\Psi(x_1, x_2)|^2 dx_1 dx_2.$$

We could use separation of variables to get the wave function and energy

$$\Psi(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2), \quad E = E_{n_1} + E_{n_2},$$

and this wave function is normalized if it satisfies

$$\iint_{\mathbb{R}^2} |\Psi(x_1, x_2)|^2 dx_1 dx_2 = 1.$$

But in quantum mechanics identical particles are indistinguishable, and the wave function must reflect this. To formalize this requirement we introduce the exchange operator, which essentially swaps all the “labels” for particle 1 with those for particle 2:

$$\hat{P}_{12}\Psi(1, 2) = \Psi(2, 1).$$

For indistinguishable particles we require that $|\Psi(1, 2)|^2 = |\Psi(2, 1)|^2$, so

$$\hat{P}_{12}\Psi(1, 2) = e^{i\delta}\Psi(1, 2).$$

We immediately get eigenfunctions—the eigenvalues can be found by noting that $\hat{P}_{12}^2\Psi(1, 2) = \Psi(1, 2)$, so $e^{i\delta} = \pm 1$. Taking $+1$ corresponds to a symmetric state and -1 corresponds to an antisymmetric state.

- When a multiparticle state is symmetric under the exchange of any two identical particles, such particles are called bosons. Bosons have integral intrinsic spin.
- When a multiparticle state is antisymmetric under the exchange of any two identical particles, such particles are called fermions. Fermions have half-integral intrinsic spin.

Note that, if two identical fermions were in the same quantum state, then the terms of the overall wave function would cancel and there would be no particle at all. So no two identical fermions can be in the same quantum state—this is known as the Pauli exclusion principle.

This discussion has important implications for atoms with multiple electrons. Consider a helium atom—if we ignore the kinetic energy of the nucleus and the repulsion between electrons, we have the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2}.$$

Solving the corresponding Schrödinger equation via separation of variables shows that the energy eigenfunctions can each be written as a product of the single-electron hydrogenic energy eigenfunctions. But since electrons are fermions, we must be careful that their overall state is antisymmetric. So, the ground state must be

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} \psi_{1s}(\mathbf{r}_1) \psi_{1s}(\mathbf{r}_2) [\chi_+(1)\chi_-(2) - \chi_-(1)\chi_+(2)].$$

Notice that the spatial part of the wave function is symmetric and that the spin state is antisymmetric, so the overall state is antisymmetric. This is an example of a singlet state—that is, a state whose overall spin

quantum number is $s = 0$. We could verify this by computing $\hat{S}^2\Psi = (\hat{S}_1^2 + \hat{S}_2^2)\Psi$, where \hat{S}_1^2 and \hat{S}_2^2 only act on particle-1 and particle-2 eigenstates, respectively.

The first-excited state of the helium atom also has a singlet state:

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) + \psi_{2s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)] [\chi_+(1)\chi_-(2) - \chi_-(1)\chi_+(2)].$$

But there are also three triplet states, which have $s = 1$:

$$\begin{aligned}\Psi(1, 2) &= \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) - \psi_{2s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)] \chi_+(1)\chi_+(2), \\ \Psi(1, 2) &= \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) - \psi_{2s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)] \chi_-(1)\chi_-(2), \\ \Psi(1, 2) &= \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) - \psi_{2s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)] [\chi_+(1)\chi_-(2) + \chi_-(1)\chi_+(2)].\end{aligned}$$

It's common to label states using the spectroscopic notation $^{2S+1}L_J$ where S , L , and J are the spin, orbital, and total angular momentum quantum numbers in the eigenvalue equations

$$\hat{S}^2\Psi = S(S+1)\hbar^2, \quad \hat{L}^2\Psi = L(L+1)\hbar^2, \quad \hat{J}^2\Psi = J(J+1)\hbar^2.$$

So in spectroscopic notation the above singlet states fall under 1S_0 , while the triplet states look like 3S_1 . (We use the letters S, P, D, F, etc. to denote orbital angular momentum.)

When we account for Coulomb repulsion, different spectroscopic labels correspond to different energies. For example, notice that the triplet states vanish when $\mathbf{r}_1 = \mathbf{r}_2$ while they don't in singlet states. So singlet electrons are more likely to overlap than triplet electrons, meaning the Coulomb repulsion contributes more to the singlet energies than the triplet energies.

If we add another electron into the mix and try writing down a ground state of the form

$$\Psi(1, 2, 3) = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)\psi_{1s}(\mathbf{r}_3)X(1, 2, 3),$$

we notice that it isn't possible to create an overall-antisymmetric state. Thus we are forced to push one of the electrons into the $2s$, and chemistry is born!

6.2 Quantum Statistics

We'll turn our attention, now, to very large multiparticle systems. A consequence of the Pauli exclusion principle is that the wave function for an entangled state of N fermions will have $N!$ terms, so if we have, say, an Avogadro's number of particles, then writing down a wave function is hopeless. The Fermi energy provides an alternative for ground-state systems, but for excited states we'll need to do some statistics.

Define $n(E)$ to be the average number of particles in a quantum state with energy E (we allow fractional n for superpositions), so

$$N = \sum_i n(E_i) \simeq \int_0^\infty n(E)D(E) dE,$$

where $D(E) dE$ is the number of states in an energy interval dE . The integral is valid in the large- N limit. The total energy is

$$E = \sum_i E_i n(E_i) \simeq \int_0^\infty E n(E)D(E) dE.$$

So what, exactly, does $n(E)$ look like for excited states? It depends on temperature! Before continuing, though, we should clarify what we mean by "temperature". It is the property of a system that determines the direction of likely energy transfer when in contact with another surface—energy flows from high to low temperatures, and there is no flow at all if both surface temperatures are the same. The "excess" energy that one system can lose to another is quantified by $k_B T$, where k_B is the Boltzmann constant. (For example, a degenerate Fermi gas would be very cold because it already has the smallest allowed energy.)

Suppose we have some particles in a potential well. If the system is in thermal equilibrium, we can now put some constraints on $n(E)$.

- For bosons and fermions, $n(E) \geq 0$.
- For fermions, $0 \leq n(E) \leq 1$.
- For bosons and fermions, $N = \sum_i n(E_i) \simeq \int_0^\infty n(E) D(E) dE$.
- $n(E)$ decreases monotonically in E .

In particular, we can quote two results from statistical mechanics:

$$n_{\text{BE}}(E) = \frac{1}{e^{\alpha} e^{E/k_B T} - 1}, \quad n_{\text{FD}}(E) = \frac{1}{e^{\alpha} e^{E/k_B T} + 1}.$$

These are the Bose-Einstein distribution (for bosons) and Fermi-Dirac distribution (for fermions), respectively. α is just a normalization constant; by convention we set $\alpha = -\mu/k_B T$, where μ is called the chemical potential. Graphically, the Fermi-Dirac distribution looks something like a logistic curve while the Bose-Einstein looks more exponential.

6.3 Cavity Radiation

We'll use this idea of an energy distribution to describe why hot things glow. In more technical terms, we'll investigate the origins of cavity (or blackbody) radiation.

Take a bunch of photons (spin-1 bosons) and plop them into a metal box with side length L . The electric field in the box satisfies

$$\nabla^2 \mathcal{E} = \frac{1}{c} \frac{\partial^2}{\partial t^2} \mathcal{E}.$$

We can break this into three separate equations for three individual components, each of which can be solved via separation of variables. Imposing the boundary conditions $\nabla \cdot \mathcal{E} = 0$ (from Gauss's law) and $\mathcal{E}_{||} = 0$ at the box boundary (since the box is conducting), we would find that, in the x -direction,

$$\mathcal{E}_x = \mathcal{E}_{0x} \cos\left(\frac{n_x \pi x}{K}\right) \sin\left(\frac{n_y \pi x}{K}\right) \sin\left(\frac{n_z \pi x}{K}\right) \sin \omega t,$$

where $n_x, n_y, n_z \in \mathbb{N}$. The same goes for \mathcal{E}_y and \mathcal{E}_z , just with the cosine shuffled around. Substituting this into the wave equation gives

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

and the photon energy is

$$E = \hbar\omega = \frac{\hbar c \pi}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{\hbar c \pi}{L} r,$$

where r is a distance in n -space.

We'll set up an integral for the total energy inside the box in order to determine the density of states for photons. It turns out that photons cannot have spin projection 0, so for each "box" in n -space we have two polarizations. Thus the number of states in a width- dr shell in this space is $2 \cdot (1/8) \cdot 4\pi r^2 dr$, so the total energy of all the states in all shells is

$$E_{\text{tot}} = \int_0^\infty E(r) n_{\text{BE}}(E(r)) \pi r^2 dr$$

The change of variables $E = (\hbar c \pi / L) r$ gives

$$\begin{aligned} &= \int_0^\infty E n_{\text{BE}}(E) \pi \left(\frac{L^2}{\hbar^2 c^2 \pi^2} E^2 \right) \left(\frac{L}{\hbar c \pi} dE \right) \\ &= \int_0^\infty E n_{\text{BE}}(E) \frac{L^3 E^2}{\hbar^3 c^3 \pi^2} dE \end{aligned}$$

From here we can pick out the density of states $D(E) = (L^3 E^2) / (\hbar^3 c^3 \pi^2)$. (We may also write this as $D(\nu) = 8\pi L^3 \nu^2 / c^3$.) But we'll go a little further and substitute $E = h\nu$ to get

$$= \int_0^\infty \frac{L^3 \nu^2 8\pi}{c^3} n_{\text{BE}}(\nu) h\nu d\nu,$$

where $\mu = 0$ for photons. Finally substituting the Bose-Einstein distribution gives

$$= \int_0^\infty \frac{8\pi h L^3}{c^3} \frac{\nu^3}{e^{h\nu/k_B T} - 1} d\nu,$$

and we pick out the Planck function

$$\rho(\nu) = \frac{8\pi h \nu^3}{c^3 (e^{h\nu/k_B T} - 1)}$$

as an energy density per unit frequency. Thus higher temperatures are associated with higher frequencies! We can also write the Planck function in terms of wavelength,

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

and solving the equation $d\rho/d\lambda = 0$ tells us that we should expect the energy density to peak at

$$\lambda_{\max} = \frac{2.9 \times 10^{-3} \text{ m K}}{T}.$$

This is known as Wien's law. It'll also be useful to know the energy density inside our cavity. A quick substitution $x = h\nu/k_B T$ gives

$$\frac{E_{\text{tot}}}{L^3} = \int_0^\infty \frac{8\pi h L}{c^3} \frac{\nu^3}{e^{h\nu/k_B T} - 1} d\nu = \frac{8\pi k_B^4 T^4}{c^3 h^3} \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{8\pi k_B^4 T^4}{c^3 h^3} \frac{\pi^4}{15}.$$

We'll define a such that $E_{\text{tot}}/L^3 = aT^4$.

We should note, at this point, that all this stuff we've done relies on the validity of the integral approximation, which itself hinges on $\lambda_{\text{peak}} \ll L$. If $\lambda > 2L$, then none of this would have any hope at working. But if we keep running with this premise, we'll arrive at a pretty neat result!

Suppose, now, that our metal box is a perfect absorber (a blackbody). The box has temperature T and the blackbody has temperature T_{BB} . At equilibrium we expect to see no net energy flow, meaning

$$R_{T,\text{inc}} = R_{T,\text{em}}$$

for the blackbody, where the radiancy $R(\nu)$ is the power per area per frequency. We claim that the radiancy incident on the box walls is the same everywhere.

Suppose we put a little area- A hole in one of the box's walls. To determine the energy per frequency that escapes this hole, we'll integrate over a hemisphere inside the box:

$$R_T(\nu) \cdot A \cdot \Delta t = \int \rho(\nu) f_{\text{esc}} dV,$$

where $f_{\text{esc}} = A \cos \theta / 4\pi r^2$ is the fraction of photons that escape and where θ corresponds to approaching the hole head-on. So in spherical coordinates we have

$$\begin{aligned} R_T A \Delta t &= \iiint \rho(\nu) \frac{A \cos \theta}{4\pi r^2} r^2 \sin \theta dr d\theta d\phi \\ &= \frac{\rho(\nu) A}{4\pi} \int_0^{c\Delta t} dr \int_0^{2\pi} d\phi \int_0^{\pi/2} \sin \theta \cos \theta d\theta \\ &= \frac{\rho(\nu) A}{4\pi} \cdot c\Delta t \cdot 2\pi \cdot \frac{1}{2} \\ R_T &= \frac{\rho(\nu) c}{4} \end{aligned}$$

This is the radiancy incident on the walls of the cavity! By conservation of energy, it's also the radiancy absorbed and emitted by the blackbody. To finish things off, we calculate the total radiancy (the flux) from a blackbody:

$$F = \int_0^\infty R_T(\nu) d\nu = \frac{c}{4} \int_0^\infty \rho(\nu) d\nu = \frac{ca}{4} T^4,$$

where a is the quantity defined earlier. This gives us the Stefan-Boltzmann constant,

$$\sigma = \frac{ca}{4} = \frac{2\pi^5 k_B^4}{15c^2 h^3},$$

and the total power (the luminosity)

$$P = FA = A\sigma T^4.$$

6.4 Bose-Einstein Condensation

Now we'll take a gas of bosons confined to a length- L box and determine the “critical temperature” below which most of the bosons are in their ground state. This turns out to have some really interesting consequences for the matter's properties!

Our first thought might be to define $k_B T_C = \Delta E$, where ΔE is the gap between a boson's ground and first-excited states. Any lower T_C and most of the atoms won't have enough energy to be excited. But this produces a critical temperature that's about a thousand times lower than the observed value, so we'll need to be a little more careful about things!

Let's begin with our expression for the total number of bosons in the gas:

$$N = \int_0^\infty n_{BE}(E) \cdot (2s+1) \cdot \frac{1}{8} \cdot 4\pi r^2 dr.$$

Taking $s = 0$ for simplicity, substituting $n_{BE}(E)$, and changing variables to $E = (\hbar^2 \pi^2 / 2mL^2) r^2$ gives

$$= \frac{V(2m)^{3/2}}{4\hbar^3 \pi^2} \int_0^\infty \frac{E^{1/2} dE}{e^{(E-\mu)/k_B T} - 1}.$$

But there's an issue here: the integrand is physically undefined for $E < \mu$, which is a problem if μ is positive. Thankfully we can work around this by estimating the value of μ when we're close enough to the critical temperature. For a very large number N_0 of bosons in the ground state, we can make the Taylor approximation

$$N_0 = n_{BE}(E_0) = \frac{1}{e^{(E_0-\mu)/k_B T} - 1} \simeq \frac{k_B T}{E_0 - \mu}.$$

Thus $\mu \simeq E_0 - k_B T / N_0 \simeq E_0$ when enough bosons are in the ground state, meaning writing the integral as

$$N = N_0 + \frac{V(2m)^{3/2}}{4\hbar^3 \pi^2} \int_{E_0}^\infty \frac{E^{1/2} dE}{e^{(E-\mu)/k_B T} - 1}$$

makes it valid. It evaluates to

$$= N_0 + 2.6V \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2}.$$

It turns out that if we define the critical temperature T_C to be that at which $\mu(T_C) = 0$, then evaluating our original integral (before fixing the $\mu > 0$ issue) gives

$$N = 2.6V \left(\frac{mk_B T_C}{2\pi \hbar^2} \right)^{3/2};$$

we can thus rewrite our general result as

$$N = N_0 + N \left(\frac{T}{T_C} \right)^{3/2}, \quad T_C = \frac{2\pi \hbar^2}{mk_B} \left(\frac{N}{2.6V} \right)^{2/3}.$$

This is the temperature below which a large fraction of bosons settle into the ground state; this fraction can be found by solving the above equation for N_0/N , and is zero for $T > T_C$.

The state of matter that the bosons take on below this temperature is called a Bose-Einstein condensate since it's reminiscent of the transition that occurs when a gas cools and condenses to a liquid. The process described here, however, is very different since it has nothing to do with attractive interactions between atoms and molecules. The critical temperature is miniscule—for dilute gases it's on the order of nanokelvin and microkelvin, respectively. In liquid helium, however, the separation between atoms is comparable to the de Broglie wavelength, meaning these quantum effects take place much more quickly (at around 2.2 K).

6.5 Lasers and Masers

Let's go back to working with photons. We know that atomic transitions can absorb and emit photons at particular wavelengths, but it turns out that there are multiple ways for this emission to occur. On one hand there's the familiar spontaneous emission, where an excited electron falls to a lower energy level. On the other hand we have stimulated emission, where an existing photon interacts with the electron and spurs the transition to a lower energy and the emission of a new, "coherent" (identical) photon.

Suppose the walls of a cavity are comprised of atoms with two energy levels E_1 and E_2 , and let $\rho(\nu, T)$ be the energy density of photons in the cavity with energy $E_2 - E_1$. Define $B_{12}\rho(\nu, T)$ and $B_{21}\rho(\nu)$ as the probability of absorption and stimulated emission, respectively, per atom per unit time. Also define A_{21} as that probability of spontaneous emission. Then we have the differential equation

$$\frac{dN_2}{dt} = -\frac{dN_1}{dt} = B_{12}\rho(\nu, T)N_1 - A_{21}N_2 - B_{21}\rho(\nu, T)N_2,$$

where N_1 and N_2 are the numbers of electrons in E_1 and E_2 , respectively. In thermal equilibrium these derivatives are zero and

$$B_{12}\rho(\nu, T)N_1 = [A_{21} + B_{21}\rho(\nu, T)]N_2.$$

Also, from statistical mechanics

$$\frac{N_2}{N_1} = -e^{(E_2 - E_1)/k_B T} = e^{-h\nu/k_B T}$$

in equilibrium, so together we get

$$\rho(\nu, T) = \frac{A_{21}}{B_{12}e^{h\nu/k_B T} - B_{21}}.$$

If we map this to the known Planck function for cavity radiation we get

$$\begin{aligned} A_{21} &= (8h\pi\nu^3/c^3)B, \\ B &= B_{21} = B_{12}. \end{aligned}$$

The rate of emission is thus given by

$$\begin{aligned} [A_{21} + B\rho(\nu, T)]N_2 &= N_2 \left[A_{21} + \frac{8\pi h\nu^3/c^3 \cdot B}{e^{h\nu/k_B T} - 1} \right] \\ &= N_2 A_{21} [1 + N_{\text{BE}}(h\nu)] \end{aligned}$$

So the rate of emission is enhanced by the presence of photons! To quantify this enhancement, suppose we have some photons incident at $x = 0$ on a volume with some atoms in it. If we ignore the effects of spontaneous emission, the evolution of the excited states is governed by

$$\frac{dN_2}{dt} = B\rho(\nu)(N_1 - N_2).$$

Noting that $d/dt(\rho(\nu)\Delta\nu) = -d/dt(N_2 h\nu/V)$, we can rewrite this as

$$\frac{d\rho(\nu)}{dt} = \frac{h\nu}{V\Delta\nu} B\rho(\nu)(N_2 - N_1).$$

Using dx/dt in the chain rule gives

$$\frac{d\rho(\nu)}{dx} = \frac{h\nu}{cV\Delta\nu} B\rho(\nu)(N_2 - N_1),$$

and absorbing everything into a constant gives

$$\frac{d\rho(\nu)}{dx} = \alpha\rho(\nu).$$

So we get the exponential solution

$$\rho(\nu, x) = \rho(\nu, 0)e^{\alpha x}, \quad \alpha = B \frac{h\nu}{cV\Delta\nu},$$

where α is called the gain constant. When $\alpha > 0$, we get exponential growth in the amount of energy in our beam of light! (In other words, the Light is Amplified via the Stimulated Emission of Radiation.)

In practice many lasers have three energy levels. Atoms are transitioned from the ground state into a highly unstable excited state, and then they fall into an intermediate metastable state with a longer lifetime. This metastable state is what we need to sustain $N_2 > N_1$ and thus lasing.

7 Applications

7.1 Band Structure of Solids

As an application of what we've done so far, we'll do a first-principles investigation into some properties of solids. Consider a block of metal; the potential in this metal is generally periodic, with asymptotes to negative infinity at each nucleus. We might simplify things by approximating each asymptote as a finite square well, but for our purposes it will do to use a series of upward delta spikes at the midpoints between atoms:

$$\frac{2mV(x)}{\hbar^2} = \frac{\alpha}{a} \sum_{n=1}^N \delta(x - na),$$

where a is the separation between the spikes and α is the “strength” of each spike. We'll build in two more elements of periodicity.

- The wave function's corresponding probability density function must be periodic with period a . Mathematically, $|\psi(x+a)|^2 = |\psi(x)|^2$, and we get $\psi(x+a) = e^{i\theta}\psi(x)$. This is called the Bloch ansatz.
- If we imagine our one-dimensional lattice to be a closed loop then the wave function itself must be single-valued and so must be periodic with period Na , where N is the number of atoms in the metal. Thus $\psi(x+Na) = \psi(x)$

Combining these, we find that $\psi(x+Na) = e^{iN\theta}\psi(x) = \psi(x)$ and $e^{iN\theta} = 1$. Thus $\theta = 2\pi r/N$, where r is an integer falling between 0 and $N-1$. Now, using the time-independent Schrödinger equation we find that, in each region between spikes, we have

$$\psi_n(x) = A_n \sin(k(x-na)) + B_n \cos(k(x-na)), \quad (n-1)a < x < na.$$

Notice that by the Bloch ansatz we have $A_{n+1} = e^{i\theta}A_n$ and $B_{n+1} = e^{i\theta}B_n$, so we really only have three unknowns: A_1 , B_1 , and k . To restrict them, we begin by applying the continuity boundary condition $\psi_n(na) = \psi_{n+1}(na)$ to get

$$B_n = B_n e^{i\theta} \cos ka - A_n e^{i\theta} \sin ka.$$

Also, ψ is not differentiable, but it does satisfy $(d\psi/dx)_{na+} - (d\psi/dx)_{na-} = (\alpha/a)\psi_n(na)$. This gives

$$\frac{\alpha}{ka} B_n = A_n e^{i\theta} \cos ka + B_n e^{i\theta} \sin ka - A_n.$$

If we rewrite both of these equations such that all A_n are on the left and all B_n on the right and then divide, we end up with

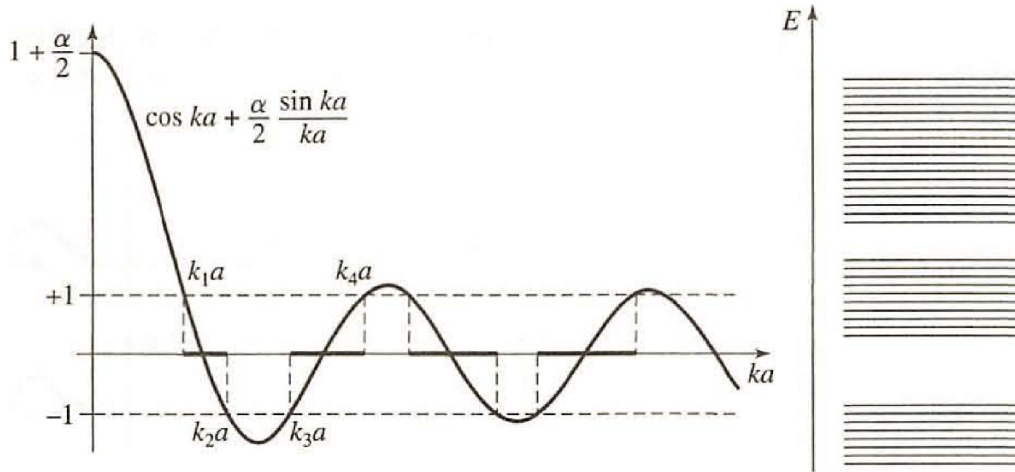
$$\cos \theta = \cos ka + \frac{\alpha}{2ka} \sin ka, \quad \theta = \frac{2\pi r}{N}.$$

Solving this equation for $k = \sqrt{2mE}/\hbar$ gives the allowed energies for the system. This cannot be done analytically, but we can glean some information using the below plot of the equation's right-hand side.

Due to the range restriction on $\cos \theta$, the only allowed ka are those for which the curve is bound by $[-1, 1]$. The energies corresponding to the allowed ka are plotted on the right. We see a structure of widening bands and narrowing gaps take form. Note that this is not an artifact of our delta potential model—if we stuck with the more realistic asymptote model we'd see something similar.

7.2 Electrical Properties of Solids

As it turns out, this is the most fundamental characteristic of conductors and insulators as groups! A material is a conductor if its Fermi energy falls inside of a band; in this case there are energies available for “accelerated” electrons to fill upon being influenced by an electric field. Otherwise the material is an insulator or a semiconductor, depending on how large the gap to the next band up is. (Also, solids with one valence electron per atom are conductors since, due to spin degeneracy, there is certainly a band that is not full. We cannot make a definite statement about solids with two valence electrons per atom.)



Sometimes the highest-allowed band is called the valence band, and the band with the next energy up is called the conducting band. In conductors these are the same, and we call it the metallic band. The distance from the Fermi energy to the top of the metallic band is called the work function.

Suppose we bring two metals into close proximity to one other, so there's a very small potential barrier between them. The metals' work functions are related by $W_a < W_b$, so the Fermi energy of metal a is greater than that of metal b . Electrons in a can thus tunnel to the lower energies in b , giving a a positive charge and b a negative charge. The potential energy of an electron in a falls, and that of an electron in b rises. This has the overall effect of shifting the metals' Fermi energies until an equilibrium is reached, at which point a contact potential

$$\phi_{\text{contact}} = \frac{W_b - W_a}{q_e}$$

exists between the two metals.

For insulators and semiconductors, at $T = 0$ K the valence band is completely filled and the conducting band is empty. Define $E = 0$ to be the top of the valence band, and E_g the gap between the bands. At a given temperature, we'd like to use the Fermi-Dirac distribution to determine the probability of occupation for a state at the bottom of the conducting band, but this requires knowing the chemical potential μ .

At temperature T , the number of atoms excited to the conduction band and holes in the valence band are respectively given by

$$\frac{1}{e^{(E_g - \mu)/k_B T} + 1} D(E_g) dE, \quad \left(1 - \frac{1}{e^{(-\mu)/k_B T} + 1}\right) D(0) dE.$$

The number of conducting electrons is equal to the number of valence holes, so

$$\frac{1}{e^{(E_g - \mu)/k_B T} + 1} D(E_g) dE = \left(1 - \frac{1}{e^{(-\mu)/k_B T} + 1}\right) D(0) dE.$$

Assuming $D(0) = D(E_g)$, solving gives $\mu = E_g/2$, right in the middle of the band gap. This quantity is also called the Fermi level, a generalization of the Fermi energy that denotes the energy of a quantum state with 50% probability of being filled at a temperature T . Note that if $E_g \gg k_B T$ we get $n_{\text{FD}}(E_g) \simeq e^{-E_g/2k_B T}$, and we see that there are correspondingly few holes in the valence band.

We can create a couple of particularly important kinds of semiconductors through a process called doping. Take a block of silicon for example; on its own this silicon is insular, but we can replace an extremely small fraction of silicon atoms with other atoms with different numbers of valence electrons. The idea is to keep the same band structure, but to change the number of electrons inhabiting that structure.

- If we dope with gallium, which has one fewer valence electron than silicon, then there is a deficit of electrons and we get some holes at the top of the valence band. This creates a p-type semiconductor, and the Fermi level is a little under the halfway point.
- If we dope with arsenic, which has one more valence electron than silicon, then we get some extra electrons at the bottom of the conducting band. This creates an n-type semiconductor, and the Fermi level is a little above the halfway point.

We can put these two semiconductors side by side in very close proximity to create a p-n junction. Just as we saw with metals, electrons from the n side move to lower energy levels on the p side until the two Fermi levels align. This creates negative and positive charges on the p and n sides, respectively, and thus an electric field exists in the depletion region between the sides.

Even in equilibrium charges are still moving, just in equal amounts. On the p side electrons are excited by thermal energy into the conduction band, where they find a downhill potential and slide onto the n side; this is called the thermal current I_0 . On the n side electrons are excited by thermal energy onto the p side, generating the recombination current I_R .

So in equilibrium we have $I_0 = I_R$. But if we apply an external potential ϕ to the junction, the recombination current must change so that a nonzero net current may flow. Depending on whether it increases or decreases, we have one of $I_R = I_0 e^{\pm |q_e| \phi / k_B T}$. Using $I = I_R - I_0$, we can express the net current in terms of I_0 . This is the foundation of technologies like LDEs, photovoltaic cells, and transistors!

We'll look at one last kind of material: superconductors. The important property here is the resistivity ρ , which is related to resistance by $R = \rho(L/A)$ where L is a tiny length of a cross section A . In any material, the electrons are scattering about due to interactions with vibrating nuclei, and this scattering gets less prevalent as temperature decreases. In particular,

$$\rho = \frac{m}{nc^2} \frac{1}{\tau},$$

where $1/\tau$ is the temperature-dependent scattering rate. For most materials the resistance simply diminishes to some R_0 . However, experiments show that there are some for which there is a critical temperature T_c after which the resistance drops to literal zero. This is what characterizes a superconductor!

The idea here is that pairs of electrons can come together to act like a boson. When two electrons in a lattice have opposite momenta, they are attracted each other via distortions in the lattice; these distortions are significant since the repulsion between two electrons is much smaller in a lattice than it is in a vacuum. In k -space, we interpret these as electrons with opposite \mathbf{k} and opposite spin being attracted and forming a bound state (with a lower energy) relative to the Fermi energy. This is what we call a Cooper pair.

If \mathbf{R}_{CM} and \mathbf{k}_{CM} are the center of mass and average k -space vectors, then it turns out that the wave function looks like

$$\Psi_{\text{pair}}(1, 2) = e^{i(\mathbf{k}_{\text{CM}} \cdot \mathbf{R}_{\text{CM}})} \Psi(\mathbf{r}_1 - \mathbf{r}_2) \chi(1, 2).$$

Since the electrons are fermions we need an overall antisymmetric state, so we take

$$\chi(1, 2) = \frac{1}{\sqrt{2}} [\chi_+(1)\chi_-(2) - \chi_-(1)\chi_+(2)].$$

So our Cooper pair behaves like a boson, and the Pauli exclusion principle no longer applies! All Cooper pairs in existence can fall into the same ground state. This is the superconducting state.

There are three hallmarks of such a state. First, as we saw, it has zero resistance. Also, a material in a superconducting state is a perfect diamagnet; specifically, it has magnetic susceptibility $\chi_m = -1$. Finally, the magnetic flux through a loop of superconducting is quantized in integer multiples of $h/2q_e$ —this is a direct consequence of requiring a single-valued wave function.

7.3 Nuclei and Binding Energy

Let's begin again by loosely discussing the structure of an atom. We know, by now, that on scales these small it doesn't really make sense to discuss definite sizes, but we can at least pin down general spheres of influence—the characteristic radius of an atom is around $R_{\text{atom}} \sim 1 \text{ \AA} = 10^{-10} \text{ m}$, and that of a nucleus is $R \sim 1 \text{ fm} = 10^{-15} \text{ m}$. The proton and neutron (together, nucleon) masses are on the order of 10^{27} kg and only differ in their fourth digits, so we approximate $m_n \simeq m_p$; the electron mass is on the order of 10^{-30} kg . Note that free neutrons are unstable and decay according to $n \rightarrow p^+ + e^- + \bar{\nu}_e$ with half-life $(610 \pm 1) \text{ s}$. (The $\bar{\nu}_e$ is called an electron antineutrino; more on that later.)

Some notation will be useful. The symbol ${}^A_Z\text{X}$ has three parts: the element symbol X, the atomic number Z , and the mass number A . (With N neutrons we have $A = Z + N$.) As shorthand, we'll often also write

$${}^1_1\text{H} = p, \quad {}^2_1\text{H} = n, \quad {}^3_1\text{H} = t, \quad {}^4_2\text{He} = \alpha.$$

Note that the mass number is always an integer, while on the periodic table we usually see decimals. This is because the periodic table values are weighted averages over all stable isotopes—in hydrogen, for example, we'd include p and d but not t. The stabilities of different isotopes are visualized very nicely with N and Z on the horizontal and vertical axes, respectively; when we color each cell according to its half-life we see a roughly linear correlation between N and Z whose slope is a little less than 1. This linearity subtly breaks down at higher N , reflecting how we need more neutrons to keep the nuclei together as we add more protons.

It's possible to roughly determine the size of a nucleus as a function of its mass number A . We can't do this using light without using crazy high-energy gamma rays, so instead some clever electron scattering experiments have been done to probe nuclear charge distributions. It turns out that these distributions are roughly constant in the interior, so if we define R as the radius at which the charge starts dropping off we get $R \simeq r_0 A^{1/3}$ with $r_0 = 1.2$ fm. This gives the volume $V = V_0 A$, where $V_0 = 7.2$ fm³ is the nucleon volume based on its characteristic radius r_0 . It follows that nuclear matter has a mass density on the order of 10^{17} kg/m³—huge!

We could do a similar thing with neutron scattering in order to probe nucleon density rather than charge density. Assuming each neutron is a point mass gives the neutron-nucleus cross section $\sigma = \pi R^2 = \pi r_0^2 A^{2/3}$. (These cross sections are usually expressed in terms of barns, where 1 barn = 1 b = 10^{-28} m².) This guess is unsurprisingly wrong, but it is on the correct order of magnitude. We could get a more accurate depiction of these interactions by relaxing the assumption that a neutron is a point particle and by using its λ_{dB} .

Now, the stability of an isotope is determined by its binding energy, which is the difference between the mass energy associated with a nucleus versus that associated with the sum of its individual parts. Mathematically,

$$E_B = (Zm_p c^2 + (A - Z)m_n c^2) - m_{\text{nuc}} c^2.$$

The higher the E_B , the more stable a nucleus is because it takes more energy to “free” the nucleons. So it will be productive to determine how, exactly, the binding energy is set.

We'll building up to the semi-empirical formula

$$E_B = a_1 A - a_2 A^{2/3} - a_3 \frac{Z^2}{A^{1/3}} - a_4 \frac{(Z - A/2)^2}{A} + \frac{a_5}{A^{1/2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix},$$

where the fitted coefficients follow $a_4 > a_1, a_2, a_5 > a_3$. The first terms can be explained using the liquid drop model in which the nuclei are spherical, incompressible, and constant-density in both mass and charge. Every nucleon interacts via a short-range attractive nuclear force with its nearest neighbors, and all protons interact with each other via the long-range Coulomb force.

1. Volume term. Due to nearest-neighbor interactions we have a positive $E_1 = An_{NN} \propto A$
2. Surface term. We've over-counted since surface nucleons have less neighbors than inner ones. Since the nuclear surface area is proportional to $A^{2/3}$ we subtract an $E_2 \propto A^{2/3}$.
3. Coulomb term. Now we account for Coulomb repulsion. From E&M we know that the energy associated with a ball of charge Ze is proportional to Z^2/R , so we subtract an $E_3 \propto Z^2/A^{1/3}$.

Now let's switch to a different, Fermi gas model. We'll model the strong nuclear force as a half-infinite square well, and we'll stuff protons and neutrons into that well according to the Pauli exclusion principle.

4. Asymmetry term. If we have N fermions, then the total energy associated with those fermions is $E_{\text{tot}} = \frac{3}{5} N E_F$. Doing this for both protons and neutrons gives

$$\begin{aligned} E_{\text{tot}} &= \frac{3}{5} Z \frac{\hbar^2}{2m_p} \left(\frac{3\pi^2 Z}{V} \right)^{2/3} + \frac{3}{5} (A - Z) \frac{\hbar^2}{2m_p} \left(\frac{3\pi^2 (A - Z)}{V} \right)^{2/3} \\ &= \frac{3}{5} \frac{\hbar^2}{2m_p} \left(\frac{3\pi^2}{V} \right)^{2/3} \left[Z^{5/3} + (A - Z)^{5/3} \right], \end{aligned}$$

approximating $m_n \simeq m_p$. Thus

$$E_{\text{tot}} \propto \frac{[Z^{5/3} + (A - Z)^{5/3}]}{A^{2/3}},$$

and minimizing this quantity with respect to Z gives $Z = A/2$. This gives

$$E_4 = E_{\text{tot}}(Z) - E_{\text{tot}}(A/2) \propto \frac{(Z - A/2)^2}{A}.$$

The origin of the last term is a little sketchy and has to do with symmetric and antisymmetric states. We'll just explain how it works here.

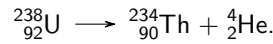
- 5. Symmetry term. If the numbers of protons and neutrons are both even then the term is positive, and if they're both odd then it's negative. If the parities don't match then the term vanishes.

All of these together provide a very good fit for the observed binding curve, including the peak at iron-56.

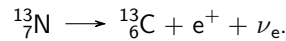
7.4 Radioactivity, Fusion, and Fission

If a nucleus is unstable, it decays toward the curve of stability on the isotope table from earlier. There are a few prominent modes by which this can happen.

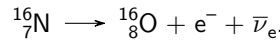
- α -decay. The nucleus emits an α -particle, which is our name for a ${}^4_2\text{He}$ nucleus. This causes $N \rightarrow N - 2$ and $Z \rightarrow Z - 2$, so we move twice down and twice left on the isotope table. As an example,



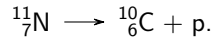
- β^+ -decay. A proton decays according to $p \rightarrow n + e^+ + \nu_e$, causing $N \rightarrow N + 1$ and $Z \rightarrow Z - 1$, a single down-right movement on the isotope table. For example,



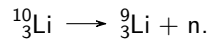
- β^- -decay. A neutron decays according to $n \rightarrow p + e^- + \bar{\nu}_e$, causing $N \rightarrow N - 1$ and $Z \rightarrow Z + 1$, a single up-left movement on the table. For example,



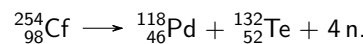
- p-decay. A proton is emitted, so $N \rightarrow N$ and $Z \rightarrow Z - 1$, causing a single downward movement:



- n-decay. A neutron is emitted, so $N \rightarrow N - 1$ and $Z \rightarrow Z$, causing a single leftward movement:



- Spontaneous fission. A nucleus randomly decays into two smaller nuclei with different masses along with a few neutrons. One example is



By the law of radioactivity, the probability R of decay per unit time is constant. There is nothing we could possibly do to tell if a nucleus is going to decay soon. So if we start with a number $N(t)$ of nuclei, we have

$$N(t + dt) = N(t) - R dt N(t) \implies N(t) = N(0)e^{-t/\tau},$$

where we τ is defined in terms of the half life: $t_{1/2} = \tau \ln 2$.

We can take advantage of this knowledge to determine the age of some very old objects! If we have a substance containing trace amounts of, say, ${}^{235}\text{U}$ and ${}^{238}\text{U}$, then if we know the half-life for each isotope and the original ratio between their amounts, then we can calculate how much time it's been sitting for. This is one of the ways we've been able to estimate the age of the solar system. It's also used to determine the age of dead organic material, in which case we compare the unstable ${}^{13}\text{C}$ and ${}^{14}\text{C}$ to the stable ${}^{12}\text{C}$.

Now, it turns out that α -decay is more common than, say, proton or neutron emission. To see why, let's model the process using an α -particle confined by the rest of the nucleus—it's in a deep square well, which at radius R jumps up and turns into a Coulomb potential. We determined, long ago, that the probability of the α -particle tunneling through a potential barrier to liberate itself is given by

$$T \simeq \exp \left[-\frac{2\sqrt{2m_\alpha}}{\hbar} \int \sqrt{V(r) - E_\alpha} dr \right] \simeq \exp \left[-\frac{4(Z-2)}{\sqrt{E_\alpha}} \right],$$

where in this case $V(r)$ is the Coulomb potential between the nucleus and α -particle. Note that E_α is measured in MeV here. So the half-life looks something like

$$t_{1/2} \sim \frac{2R}{v} \cdot \frac{1}{T},$$

where $2R/v$ is the time between encounters with the potential barrier and $1/T$ is the number of encounters before tunneling. Despite all the approximations we made, on a log-log plot this aligns very well with experimental results!

We can use this same model to describe other processes, like fusion. Suppose, in the simplest case, that one proton is at rest and another is flying towards it; in order for the approaching proton to overcome the Coulomb barrier we must have

$$\frac{3}{2}k_B T \gtrsim \frac{q_e^2}{4\pi\epsilon_0 R}.$$

This would require a temperature above 6×10^9 K. But this process happens in the Sun all the time, and we know that the Sun's interior isn't that hot! Quantum tunneling once again saves the day—it turns out that the temperature required for there to be a reasonable chance of tunneling is on the order of 10^7 K, which is just about what we observe. (Processes like these are what give stars their luminosity! It's also where all naturally-occurring elements after lithium come from.)

Fission is the opposite of this process. Sometimes it happens spontaneously, and other times it's induced by adding a neutron to create an unstable nucleus. Either way, we end up with two different nuclei and some extra neutrons shooting out. The reason these nuclei are usually different is, once again, quantum tunneling! Classically, the “activation energy” for fission (based on the change in binding energy) may be too high, but we've seen that the tunneling probability T is highly sensitive to mass based on the presence of \sqrt{m} in the exponential. So if one of the resultant nuclei is light enough it can tunnel through the heavier's potential barrier and break apart.

7.5 Particle Physics

Now we'll go even smaller and look at some particle physics! We'll start by talking through the Standard Model, which is summarized in the table below. The first three columns contain the fermions, which are generally associated with matter. They are subdivided into two groups, quarks and leptons, based on whether they can interact with particles via the strong force.

- Quarks feel the strong force. The up-type quarks in the first row all have charge $+(2/3)q_e$, and the down-type quarks in the second row have $-(1/3)q_e$. All charges that we'll discuss here are multiples of q_e , so we'll often drop it for simplicity.
- Leptons do not feel the strong force. The charged quarks in the third row all have charge -1 , while their corresponding neutrinos in the fourth row have no charge. (Note that, in this course, we'll denote the charged leptons as e^-, μ^-, τ^- .)

All of these particles also have corresponding antiparticles, which are represented by bars or plus signs. For example, an up antiquark is denoted \bar{u} and an electron antineutrino is denoted e^+ .

The bosons in the fourth column are the force carriers of the Standard Model. For the electromagnetic force we have the photon γ , which does not self-interact; for the strong force we have the gluon g , which does self-interact; and for the weak force we have the W and Z bosons W^\pm, Z^0 , which also self-interact. (The last boson is the Higgs boson and is associated with mass; we'll respectfully ignore it in this discussion.)

We'll dive deeper into all of these, but first, a few caveats to the approach we've been taking in this course. First, the Schrödinger equation is nonrelativistic, while many of the phenomena that exist in the realm of particle physics are inherently relativistic. Also, this equation conserves probability and thus does not allow for the creation and annihilation of particles, another phenomenon intrinsic to the field. All of this is to simply say that we must proceed with caution.

mass →	≈2.3 MeV/c ²	≈1.275 GeV/c ²	≈173.07 GeV/c ²	0	≈126 GeV/c ²
charge →	2/3	2/3	2/3	0	0
spin →	1/2	1/2	1/2	1	0
	u up	c charm	t top	g gluon	H Higgs boson
QUARKS	≈4.8 MeV/c ²	≈95 MeV/c ²	≈4.18 GeV/c ²	0	
	-1/3	-1/3	-1/3	0	
	1/2	1/2	1/2	1	
	d down	s strange	b bottom	γ photon	
	0.511 MeV/c ²	105.7 MeV/c ²	1.777 GeV/c ²	0	
	-1	-1	-1	0	
	1/2	1/2	1/2	1	
	e electron	μ muon	τ tau	Z Z boson	
LEPTONS	<2.2 eV/c ²	<0.17 MeV/c ²	<15.5 MeV/c ²	±1	
	0	0	0	1	
	1/2	1/2	1/2		
	ν_e electron neutrino	ν_μ muon neutrino	ν_τ tau neutrino	W W boson	
					GAUGE BOSONS

With that out of the way, we'll continue our discussion of the fundamental forces, sans gravity.

- Electromagnetic force. We're familiar with the associated potential function

$$V(r) = \frac{(Q_1 e)(Q_2 e)}{4\pi\epsilon_0 \hbar c} \frac{\hbar c}{r} = Q_1 Q_2 \left(\frac{e^2}{4\pi\epsilon_0 \hbar c} \right) \frac{\hbar c}{r},$$

where $q_i = Q_i q_e$. We'll also package the parenthetical into a dimensionless coupling constant α_γ to get

$$V(r) = Q_1 Q_2 \alpha_\gamma \frac{\hbar c}{r}.$$

In summary we have $\alpha_\gamma \simeq 1/137 \simeq 0.0073$, $m_\gamma = Q_\gamma = 0$, and an infinite range.

- Weak force. This more unfamiliar force is responsible for radioactive decay. Its potential takes a similar form, but this time there is a massive force carrier so we tack on an extra factor:

$$V(r) = Q_1^W Q_2^W \alpha_W \frac{\hbar c}{r} e^{-cm_W r/\hbar}.$$

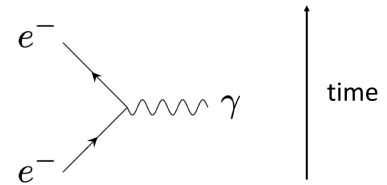
The exponential causes the force to essentially vanish for $r \sim \hbar/cm_W$, where the W and Z masses are each about 100 times bigger than that of a proton. The weak force has $\alpha_W \simeq 0.032$, and the charge is simply called "weak charge".

- Strong force. This force is chiefly responsible for holding nucleons together, but its effects spill out and build full nuclei, too. Its coupling strength is not constant due to self-interaction, but it tends to be around $\alpha_S \simeq 0.1$. The charge is called color, and it turns out that the gluon itself has color! (Self-interaction also leads to the strange observation that the strong force, to a point, gets stronger with distance and with decreasing energy.)

It turns out that quarks and gluons always get bound together into color-neutral states called mesons or baryons, together hadrons. Mesons are comprised of a quark and an antiquark, while a baryon is comprised of three ordinary quarks.

Now, at high energies both matter and force carriers behave like these individual particles rather than waves. Working with potentials becomes less useful, so we instead turn to computing probabilities of certain particle interactions taking place. These probabilities are encoded in Feynman diagrams, which have an amount of mathematical complexity that is beyond the scope of this course; for now we'll focus on the surface level.

At right is an example of a Feynman diagram. There are few things to notice here. First is that the diagram is read from bottom to top; here we start with an electron, then a photon is produced, and we end with an electron. So this diagram represents the emission of a photon when an electron falls to a lower energy state!



Also, the arrowheads on the two electron lines have nothing to do with the passage of time or movement in space. Instead, the fact that they point in the same direction as time simply emphasizes that we are talking about electrons rather than positrons, whose arrows point against time.

We can also use Feynman diagrams to represent unknown processes. We write down the inputs to the processes, send them into a “black box” (however we decide to draw that), and get back some outputs. Roughly speaking, each possibility for the contents of the black box is associated with a probability amplitude; we can add them, norm them, and square them to determine the probability of this arbitrary process occurring.

Most relevant to us right now, we can use Feynman diagrams to represent some key insights about the nature of the weak force. First, the W^\pm interactions are the only ones in the Standard Model that change the type of a particle—for example, an e^- might interact with a W^- to create an ν_e . Thus these bosons are the only force carriers that allow matter particles to decay! For leptons, however, this comes with the caveat that the W^\pm only couple charged leptons and neutrinos of the same generation, so we couldn't have an interaction involving $e^- \rightarrow \nu_\mu$, for example.

Speaking of neutrinos, their observations have been plagued by a puzzle that goes beyond the Standard Model—on Earth, we only observe a third of the predicted number of solar neutrinos! This was a complex problem for a long time, but it turns out to have a simple solution: neutrinos cannot be in energy eigenstates. Focusing just on the electron and muon neutrinos, consider two actual eigenstates ψ_1, ψ_2 . Then we have

$$\begin{aligned}\psi_{\nu_e} &= (\cos \theta)\psi_1 + (\sin \theta)\psi_2 \\ \psi_{\nu_\mu} &= (-\sin \theta)\psi_1 + (\cos \theta)\psi_2\end{aligned}$$

We can put these together to find the most general wave function:

$$\begin{aligned}\Psi(t) &= (\cos \theta)e^{-iE_1 t/\hbar}\psi_1 + (\sin \theta)e^{-iE_2 t/\hbar}\psi_2 \\ &= c_e(t)\psi_{\nu_e} + c_\mu(t)\psi_{\nu_\mu}\end{aligned}$$

As $\Psi(t)$ evolves, the probability associated with each term evolves too, and we come to the startling conclusion that neutrinos can change type as time passes! This completely explains the perceived deficit in neutrinos.

7.6 Compact Extra Dimensions

Now we'll investigate one last problem: why is gravity so puny compared to the other fundamental forces? One purely theoretical hypothesis is that its influence is being eaten up by some other spatial dimensions that we can't see. Let's run with this and see where it goes!

Recall Gauss's law $\nabla \cdot \mathbf{E} = \rho/\epsilon_0$, and how we can use it to derive Coulomb's law. It turns out that there is an analog for gravitation: $\nabla \cdot \mathbf{g} = -4\pi G\rho_m$, where ρ_m is mass density. Integrating over a volume V gives

$$\int_{\partial V} \mathbf{g} \cdot d\mathbf{A} = -4\pi Gm \implies \mathbf{g} = -\frac{GM}{r^2}\hat{r},$$

where the second statement comes from placing a point mass inside a radius- r sphere. If we generalize this process to $(3 + n)$ -dimensional space we get

$$\mathbf{g} = -\frac{G_n M}{r^{2+n}}\hat{r},$$

where G_n is a generalized gravitational constant.

Now, suppose that these n extra dimensions are compact with characteristic “radius” R . To understand this, we might draw an analogy to a person and ant walking on a radius- R tightrope. The walker can only experience forward-backward motion, but a creature as small as an ant would notice that it can walk all the

way around the tightrope, effectively adding a new compact dimension to the picture. See how, despite the existence of such dimensions, over long distances $r \gg R$ in the visible dimensions we recover the somewhat familiar

$$g = -\frac{G_n M}{R^n r^2} \equiv \frac{G_N^{\text{3D}} M}{r^2}.$$

This is great, but gravity is fundamentally tied to relativity, which we know is incompatible with the Schrödinger equation. What we need is a relativistic wave equation, and the Klein-Gordon equation does the trick:

$$-\hbar^2 c^2 \nabla^2 \Psi + m^2 c^4 \Psi = -\hbar^2 \frac{\partial^2 \Psi}{\partial t^2}.$$

Note that this equation has the dispersion relation $\hbar\omega = \sqrt{\hbar^2 k^2 c^2 + m^2 c^4}$, as we'd hope based on our knowledge of special relativity. Now, suppose we introduce a fourth compact coordinate u , so the Laplacian turns into

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

We'll rewrite the Klein-Gordon equation:

$$\hbar^2 c^2 \left[\frac{1}{c^2} \frac{\partial^2 \Psi}{\partial t^2} - \nabla^2 \Psi \right] + m^2 c^4 \Psi = 0.$$

The solution looks like

$$\begin{aligned} \Psi(x, y, z, u, t) &= e^{-iEt/\hbar} e^{i(k_x x + k_y y + k_z z + k_u u)} \\ &= e^{-iEt/\hbar} e^{i(\mathbf{k} \cdot \mathbf{x} + k_u u)}. \end{aligned}$$

As a gut check, we could substitute this back into the equation to confirm that Ψ obeys the expected energy-momentum relation. Now we apply a boundary condition; specifically, u is a compact dimension, so to keep our wave function single-valued we require that $\Psi(\mathbf{x}, u, t) = \Psi(\mathbf{x}, u + 2\pi R, t)$. Substituting the solution we just found gives

$$e^{ik_u u} = e^{ik_u (u + 2\pi R)} \implies k_u = \frac{n}{R}, \quad n \in \mathbb{Z}.$$

So the energy eigenfunctions and eigenvalues are still quantized here! The squared eigenvalues are

$$E_n^2 = \hbar^2 |\mathbf{k}|^2 c^2 + \frac{\hbar^2 c^2 n^2}{R^2} + m^2 c^4.$$

In the rest frame of the particle, the first term vanishes and we get

$$m_n = \sqrt{m^2 + \frac{\hbar^2 n^2}{R^2 c^2}}.$$

This is the apparent mass of the particle in three dimensions! All this is a peek into the world of things like string theory, where predictions only work out for universes with more than three dimensions.