

# PHYS 52: Quantum Physics

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# Chapter 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  $\nu$  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 an angle  $\theta$  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  $\theta$  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.

**Summary**

Light is comprised of massless packets called photons, each with energy  $E = h\nu$ . The probabilistic behavior of these photons are described by complex numbers called probability amplitudes, and they accurately predict double- and single-slit interference patterns.

It turns out that matter exhibits interference, too; to quantify it, we define the de Broglie wavelength  $\lambda_{dB} = h/mv$ . An application is the Bragg relation  $2d \sin \theta = n\lambda$ , where matter of de Broglie wavelength  $\lambda$  is incident at an angle  $\theta$  upon a two-layer crystal with spacing  $d$ .

## 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  $\omega$ , 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

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

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?

**Summary**

De Broglie's matter wave hypothesis immediately leads to the equations  $E = \hbar\omega$  and  $p = \hbar k$ . An application of the classical energy-momentum relation gives the dispersion relation  $\omega = \hbar k^2/2m$ . Given this, one might deduce that the correct equation for nonrelativistic matter waves 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 the complex-valued wave function  $\Psi$  encodes the wave property of a particle. The complex exponential  $\Psi(x, t) = e^{i(kx - \omega t)}$  is one important solution to this equation.

**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  $\rho$  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  $x \rightarrow \pm\infty$ .)

### Summary

The wave function is a probability amplitude density function: the Born rule states that  $dP(x, t) = |\Psi(x, t)|^2 dx$ , and we can determine the probability of detection in some spatial interval by integrating this differential over that interval. Any meaningful wave function must be normalized so that its integral over all space is equal to one.

Probability is conserved locally—if the probability in a particular interval changes, there must be an equal and opposite change somewhere else. The flow of probability is described by the probability current

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

Probability is also conserved globally, so the wave function remains normalized for all time.

## 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  $\Psi$  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:

$$\begin{aligned}\Psi(x, 0) &= \int_{k_0 - \frac{\Delta k}{2}}^{k_0 + \frac{\Delta k}{2}} A e^{ikx} dk \\ &= \frac{A}{ix} \left( e^{i(k_0 + \frac{\Delta k}{2})x} - e^{i(k_0 - \frac{\Delta k}{2})x} \right) \\ &= \frac{2Ae^{ik_0x}}{x} \sin\left(\frac{\Delta kx}{2}\right)\end{aligned}$$

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  $\Delta x$  of the wave packet and the range  $\Delta k$  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  $\Delta x$  and  $\Delta p_x$  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  $\Delta k$  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!

### Summary

We can get a normalizable solution to the Schrödinger equation by linearly combining a continuum of complex exponentials. Such a solution is called a wave packet, and the speed at which it propagates is the group velocity  $d\omega/dk$ . By considering the width of this packet and the range of integrated wavenumbers, we can make a crude argument for the Heisenberg uncertainty principle

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

where  $\Delta x$  and  $\Delta p_x$  are uncertainties in a particle's position and momentum, respectively.

## 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.)

### Summary

Despite the unintuitive nature of quantum mechanics, it must correctly describe the behavior of macroscopic objects. We can capture the "classical limit" using expectation values; the relevant ones for position and momentum are given below.

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

These can be used to calculate the uncertainties in position and momentum:

$$\begin{aligned} (\Delta x)^2 &= \langle x^2 \rangle - \langle x \rangle^2 \\ (\Delta p_x)^2 &= \langle p_x^2 \rangle - \langle p_x \rangle^2 \end{aligned}$$

According to Ehrenfest's theorem, we can write the quantum analog of Newton's second law,

$$\frac{d\langle p_x \rangle}{dt} = - \left\langle \frac{\partial V}{\partial x} \right\rangle.$$



## Chapter 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.

**Summary**

Using separation of variables on the Schrödinger equation gives  $\Psi(x, t) = e^{-i\omega t}\psi(x)$ , where  $\psi$  is a solution to the time-independent Schrödinger equation

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

These  $\Psi$  are not the only solutions to the Schrödinger equation, but they are the building blocks for all others. Since their  $|\Psi|^2$  are time-independent, these solutions are often called stationary states.

## 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  $\Psi_n$  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.)

### Summary

The infinite square well is a very simple choice of  $V(x)$ . Applying continuity boundary conditions gives the quantized stationary states and energies

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

for positive integers  $n$ .

## 2.3 Time Evolution and Measurement Properties

In general, the time-independent Schrödinger equation gives a discrete set of solutions  $\psi_n$ , 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

$$\begin{aligned} \Psi(x, t) &= \frac{1}{\sqrt{2}} \Psi_1(x, t) + \frac{1}{\sqrt{2}} \Psi_2(x, t) \\ &= \frac{1}{\sqrt{2}} e^{-iE_1 t/\hbar} \psi_1(x) + \frac{1}{\sqrt{2}} e^{-iE_2 t/\hbar} \psi_2(x) \\ &= \frac{1}{\sqrt{2}} e^{-iE_1 t/\hbar} \left[ \psi_1 + e^{-i(E_2 - E_1)t/\hbar} \psi_2 \right]. \end{aligned}$$

The corresponding probability density function described turns out to be

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

where the last step is valid because  $\psi_n$  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.

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

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  $\Psi$  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  $\psi_m$  and  $\psi_n$  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  $\Psi$ ,  $c_n$  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:

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

### Summary

In general, the time-independent Schrödinger equation gives a discrete set of mutually orthonormal solutions  $\psi_n$ , each with an associated energy  $E_n$  and phase factor  $e^{-i\omega_n t}$ . We can linearly combine these stationary states to get solutions that evolve in time. The coefficients of such a linear combination is given by the inner product

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

Each  $|c_n|^2$  represents the probability of finding  $E_n$  upon a measurement of a particle's energy. So we have

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

## 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  $\Psi$ , and then doing stuff with the result. So we expect that there is some energy operator  $E_{\text{op}}$  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  $\psi_n$  found via separation of variables, and its eigenvalues are their corresponding energies  $E_n$ ! We'll often refer to  $\psi_n$  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  $p_{\text{op}}$  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  $p_{\text{op}}$ , and its corresponding eigenvalue is the momentum  $\hbar k$ . Since  $k$  can vary continuously, this tells us that momentum is continuous (unlike energy!).

### Summary

We have the position, momentum, and energy operators:

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

The time-independent Schrödinger equation can be written as  $H\psi = E\psi$ , so the eigenvectors of the Hamiltonian  $H$  are stationary states and the eigenvalues are their associated energies. In general, the eigenvalues of an operator correspond to the possible outcomes of the measurement of some observable. Here are the relevant expectation values for energy:

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

## Chapter 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  $\psi$  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  $\psi$  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  $\psi$  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  $\psi$  and  $\psi'$  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:

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

Notice that the  $\psi$  on the left is even while the  $\psi$  on the right is odd.

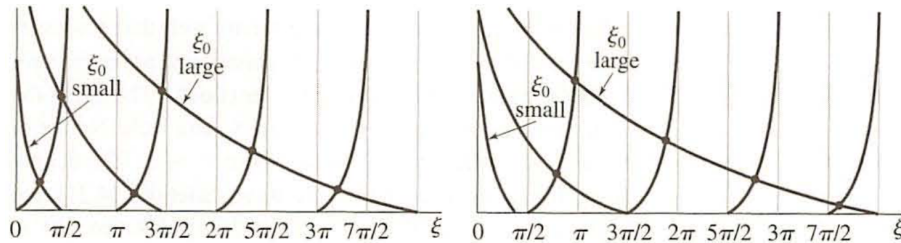
At this point we still haven't quantized anything. To change this, let's go back to dividing (1)/(2) and (3)/(4):

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

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  $\xi_0$  corresponding to more allowed energies. This hopefully makes some intuitive sense:  $\xi_0$  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.

### Summary

The finite square well has oscillatory solutions on its interior and exponential ones on its exterior. To determine precisely the behavior of these solutions, we apply continuity and differentiability boundary conditions, requiring that we eliminate any divergent terms which would otherwise ruin normalizability. We eventually get a pair of equations that lack analytic solutions, but together they show that the allowed energies are once again quantized and that there are finitely many of them.

## 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  $\psi$  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.

### Summary

Given a state with energy  $E$ , there are two key regions to consider.

- In the  $E > V$  regions, solutions are oscillatory. As  $E - V$  increases, the frequency of oscillation increases and the amplitude decreases. If  $E > V$  everywhere then we have a continuum of solutions that we can combine to create a normalizable wave packet.
- In the  $E < V$  regions, solutions are exponential. As  $V - E$  increases, the “decay length” decreases. If  $E < V$  everywhere then there are no solutions because  $\psi$  will diverge.

At  $E = V$  we often see inflection points; this is where we apply continuity and differentiability boundary conditions to get quantized solutions and energies. The  $n$ th bound state has  $n - 1$  nodes.

## 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  $\psi_0$ . 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  $\psi_0$  is a stationary state, the energy has a definite value  $E_0$ . Also, since  $\psi_0$  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  $\Delta x$  and  $\Delta p_x$ , 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  $\psi_0$  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  $\psi_0$  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

$$1 = \int_{-\infty}^{\infty} |A_0|^2 e^{-m\omega_0 x^2/\hbar} dx$$

$$\frac{1}{|A_0|^2} = \int_{-\infty}^{\infty} e^{-bx^2} dx,$$

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  $|A_0| = (b/\pi)^{1/4}$ .

Once 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  $\psi_n$  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!

### Summary

According to the Heisenberg uncertainty principle, the quantum harmonic oscillator must have a nonzero minimum allowed energy. In particular,  $E_0 = \hbar\omega_0/2$ , and  $\psi_0(x) = A_0 e^{-m\omega_0 x^2/2\hbar}$ . The other energies are evenly-spaced up the potential well, but their associated eigenfunctions take a more complex form involving Hermite polynomials.

## 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  $\alpha$  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  $\delta$  implies that  $\delta$  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  $\psi$  is continuous,  $A = B$ . But since we have an infinity here,  $\psi$  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  $\psi'$  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

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

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.

### Summary

The Dirac delta potential has exponential solutions on either side of the spike. These solutions piece together to create a continuous solution. There is also a differentiability boundary condition that is uncovered by integrating either side of the Schrödinger equation over an infinitesimal neighborhood around the potential spike. If we do a similar thing with a double delta well we get a solution that is more tightly bound (i.e., one that has a lower energy).

## 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

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{ik_0x} + De^{-ik_0x} & x > 0 \end{cases} \implies \psi'(x) = \begin{cases} ik(Ae^{ikx} - Be^{-ikx}) & x < 0 \\ ik_0(Ce^{ik_0x} - De^{-ik_0x}) & x > 0 \end{cases}$$

The continuity of  $\psi$  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

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

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”.)

### Summary

When a wave function is incident on some sudden step in potential satisfying  $V_0 < E$ , some probability is transmitted through the step and the rest is reflected. These amounts are quantified by the reflection and transmission coefficients

$$R = \frac{j_{\text{ref}}}{j_{\text{inc}}}, \quad T = \frac{j_{\text{trans}}}{j_{\text{inc}}},$$

where each  $j$  is the relevant component of the probability current. When  $V_0 > E$ , the region within the potential step has no probability current because the wave function is real-valued there.

## 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  $\kappa^2$  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  $k$ .

### Summary

When a wave function is incident on a potential barrier (rather than a simple step) satisfying  $V_0 > E$ , then there is some transmitted probability. Using the same analysis as before, we can find that the transmission coefficient through the barrier goes to 1 in the thin limit and to 0 in the thick limit.

## Chapter 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  $\Pi$ , defined by

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

The eigenvalues  $\lambda = \pm 1$  of  $\Pi$  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 super position 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  $\Phi$  and  $\Psi$  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  $\psi_a$  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  $\psi_1$  and  $\psi_2$  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  $\Psi$ , 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

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

### Summary

The parity operator  $\Pi$  simply reflects its inputs over the vertical axis. Its eigenfunctions are the even and odd functions, which respectively correspond to eigenvalues of 1 and  $-1$ .

This, along with the operators we've discussed so far, is an example of a Hermitian operator  $A$ , which is one that satisfies

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

For our purposes, Hermitian operators are ones that have real eigenvalues, meaning  $\langle A \rangle = \langle A \rangle^*$ . The eigenfunctions of Hermitian operators are mutually orthogonal, and they form a basis for the set of all wave functions. The coefficients on a linear combination of eigenfunctions are given by

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

and each  $|c_n|^2$  represents the probability of finding the eigenvalue  $a_n$  upon a measurement of  $A$ . The relevant expectation values are

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

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

### Summary

The commutator  $[A, B] = AB - BA$  of two Hermitian operators is equal to zero if and only if they commute. In this case, the operators have the same eigenspaces; further, if their eigenvalues are nondegenerate, then they have the same eigenfunctions. Uncertainty arises when the commutator is nonzero—in particular, if  $[A, B] = iC$ , then we have the generalized uncertainty principle

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

We also have

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

where  $\Delta t$  is the amount of time it takes  $\langle E \rangle$  to change by an amount equal to its uncertainty.

### 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  $\Psi$  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.

## Chapter 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  $\Psi$  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  $\psi$  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  $\psi$  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

$$\psi_{n_x, n_y, n_z}(x, y, z) = \left(\frac{2}{L}\right)^{\frac{3}{2}} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

$$E = (n_x^2 + n_y^2 + n_z^2) \frac{\hbar^2 \pi^2}{2mL^2}$$

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

$$E_F = \frac{\hbar^2}{2m} (3\pi^2)^{\frac{2}{3}} \left(\frac{N}{L^3}\right)^{\frac{1}{3}}.$$

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  $\theta$  to be the polar angle (from the  $z$ -axis) and  $\phi$  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,

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

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

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

Let's take another step down the ladder.  $\hat{\mathbf{L}}^2$  commutes with  $\hat{L}_z$ , and  $\hat{L}_z$  depends only on  $\phi$ , 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  $\Phi$  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,  $\Phi$  must be periodic with period  $2\pi$ . 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  $\theta$ -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  $\Theta$  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  $\Theta$  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

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

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  $\psi$  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

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

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  $\lambda$  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

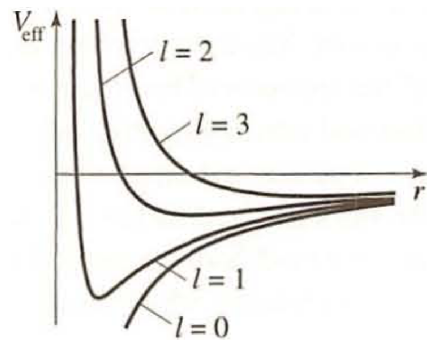
$$E_n = -\frac{Z^2 \hbar^2}{2ma_0^2} \frac{1}{n^2} = -\frac{Z^2 e^4 m}{2(4\pi\epsilon_0)^2 \hbar^2} \frac{1}{n^2}, \quad n = \lambda = l+1, l+2, \dots$$

$$R_{n,l}(r) = \frac{u(r)}{r} = N_{n,l} r^l F_{n-(l+1)}(r) e^{-Zr/\lambda a_0},$$

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,

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

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  $\theta$  or  $\phi$  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  $\nu$  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

$$\begin{aligned} \mathbf{j} &= \frac{\hbar}{2mi} (\psi^* \nabla \psi - \psi \nabla \psi^*) \\ &= \frac{\hbar m_l}{mr \sin \theta} |\psi_{n,l,m_l}(r, \theta, \phi)|^2 \hat{\phi} \end{aligned}$$

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  $(eB/2m)\hat{L}_z$  term to the Hamiltonian. So we have

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



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

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

where  $E_n$  are the energies without the magnetic field and  $\mu_B = e\hbar/2m$  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

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

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:

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

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  $\chi_+$  (“spin up”) and  $\chi_-$  (“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

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

just like with orbital angular momentum, so  $\hat{S}_z$  and  $\hat{\mathbf{S}}^2$  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

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

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  $E_{\text{fs}} = \boldsymbol{\mu}_S \cdot \mathbf{B}_{\text{int}} \propto \mathbf{S} \cdot \mathbf{L}$ . 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  $j$ .

## Chapter 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 only possibility for the ground state is

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

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 letters rather than numbers 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 the integral is valid in the large- $N$  limit. The total energy is given by

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

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.  $\alpha$  is just a normalization constant; by convention we set  $\alpha = -\mu/k_B T$ , where  $\mu$  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. Note 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

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

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

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

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

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

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  $T_{\text{BB}}$ . 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  $\theta$  corresponds to approaching

the hole head-on. So in spherical coordinates we have

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

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” at 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  $\Delta E$  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:

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

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  $\mu$  is positive. Thankfully we can work around this by estimating the value of  $\mu$  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 totally valid. In fact, 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

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

The rate of emission is thus given by

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



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  $\alpha$  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.