

# 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 electroamgnetic 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

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

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

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

substituting our de Broglie relations gives the dispersion relation

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

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

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

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

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

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

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

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

**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.

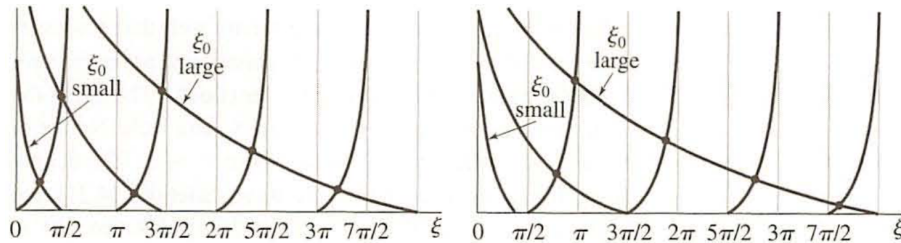
At this point we still haven't quantized anything. To change this, let's go back to dividing (1)/(2) and (3)/(4):

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

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 observables 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.