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 particles that compose light are called photons. Each photon has energy $E = h\nu$, where ν is the photon's frequency and h is Planck's constant. The inherently probabilistic nature of the photon is described by complex numbers called probability amplitudes.

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

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

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

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

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

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

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

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

This is called the Bragg relation.

1.2 The Schrödinger Equation

We've seen that light (i.e., an 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 $k = \frac{2\pi}{\lambda}$ and $\omega = \frac{2\pi}{T}$ are the light's spatial and temporal angular frequencies, respectively. We can't just pick any values of k and ω, however; specifically, the quantities must satisfy the equation

$$\omega = ck.$$

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

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

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

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

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

substituting our de Broglie relations gives the dispersion relation

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

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

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

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

For a free particle ($V = 0$),

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

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

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

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

1.3 Wave Functions

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

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

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

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

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

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

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. (This is not a consequence of the Schrödinger equation, but rather the physical interpretation of the wave function.)

Example: Wave function normalization

Suppose we want to normalize the wave function

$$\psi(x) = \begin{cases} Nx(L-x) & 0 < x < L \\ 0 & \text{elsewhere.} \end{cases}$$

We know that

$$\begin{aligned} \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1 \\ \int_0^L |N|^2 x^2 (L^2 - 2xL + x^2) dx = 1 \\ |N|^2 L^5 \cdot \frac{1}{30} \end{aligned}$$

Therefore, $N = \sqrt{\frac{30}{L^5}} e^{i\theta}$, where $\theta \in \mathbb{R}$ is an arbitrary phase.

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:

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

From the Schrödinger equation we get

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

Substituting gives

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

When we rewrite this as

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

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

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

that describes the flow of probability throughout space. So any change in probability density at a point in space is matched with an inward 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 $\Psi(x,t) \to 0$ as $x \to \pm\infty$.)

1.4 Physical Wave Solutions

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

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

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

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

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

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

Example: Wave packets

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

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

We simply integrate:

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

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

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

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

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

Here we can interpret Δx and Δp 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

$$v_{\mathrm{p}} = \frac{\omega}{k} \quad \text{and} \quad v_{\mathrm{g}} = \lim_{\Delta\to 0} \frac{\Delta\omega}{\Delta k} = \frac{d\omega}{dk},$$

respectively. (Recall how, when we superpose two waves, the resulting envelope has wavenumber Δk and frequence $\Delta\omega$; 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,

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

However, the group velocity gives

$$v_{\mathrm{g}} = \frac{d\omega}{dk} = \frac{\hbar k}{m} = \frac{p}{m} = v,$$

so this is the velocity we seek!

1.5 Quantum Averages and the Classical Limit

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

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

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:

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

Example: Expectation value and uncertainty

Suppose we want to determine $\langle x \rangle$, Δx for

$$\Psi(x) = \begin{cases} \sqrt{\frac{30}{L^5}}\, x(L-x) & 0 < x < L, \\ 0 & \text{elsewhere.} \end{cases}$$

By symmetry, we can see that $\langle x\rangle = L/2$. To calculate Δx, we also need to know $\langle x^2\rangle$. Integrating:

$$\begin{aligned}\langle x^2\rangle &= \int_{-\infty}^{\infty} x^2|\Psi|^2 dx\\ &= \int_0^L x^2\frac{30}{L^5}x^2(L-x)^2 dx\\ &= \frac{2}{7}L^2\end{aligned}$$

Finally, we can calculate the square of the uncertainty

$$(\Delta x)^2 = \langle x^2\rangle - \langle x\rangle^2 = \frac{1}{28}L^2.$$

This gives $\Delta x = \frac{1}{\sqrt{28}}L$.

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 determine $\frac{d\langle x\rangle}{dt}$.

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

By conservation of probability:

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

Proceeding with integration by parts:

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

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

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

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

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

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

Chapter 2

The Time-Indpendent Schrödinger Equation

2.1 Separation of Variables

With a solid foundation in wave mechanics, we can now move into actually producing solutions to the Shrödinger 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:

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

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 $\psi(t)$ to get the wave function

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

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

2.2 The Infinite Square Well

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

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

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 $k^2 = \frac{2mE}{\hbar^2}$, 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

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

Negative values of n don't lead to new (linearly indpendent) 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

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

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

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

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 periodcially wriggle up and down with a set amplitude.

- Each wave function Ψ_n is associated with a different amount of energy E_n; since these wave functions are "discrete", only supporting a half-integer number of wavelengths, their associated energy levels are also discrete!

- There is no $E = 0$ state. Even in the ground state $n = 1$, the wave function still needs to oscillate so that it's connected to each wall of the well. (We don't consider $n = 0$ because it isn't normalizable.)

2.3 Time Evolution and Measurement Properties

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

Example

Suppose we construct a wave function using the linear combination

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

The corresponding probability density function described turns out to be

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

So we can write expectation values for energy:

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

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:

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

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

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

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

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

So the important expectation values for E are

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

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

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

This reveals that the eigenfunctions of H are the ψ_n found via separation of variabes, and its eigenvalues are their corresponding energies E_n! This is why we'll often refer to ψ_n as energy eigenfunctions and E_n as energy eigenvalues.

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

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

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

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 contitions are going to change a bit. We'll still require that ψ be normalizable, so it must go to zero in its infinite limits. It should also be continuous, but now that we're dealing with a finite potential, we also want ψ to be smooth (so its first derivative is continuous).

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

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

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

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

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

$$\psi(x) = \begin{cases} Ce^{\kappa x} & x < -a/2 \\ Ae^{ikx} + Be^{-ikx} & |x| < a/2 \\ De^{-\kappa x} & x > a/2 \end{cases} \implies \frac{d\psi}{dx} = \begin{cases} \kappa Ce^{\kappa x} & x < -a/2 \\ ikAe^{ikx} - ikBe^{-ikx} & |x| < a/2 \\ -\kappa De^{-\kappa x} & x > a/2 \end{cases}$$

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

$$\begin{aligned} &(1) \quad Ce^{-\kappa a/2} = Ae^{-ika/2} + Be^{ika/2} && (3) \quad De^{-\kappa a/2} = Ae^{ika/2} + Be^{-ika/2} \\ &(2) \; \kappa Ce^{-\kappa a/2} = ikAe^{-ika/2} - ikBe^{ika/2} && (4) - \kappa De^{-\kappa a/2} = ikAe^{ika/2} - ikBe^{-ika/2} \end{aligned}$$

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

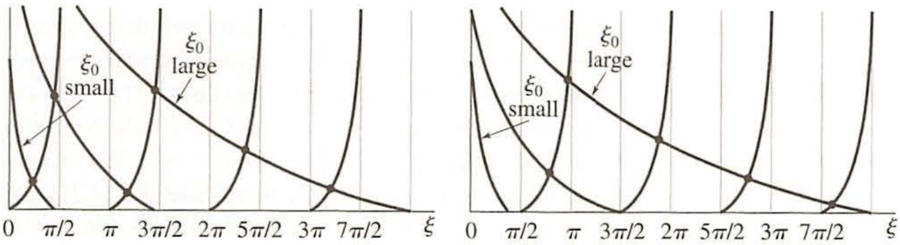
At this point we still haven't quantized anything. To change this, let's go back to dividing (1)/(2) and (3)/(4):

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

Here we've defined the dimensionless variables

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

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



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

3.2 General Potential Wells

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

Again, we're mostly interested in bound states. For such a state there is a finite region for which $E > V$, which we'll call the classically bound region, and another for which $E < V$, which is classically forbidden.

Taking inspiration from the finite square well, we can rewrite the time-independent Schrödinger equation in convenient ways—one for $E > V$ and another for $E < V$.

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

These differential equations have oscillatory and exponential solutions, respectively.

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

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

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

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

whose derivative is

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

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

3.3 The Quantum Harmonic Oscillator

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

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

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

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

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

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

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

By the Heisenberg uncertainty principle,

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

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

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

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

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

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

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

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

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

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

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

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

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

Example: Gaussian integral

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

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

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

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

Rewriting in polar form,

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

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

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

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

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

3.4 Delta Function Potentials

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

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

then the integral over a delta spike is one. Thus

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

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

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

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

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

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

Anyway, now we'll consider the point potential

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

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

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

the solution of which is

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

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

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

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

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

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

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

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

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

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

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

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.

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,

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

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 ψ and its derivative require that

$$A + B = C + D$$
$$ik(A - B) = ik_0(C - D)$$

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

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

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:

$$A + B = C$$
$$k(A - B) = k_0C$$

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

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

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

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

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

3.6 Quantum Tunneling

Now consider the finite barrier

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

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

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

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

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

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

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

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

From here we could show, with some nasty algebra, that the transmission coefficent 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, $\sinh^2 \kappa x \approx e^{2\kappa a}/2$, 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.