Chapter 12. Introduction to the Schrödinger Equation.

12.1 Einstein's Theory of Relativity. Occasionally mainstream news, whether TV or internet, like to report on scientific phenomena and recent findings. However, they invariably simplify things to the point that the information is wrong. The two greatest victims of these unfortunate oversimplifications are the theories of relativity and quantum mechanics. For example, $E = mc^2$ anyone? Not hardly, Einstein derived the following:

$$E^2 = c^2p^2 + m^2c^4$$

where E is energy, m is mass, c is the speed of light, and p is momentum. The above is clearly a mouthful; however, if the particle isn't moving (p=0), then $E^2 = m^2c^4$ which simplifies to:

$$E = mc^2$$

Thus, this ultra-famous equation is only correct for a particle at rest. And as you will see shortly, quantum mechanics stipulates that everything is always moving.

Einstein's equation provides a launching point for the development of quantum mechanics. In this regard, let's say that we are studying a particle with no mass such as a photon ($m = 0$ kg). In that case:

$$E^2 = c^2p^2 \rightarrow E = cp$$

The energy of a photon is known to be hυ, where h is Planck's constant and υ is frequency which is: $\upsilon = \frac{c}{\lambda}$ and λ is the wavelength. We can thus show that $E = h\frac{c}{\lambda} = cp$, which means that a massless particle such as a photon has a momentum: $p = \frac{h}{\lambda}$. Even though momentum is mass times velocity, and a photon has no mass, it still has a momentum. And now you should also know that many of the things you were told were absolutely true are, in fact, not true at all. Also, this is just our beginning of the discussion of Stranger Things.

12.1.1 Why waves? The theory of small things introduces concepts that seem preposterous to those indoctrinated into classical mechanics, defined as Isaac Newton's equation: force = mass × acceleration. It should be made clear on the outset that the theory of quantum mechanics as formulated by the Schrödinger equation is known to be incorrect. However, for chemistry the form of quantum mechanics introduced here is as accurate as can be measured, so its "good enough" for developing a thorough understanding of chemical phenomena.

The most important concept is that small things (mostly electrons) often act more like waves than particles. For example, if a truck hits a wall, it will break through it if it is travelling fast enough (or faster than that!). However, if the truck is actually an electron, it may break through the wall even if it is going very slowly. Alternatively, if it has the right speed to break through the wall, it might instead just bounce off it. Confused yet? Here is a better analogy- an electron trying to get through a barrier is like light skimming off the surface of water. And that is because of the wave equation.

12.2 The Schrödinger Equation. We started to understand waves once Maxwell's equations for electromagnetism were developed. They are:

$$\nabla \times \mathcal{E} = -\frac{\partial B}{\partial t}$$

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

$$\nabla \mathcal{E} = 0$$

$$\nabla B = 0$$

where $\mathcal{E}$ and B are electric and magnetic fields and t is time. You worked with these equations when you took Physics II to understand how an oscillating magnetic field creates electricity (alternatively, how an electric motor spins). You probably had to calculate the electric field from a dipole as well. The wave equation comes about when you combine these equations to show that:

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

A function for the electric field $\mathcal{E}$ that can solve the above is: $\mathcal{E}(x,t) = \cos\left(\frac{2\pi}{\lambda}x - \omega t\right)$, where ω is the angular frequency ($\omega = 2\pi\nu$). This describes a wave travelling to the right. If we input this function into: $\frac{\partial^2}{\partial x^2}\mathcal{E} = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathcal{E}$, and by calculating the double derivatives we can show that:

$$\frac{\partial^2}{\partial x^2}\cos\left(\frac{2\pi}{\lambda}x - \omega t\right) = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\cos\left(\frac{2\pi}{\lambda}x - \omega t\right)$$

And therefore:

$$\left(\frac{2\pi}{\lambda}\right)^2 \cos\left(\frac{2\pi}{\lambda}x - \omega t\right) = \frac{\omega^2}{c^2}\cos\left(\frac{2\pi}{\lambda}x - \omega t\right)$$

Since you can eliminate the function $\cos\left(\frac{2\pi}{\lambda}x - \omega t\right)$ from both sides the remainder is: $\left(\frac{2\pi}{\lambda}\right)^2 = \frac{\omega^2}{c^2}$, and thus $\lambda\omega = 2\pi c$. This is a well-known description of how wavelength and frequency of light are related.

Travelling vs. Standing waves

Equations such as:

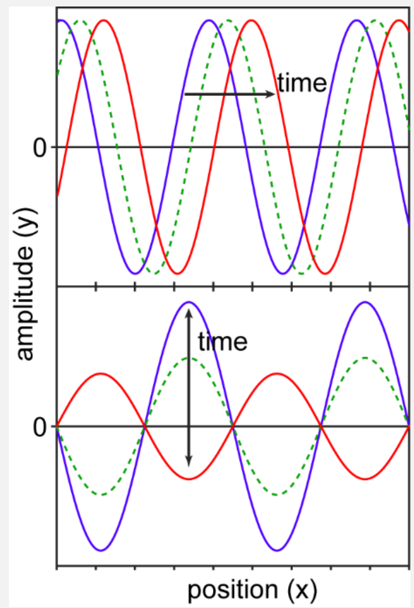
$$\cos\left(2\pi \cdot \frac{x}{\lambda} - \omega \cdot t\right)$$

represent travelling waves, which is obvious if you look at a figure of this function over time as shown below (top). The above example is for a wave moving to the right. However, you are also aware of standing waves, you probably created one when you shook a rope up and down at the right frequency. The reason a standing wave forms is that the waves you input reflect off the end and travel back to you. The addition of the left and right moving waves:

$$\cos\left(2\pi \cdot \frac{x}{\lambda} - \omega \cdot t\right) + \cos\left(2\pi \cdot \frac{x}{\lambda} + \omega \cdot t\right) =$$

$$2 \cdot \cos\left(2\pi \cdot \frac{x}{\lambda}\right) \cdot \sin(\omega \cdot t)$$

creates the standing wave as shown on the bottom of the figure . In quantum mechanics we have both types, where a travelling wave carries energy with it like an electron shot out of a hot wire filament. A standing wave represents a quantum entity that is sitting "still". An example is the hydrogen atom, which has an electron that cannot "escape" because it remains bound to the nucleus by the Coulombic interaction.



Here we will examine how to adjust the parameters of the wave equation to include mass, which will lead us to quantum mechanics for particles. If we look back at: $\mathcal{E}(x, t) = \cos\left(\frac{2\pi}{\lambda}x - \omega t\right)$, we can multiply and divide the argument of cosine by the Plank constant h:

$$\mathcal{E} = \cos\left[\frac{1}{h}\left(\frac{2\pi h}{\lambda}x - h2\pi\nu t\right)\right]$$

If we introduce a new constant $\hbar = \frac{h}{2\pi}$, we have:

$$\cos\left[\frac{1}{\hbar}\left(\frac{h}{\lambda} \cdot x - h\nu \cdot t\right)\right]$$

where we see the formula for momentum $p = \frac{h}{\lambda}$ from the discussion on relativity in the previous section and we of course know that hν is the energy (E) of a photon (or any wave). Thus:

$$\psi(x,t) = \cos\left[\frac{1}{\hbar}(p \cdot x - E \cdot t)\right]$$

where we have used a new symbol (ψ) to replace $\mathcal{E}(x,t)$ as we are moving further away from describing the electric field of photons. If we plug this $\psi(x,t)$ wavefunction back into our starting point:

$$\frac{\partial^2}{\partial x^2}\psi = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\psi$$

Since $\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\psi = \frac{E^2}{\hbar^2 c^2}\psi$:

$$c^2\hbar^2\frac{\partial^2}{\partial x^2}\psi \ = E^2\psi$$

and as $\frac{\partial^2}{\partial x^2}\psi = \frac{p^2}{\hbar^2}\psi$ we can see that the above translates into: $c^2p^2 = E^2$. This is just Einstein's equation for energy of a massless particle! However, the point of this derivation is to introduce mass into the wave equation. To do so we look back at the real equation for relativistic energy: $c^2p^2 + m^2c^4 = E^2$ and take the square root to approximate: $\frac{p^2}{2m} + mc^2 \approx E$. The next few steps are a bit too onerous to review here; regardless, the end result is the 1-dimensional non-relativistic Schrödinger equation:

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = E\psi$$

where the approximations made remove the effects of relativity; this is why the speed of light no longer appears in the equation. Since this equation is for a moving particle with no potential energy, the total energy is just kinetic, i.e. $E = \frac{p^2}{2m}$. The last thing to note is that, to extend the above to three dimensions you simply add in the double derivatives in y and z:

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

12.2.1 Where's the potential? In the previous derivation we never considered potential energy. Where does it go into the equation? We showed above that: $\frac{-\hbar^2}{2m}\nabla^2$ is related to: $\frac{p^2}{2m}$, which is the kinetic energy because: $\frac{p^2}{2m}$ and: $\frac{1}{2}mv^2$ are the same thing! With this knowledge it becomes more apparent that the Schrödinger equation resembles a well-known formula from freshman physics:

$$\text{Kinetic Energy} + \text{Potential Energy} = \text{Total Energy}$$

As a result, if we simply state that the potential energy is just a function: V(x,y,z), then the full Schrödinger equation is:

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

12.1.2 Consistency with the de Broglie relation. In 1923 Louis de Broglie proposed that, if wavy light can have particle-like properties (i.e. momentum), then perhaps particles can be wavy. To this end he derived the following, starting with Einstein's equation of energy for a particle at rest: mc^2 and equating that to the energy $h\upsilon$ of a wave:

$$mc^2 = h\upsilon$$

As the frequency of light υ is related to the wavelength by: $\lambda\upsilon = c$, the energy of the wave can be converted into: $h\upsilon = h\frac{c}{\lambda}$. This means we can solve the wavelength from: $mc^2 = h\frac{c}{\lambda}$:

$$\lambda = \frac{h}{mc}$$

Since a particle with mass can't travel the speed of light, de Broglie substituted in the velocity v for the speed of light: $\lambda = \frac{h}{mv}$. Since momentum is: $p = mv$, we are left with a relationship for the wavelength of a particle as determined by its momentum:

$$\lambda = \frac{h}{p}$$

When de Broglie determined that matter has an associated wavelength in 1924 at first no one paid much attention (and likely didn't understand the implications). However, Albert

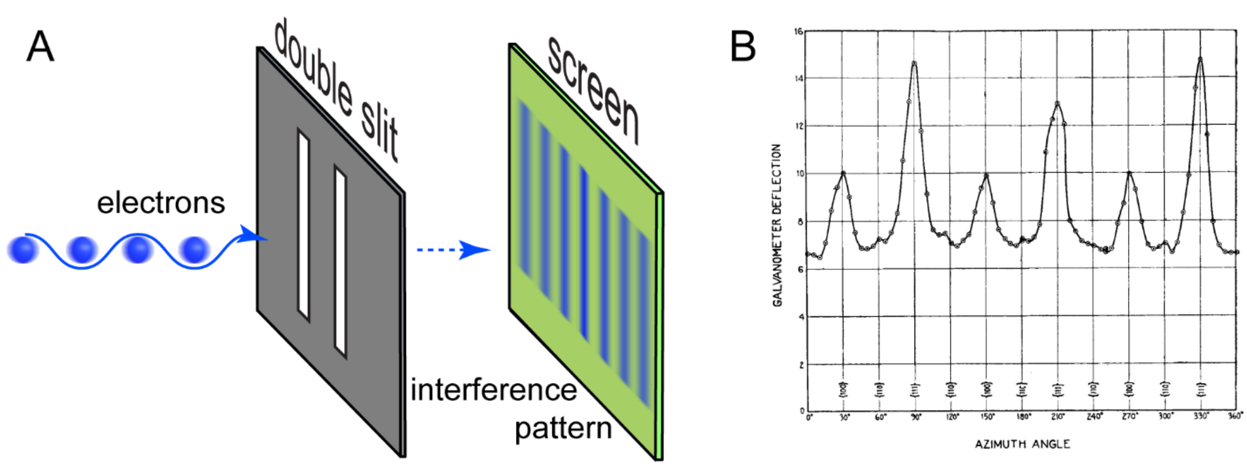


Figure 12.1. A. Davisson and Germer discovered that electrons can diffract through a material and create a diffraction pattern, proving that matter has wave like properties. **B.** Davisson and Germer's original data from 1927.

Einstein noted de Broglie's work, which generated interest and as such three years later Clinton Davisson and Lester Germer were able to prove the de Broglie hypothesis by diffracting electrons off a piece of metal. Shown in Figure 12.1 is an example of electron diffraction. Normally, one would expect electrons pointing at two slits in a material to go through like bullets; they ought to simply create a shadow of the two slits on the screen behind. However, since electrons have wavelength the two slits form an interference pattern just like light through a diffraction grating. Also shown in Figure 12.1 are Davisson and Germer's original data. Vindicated, de Broglie won the Nobel Prize in 1929.

What is most interesting about the Schrödinger equation is that it can return the de Broglie hypothesis if you "ask" it properly. Hopefully, you are wondering what does it mean for an equation to "ask"? In other words, how do you tease out: $\lambda = \frac{h}{p}$ (de Broglie) from: $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = \frac{p^2}{2m}\psi$ (Schrödinger)? Starting with the latter, we must insert something for ψ, which is our model for a particle. To this end we use the most simple wave equation possible, which is: $\psi = \cos\left(2\pi\frac{x}{\lambda}\right)$. This wave equation is subject to the Schrödinger equation's double derivative $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$ as follows:

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\cos\left(2\pi\frac{x}{\lambda}\right) = \frac{4\pi^2\hbar^2}{2m\cdot\lambda^2}\cos\left(2\pi\frac{x}{\lambda}\right)$$

Since $\hbar = \frac{h}{2\pi}$:

$$\frac{4\pi^2\hbar^2}{2m\cdot\lambda^2}\cos\left(2\pi\frac{x}{\lambda}\right) = \frac{h^2}{2m\lambda^2}\psi$$

Based on the Schrödinger equation: $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = \frac{p^2}{2m}\psi$, it must be true that: $\frac{h^2}{2m\lambda^2} = \frac{p^2}{2m}$. Simplifying further shows: $\lambda^2 = \frac{2m\cdot h^2}{2m\cdot p^2}$, which reveals de Broglie's wavelength $\lambda = \frac{h}{p}$.

The demonstration above reveals that the Schrödinger equation is consistent with the de Broglie relationship. It also shows that: $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$, which we will call an "operator" for now on, provides the kinetic energy as we presumed already. To make these types of derivations easier in the future we will simplify the wave equation as:

$$\psi = \cos\left(2\pi\frac{x}{\lambda}\right) \rightarrow \cos(kx)$$

where $k = \frac{2\pi}{\lambda}$, and is called the "wavevector". In three dimensions k is truly a vector and points in the direction that the wave is travelling in. We can determine some relationships between the wavevector k, momentum, and energy via application of the Schrödinger equation:

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\cos(kx) = \frac{\hbar^2 k^2}{2m}\cos(kx) = E \cdot \cos(kx)$$

From the above it must be true that: $\frac{\hbar^2 k^2}{2m} = E$, and as a result: $k = \frac{\sqrt{2mE}}{\hbar}$ and $\psi = \cos\left(\frac{\sqrt{2mE}}{\hbar}x\right)$. You may also notice from the above that: $p^2 = \hbar^2 k^2$, and since $k = \frac{2\pi}{\lambda}$ and $\hbar = \frac{h}{2\pi}$ we have: $p^2 = \left(\frac{h}{2\pi}\right)^2\left(\frac{2\pi}{\lambda}\right)^2$ which simplifies to the de Broglie relationship: $\lambda = \frac{h}{p}$. Everything is self-consistent!

12.3 Born interpretation. Back in the mid 1920's there was some confusion as to the purpose of the wave equation ψ. While it can deliver a numerical value for energy (quite useful), some questioned if they have any intrinsic meaning. For example, my Aunt Mary's dog only turns right when walking, hence an equation for the angle of his turns is $-|\theta|$. This implies that he tries to turn left (positive θ) an unseen force causes him to reverse (the negative of the absolute value). What do we call this doggie force? Is it fundamental, like gravity or electromagnetism, and can we measure this force acting on other dogs? *What about cats?*

In reality, the dog had surgery on his left paw and that is why he only turns right, a fact that isn't captured by $-|\theta|$. Hence, we shouldn't over interpret an equation that describes him. Are we doing the same thing with wave equations?

Max Born was the first to state that wave equations have substantial meaning, which is to say that they represent probability distributions. Specifically, if you square the wavefunction to make sure it is always positive as shown in Figure 12.2, it represents the probability that you

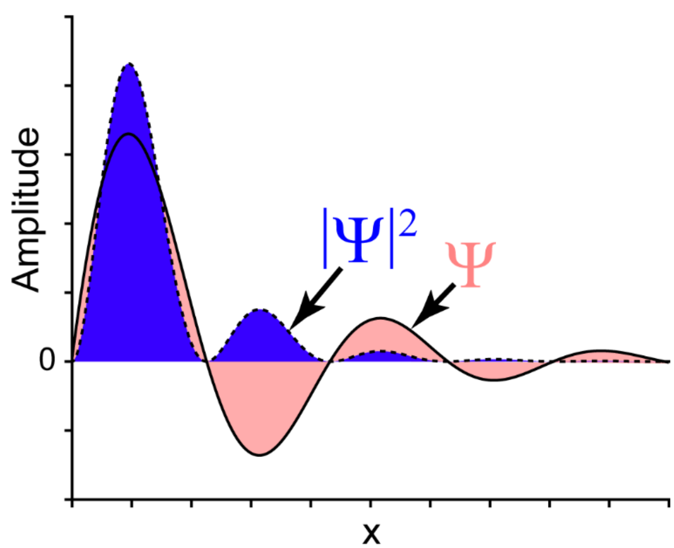


Figure 12.2. The Born interpretation is that the absolute value of a wavefunction |Ψ|² is a probability density.

can find the particle at some point in space (probability distributions were discussed at length in Chapter 10). The fact that the wavefunction squared is a probability distribution requires that it be "normalized", which means:

$$\int_{\text{lower limit}}^{\text{upper limit}} |\psi|^2\, \partial\tau = \int_{\text{lower limit}}^{\text{upper limit}} \psi^*\psi\, \partial\tau = 1.0$$

where ψ^* is the complex conjugate of the wavefunction, which needs to be used because most wavefunctions are complex (i.e. they have $i = \sqrt{-1}$ in them). There is a substantial amount to unpack from this normalization equation. First, we didn't specify the limits because they depend on what is being represented and how "big" the wave equation is allowed to be. For example, if we are using quantum mechanics to describe a particle trapped in a box of length L, then the lower limit would likely be x=0 and the upper x=L. Also note the partial $\partial\tau$ in the integral. This is a symbol that is generic for the dimensionality of the wave equation. Thus far, we have been dealing with a wave in the x direction, so $\partial\tau = \partial x$. If we were trying to solve a quantum mechanical problem for a particle in three dimensions, then $\partial\tau = \partial x\, \partial y\, \partial z$, and of course that means that normalization integral is actually a triple integral. If we were working in radial coordinates then $\partial\tau = r^2 \sin(\theta)\, \partial r\, \partial\phi\, \partial\theta$, where $r^2 \sin(\theta)$ is the Jacobian that property accounts for the volume. If there is no angular dependence to a problem that involves radius, then $\partial\tau = 4\pi r^2\, \partial r$. Last, you should know that we are going to have to use complex mathematics to work quantum mechanical problems. If you are not familiar, there is a short description of most of what you need to know on the next page; more can be found on the "internet". While this may seem like more to learn (and it is), the value is that complex mathematics makes solving quantum mechanical problems much easier.

12.3.1 Normalization. Let's take a look back at what it means for a wave equation to be normalized. Generally, when we determine that a wavefunction is something like: $\psi = \cos(kx)$, for example, it is unlikely to be normalized. As a result, we have to make it normalized. To do so you multiply ψ by a normalization constant (N) as:

$$\psi_{\text{norm}} = N\psi = \frac{1}{\sqrt{\int |\psi|^2\, \partial\tau}}\psi$$

As a result:

$$\int \psi_{\text{norm}}^2 \,\partial\tau = \frac{\int \psi^* \psi \,\partial\tau}{\sqrt{\int |\psi|^2 \,\partial\tau}\sqrt{\int |\psi|^2 \,\partial\tau}} = \frac{\int \psi^* \psi \,\partial\tau}{\int \psi^* \psi \,\partial\tau} = 1$$

and clearly $N = \frac{1}{\sqrt{\int \psi^2 \,\partial\tau}}$. It is often the case that we first figure out what kind of function (sine, cosine etc.) is the solution to the wave equation, and then normalize it after the fact. Sometimes we don't need to normalize the wave equation to answer problems, but it is a good practice. In fact, we will generally assume that wave equations have been properly normalized in our further discussions. It is interesting to note that the requirement for normalization means that not any function can be a wavefunction; in fact there are a few restrictions on solutions as discussed below.

12.3.2 Wave equation restrictions. Since the absolute value, i.e. the square of the wave equation, must be related to probability there are some restrictions on what wave equations can and cannot do as shown in Figure 12.3. First, they cannot be 0 everywhere. This is sort of silly, since $\psi = 0$ doesn't leave much room for solving any problems. Second, they must be continuous. Otherwise, there are basically two probabilities for a particle to be found at a certain point in space- what kind of nonsense is that? Third, the wavefunctions must be smooth, which means that the derivative cannot approach ∞ at any point. As you will see later, if the derivative did so then the particle would have more kinetic energy that the Universe holds. Last, wavefunctions cannot be divergent, which means that they can be integrated to a finite value. If not, then the wavefunction could not be normalized, which would not be consistent with the rules of probability distributions.

One of the tricks of quantum mechanics is to use these restrictions to solve problems. Generally, the most relevant are the smooth and continuous stipulation at some sort of boundary. Often that boundary takes the form of a sudden change in the potential energy at a point in space. Another observation is that these boundary conditions mean that a solution for the wave equation can't be found for any energy, rather, often discrete energy values. This is the source of the "quantum" in quantum

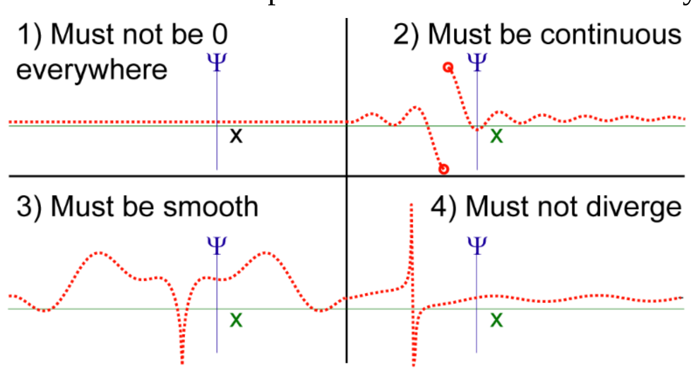


Figure 12.3. Quantum mechanical wavefunctions must follow the rules shown here to properly behave according to the rules of probability.

mechanics, and the solutions are likely to look like standing waves discussed earlier.

12.4 The Eigenvalue Equation and operators. Previously we referred to the kinetic energy part: $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$ of the Schrödinger equation as an "operator". This is a good name because the double derivative causes you to "do" something to the wave equation, i.e. you operate on it. There are many different types of operators because there has to be one for anything that is "real" and can be measured. You will learn many of them, and we will give them a generic symbol: $\widehat{\Omega}$, where the "hat" signifies a quantum mechanical operator. We will use the Φ symbol for the wave equation that $\widehat{\Omega}$ operates on (and unfortunately Φ are also called eigenfunctions, because people like to give names to things that already have names). You may also have noticed that when we applied the kinetic energy operator: $\widehat{\Omega} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$ to the wave equation: $\Phi = \cos\left(\frac{2\pi}{\lambda}x\right)$ that we were able to calculate the energy via what is called the "eigenvalue equation":

$$\widehat{\Omega}\Phi = \omega\Phi$$

where "ω" is the result of the eigenvalue equation and is creatively called the eigenvalue. For instance, application of the kinetic energy operator returned an eigenvalue ω, which happened to be the kinetic energy. Quite useful if you want to know the kinetic energy.

Eigen is German for "same", which refers to the fact that the wave equation Φ appears to the left and right side of the eigenvalue equation. This reveals an absolutely crucial aspect of quantum mechanics, which is that ***if the wave equation doesn't appear exactly as is on both the left and right, then the eigenvalue is meaningless***. For example, if we have an operator $\widehat{\Omega}$ that acts on $\Phi = N \cdot \cos\left(\frac{2\pi}{\lambda}x\right)$ as follows:

$$\widehat{\Omega}\Phi = \widehat{\Omega}\cos\left(\frac{2\pi}{\lambda}x\right) = \frac{2\pi}{\lambda}\cdot\sin\left(\frac{2\pi}{\lambda}x\right) \neq \omega\Phi \quad \text{or} \quad \widehat{\Omega}\Phi = \widehat{\Omega}\cos\left(\frac{2\pi}{\lambda}x\right) = x\cdot\cos\left(\frac{2\pi}{\lambda}x\right) \neq \omega\Phi$$

then these examples are quantum mechanical "fails", and nothing can be learned from the results. If the wave equation appears exactly the same on left and right side, then we say that the wave equation Φ is an eigenfunction of the operator $\widehat{\Omega}$. To verify our understanding, we will measure the kinetic energy once again:

$$\widehat{\Omega}\Phi = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\cos\left(\frac{2\pi}{\lambda}x\right)\omega\Phi = \frac{2\pi^2\hbar^2}{m\lambda^2}\cos\left(\frac{2\pi}{\lambda}x\right) = \omega\Phi$$

Complex mathematics

Despite the name, complex mathematics is not that hard. It's all about the letter "i", which is equal to $\sqrt{-1}$. As a result, $i^2 = -1$. Likewise: $i^3 = -i$ and $i^4 = 1$. Here are some additional indentities:

If: $e^x = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \frac{x^4}{24} + \frac{x^5}{120}$ ...

therefore: $e^{ix} = 1 + ix + \frac{i^2x^2}{2} + \frac{i^3x^3}{6} + \frac{i^4x^4}{24} + \frac{i^5x^5}{120} + \cdots$

If you separate real from imaginary: $e^{ix} = \left(1 - \frac{x^2}{2} + \frac{x^4}{24}\right) + i\left(x - \frac{x^3}{6} + \frac{i^5x^5}{120}\right) + \cdots$, and from what you might recall of $\cos(x) = 1 - \frac{x^2}{2} + \frac{x^4}{24}$ ... and $\sin(x) = x - \frac{x^3}{6} + \frac{i^5x^5}{120}$ ... you can show:

$$e^{ix} = \cos(x) + i \cdot \sin(x)$$

Likewise, $e^{-ix} = \cos(x) - i \cdot \sin(x)$. These relationships can be combined into:

$$\sin(x) = \frac{e^{ix} - e^{-ix}}{2i} \text{ and } \cos(x) = \frac{e^{ix} + e^{-ix}}{2}$$

Another valuable relationship is the complex conjugate, which is $\psi^*(i) = \psi(i)$. Therefore $\psi^2 = \psi^*\psi$. Here is an example, if $\psi = e^{ikx} = \cos(kx) + i \cdot \sin(kx)$ and $\psi^* = \cos(kx) - i \cdot \sin(kx)$, then it is easy to show that:

$$\psi^*\psi = \cos(kx) + i \cdot \sin(kx)\big(\cos(kx) - i \cdot \sin(kx)\big) =$$
$$\cos^2(kx) - i \cdot \cos(kx)\sin(kx) + i \cdot \cos(kx)\sin(kx) + \sin^2(kx) = 1$$

A graph of $\psi = e^{ikx}$ is shown here. Note how the real and imaginary parts of the function have to be graphed separately.

This is a good example, and we know that the kinetic energy of the particle that is described by the wave equation $\Phi = \cos\left(\frac{2\pi}{\lambda}x\right)$ is: $\frac{2\pi^2\hbar^2}{m\lambda^2}$. The wave equation(s) that work with an operator are often referred to as "belonging" to that operator; the proper way of saying this is to state, "the set of one or more functions Φ are eigenfunctions of the operator $\widehat{\Omega}$".

As we move forward you will learn many more operators. Some of them are very special, such as the Hamiltonian operator that returns the total energy. The Hamiltonian is given the symbol $\widehat{H}$; likewise, the wave equations of the Hamiltonian are called "wavefunctions" and are given the symbol ψ. Thus, the eigenvalue equation for the Hamiltonian is properly expressed as:

$\hat{H}\psi = E\psi$, where we also changed the symbol for the eigenvalue (ω) to "E" for energy. Recall that you have already seen the Hamiltonian operator

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + \hat{V}$$

where $\hat{V}$ is the potential energy operator, which is usually a function of position. We believe the wavefunctions ψ of the Hamiltonian operator are the most meaningful results of quantum mechanics because we believe that they are "real". In fact, all the learnings you have had previously about atomic structure, such as s- and p-orbitals of hydrogen and heavier elements, are in fact wavefunctions of the atom's Hamiltonian.

Let's see a few more operators. Given that particles have momentum, and that is something we can definitely measure, there must be an associated quantum mechanical operator for it. In fact, the momentum operator ($\hat{p}$) is:

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

This is fully consistent with our kinetic energy operator $\frac{\hat{p}^2}{2m}$ as follows:

$$\frac{\hat{p}\hat{p}}{2m} = \frac{\hat{p}^2}{2m} = \frac{1}{2m}\frac{\hbar}{i}\frac{\partial}{\partial x}\frac{\hbar}{i}\frac{\partial}{\partial x} = \frac{1}{2m}\frac{\hbar^2}{i^2}\frac{\partial^2}{\partial x^2} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

Another operator is the position operator $\hat{x}$, which is quite simple: $\hat{x} = x$. More complex operators include the z-component of angular momentum $\widehat{J_z} = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$, which we will cover in a later chapter. The important thing to know is that there are many operators for calculating many different properties from quantum mechanical objects such as electrons and molecules.

12.4.1 Eigenfunctions of different operators. There is one last, very important lesson about operators and eigenfunctions which is one of the most complicated things about quantum mechanics. And that is the fact that the eigenfunctions of one operator may, or may not, be the eigenfunctions of another operator. This is shown by the Venn diagram in Figure 12.4, and as an example let's go

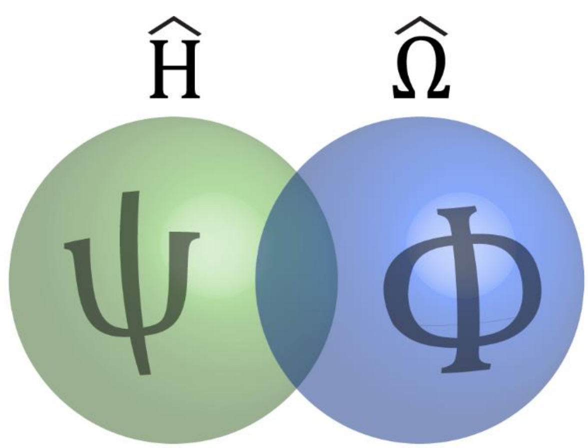


Figure 12.4. Eigenfunctions of one operator may, nor may not be eigenfunctions of another operator.

back to the example of a Hamiltonian operator with no potential energy, i.e. $\widehat{\mathrm{H}} = \frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}$. A wavefunction of this Hamiltonian is $\psi = \cos\left(\frac{2\pi}{\lambda}\mathrm{x}\right)$, and has an energy as we showed on the previous page. Now, if we apply the momentum operator to the same state:

$$\hat{\mathrm{p}}\psi = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \mathrm{x}}\cos\left(\frac{2\pi}{\lambda}\mathrm{x}\right) = \frac{2\pi}{\lambda}\cdot\sin\left(\frac{2\pi}{\lambda}\mathrm{x}\right) \neq \omega\psi$$

Then you should know that the momentum of the state ***most definitely is not*** $\frac{2\pi}{\lambda}$. The next section will discuss in great detail how we deal with this uncomfortable situation.

12.4.2 Practice with the Eigenvalue Equation and Complex Wave Equations. We have already shown that wave equations, when squared, provides a measure of probability that a quantum mechanical particle is at a particular position. We have also shown how a wave equation can provide additional information, that being what is returned when it is operated on by, oddly, operators. We will make this more concrete with examples here. Let's say that the normalized wavefunction for an electron is: $\psi = \mathrm{N}\cdot\cos(\mathrm{kx})$ where N is the normalization constant and k is the wavevector $\frac{2\pi}{\lambda}$. We know how to square this function, which then tells us the probability that the electron is at a position x that we are curious about (for whatever reason). What about the energy of this electron? Just like in the previous examples we apply the potential energy free (i.e. $\widehat{\mathrm{V}} = 0$) Hamiltonian:

$$\widehat{\mathrm{H}}\psi = -\frac{\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}\{\mathrm{N}\cdot\cos(\mathrm{kx})\} = -\frac{\hbar^2}{2\mathrm{m}}\frac{\partial}{\partial \mathrm{x}}\{\mathrm{N}\cdot\mathrm{k}\cdot\sin(\mathrm{kx})\} = \frac{\hbar^2\mathrm{k}^2}{2\mathrm{m}}\{\mathrm{N}\cdot\cos(\mathrm{kx})\}$$

Comparison to the eigenvalue equation $\widehat{\mathrm{H}}\psi = \mathrm{E}\psi$ reveals that the above is in the proper form, so we can be sure that the energy is: $\frac{\hbar^2\mathrm{k}^2}{2\mathrm{m}}$.

Now let's repeat the above using the complex mathematical version of the wavefunction shown previously, $\mathrm{N}\cdot\cos(\mathrm{kx}) = \mathrm{N}\cdot\left(\frac{1}{2}\mathrm{e}^{\mathrm{ikx}} + \frac{1}{2}\mathrm{e}^{-\mathrm{ikx}}\right)$:

$$\widehat{\mathrm{H}}\psi = -\frac{\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}\left\{\mathrm{N}\cdot\left(\frac{1}{2}\mathrm{e}^{\mathrm{ikx}} + \frac{1}{2}\mathrm{e}^{-\mathrm{ikx}}\right)\right\} = -\frac{\hbar^2}{2\mathrm{m}}\frac{\partial}{\partial \mathrm{x}}\left\{\mathrm{N}\cdot\left(\frac{\mathrm{ik}}{2}\mathrm{e}^{\mathrm{ikx}} + \frac{-\mathrm{ik}}{2}\mathrm{e}^{-\mathrm{ikx}}\right)\right\}$$

$$= -\frac{\hbar^2}{2\mathrm{m}}\left\{\mathrm{N}\cdot\left(\frac{-\mathrm{k}^2}{2}\mathrm{e}^{\mathrm{ikx}} + \frac{-\mathrm{k}^2}{2}\mathrm{e}^{-\mathrm{ikx}}\right)\right\}$$

The next step is to factor out $-\mathrm{k}^2$ which gives us:

$$\widehat{\mathrm{H}}\psi = \frac{\hbar^2\mathrm{k}^2}{2\mathrm{m}}\left\{\mathrm{N}\cdot\left(\frac{1}{2}\mathrm{e}^{\mathrm{ikx}} + \frac{1}{2}\mathrm{e}^{-\mathrm{ikx}}\right)\right\} = \mathrm{E}\psi$$

where again we see that $E = \frac{\hbar^2 k^2}{2m}$. So, everything seems fine, but why are we using this approach? While solving $\widehat{H}\psi$ using the complex representation of $\psi = N \cdot \cos(kx)$ seems more difficult, there are going to be many examples coming up where the complex representation is far easier to work with. For example, the electron's wavefunction could have been $\psi = N \cdot e^{ikx}$. In this case, which do you think is harder to solve:

$$\widehat{H}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\{N \cdot e^{ikx}\}$$

or:

$$\widehat{H}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\{N \cdot \cos(kx) + i \cdot \sin(kx)\}$$

Just for the heck of it let's solve the former:

$$\widehat{H}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\{N \cdot e^{ikx}\} = -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\{ik \cdot N \cdot e^{ikx}\} = -\frac{\hbar^2}{2m}\{i^2 k^2 \cdot N \cdot e^{ikx}\} = \frac{\hbar^2 k^2}{2m}\{N \cdot e^{ikx}\}$$

Taking the derivative of an exponential is easy, and just like the previous example, we see that $E = \frac{\hbar^2 k^2}{2m}$. This wasn't nearly as hard as taking the double derivative of two trig functions!

12.4.2.1 Applications of other operators: Let's continue to work with $\psi = N \cdot e^{ikx}$, from which we will extract the momentum via $\hat{p}$:

$$\hat{p}\psi = \frac{\hbar}{i}\frac{\partial}{\partial x}\{N \cdot e^{ikx}\} = \frac{\hbar}{i}\{ik \cdot N \cdot e^{ikx}\} = \hbar k\{N \cdot e^{ikx}\}$$

We can see that this wavefunction represents an electron with $\frac{\hbar^2 k^2}{2m}$ of energy and $\hbar k$ of momentum. Notice the consistency, as in the absence of potential the total energy is $E = \frac{p^2}{2m}$, and inserting p= $\hbar k$ yields $E = \frac{\hbar^2 k^2}{2m}$. If the wavefunction of the electron was $\psi = N \cdot e^{-ikx}$, we would have still found $\frac{\hbar^2 k^2}{2m}$ of energy but $-\hbar k$ of momentum (note that this is still consistent with $E = \frac{p^2}{2m}$). Why would one wavefunction have a positive momentum and the other negative? Why, the interpretation is simple, $\psi = N \cdot e^{ikx}$ represents a particle moving forward and $\psi = N \cdot e^{-ikx}$ is moving backwards!

Now let's double check our math abilities one last time with $\psi = N \cdot \cos(kx)$, from which we will calculate the momentum.

$$\hat{p}\psi = \frac{\hbar}{i}\frac{\partial}{\partial x}\{N \cdot \cos(kx)\} = \frac{-\hbar k}{i}\{N \cdot \sin(kx)\} = -i\hbar k\{N \cdot \sin(kx)\}$$

where we used the identity $\frac{-1}{i} = i$ in the last step. Therefore, this electron is moving to the left with an imaginary amount of momentum. What does it mean for this electron to have imaginary momentum? Why, it means absolutely nothing- there is no such thing as imaginary momentum, which should be a clue that you screwed up the question. What did you do wrong? You didn't get the correct eigenvalue equation form:

$$\widehat{\Omega}\Phi = \omega \cdot \Phi$$

as you don't have the wavefunction on the left- and right-hand side equal to each other:

$$\hat{p}\{N \cdot \cos(kx)\} \neq \hat{p}\{N \cdot \sin(kx)\}$$

After all, cosine and sine are not the same thing.

As discussed in the previous section, the eigenfunctions of one operator may, or may not, be the eigenfunctions of another operator. Here, the wavefunctions $\psi = N \cdot e^{ikx}, N \cdot e^{-ikx}$, and $N \cdot \cos{(kx)}$ are all "good" with the Hamiltonian because they all deliver on $\widehat{H}\psi = E\psi$. However, only $\psi = N \cdot e^{ikx}$ and $N \cdot e^{-ikx}$ are eigenfunctions of the momentum operator, but $\psi = N \cdot \cos{(kx)}$ is not.

12.4.2 Expectation Values. How do we figure out the momentum of a particle with a wavefunction of the form $\psi = N \cdot \cos{(kx)}$? Give up? Sometimes! After all quantum mechanics is all about probability, and you cannot know everything. In this case, instead of giving up you can often solve these types of problems using the following approach. If we write out:

$$\psi = N \cdot \cos(kx) = \frac{N}{2} e^{ikx} + \frac{N}{2} e^{-ikx}$$

you notice that particle's wavefunction is composed of two equal momentum eigenfunctions, one that is moving to the right (e^{ikx}) and the other to the left (e^{-ikx}). Now you can guess that the total momentum is 0. Good intuition, but quantum class is sort of a math class, so how do we prove it? Here we introduce a new expression that is called the "expectation value" for an operator $\widehat{\Omega}$:

$$\langle \widehat{\Omega} \rangle = \int_{\text{lower limit}}^{\text{upper limit}} \psi^* \widehat{\Omega}\, \psi \cdot \partial\tau$$

where ψ may, or may not, be the eigenfunction of the operator $\widehat{\Omega}$. What is great about expectation values is that it doesn't matter- in either case you will get the right answer. Let's apply this to our current problem with determining the momentum of $\psi = N \cdot \cos(kx)$:

$$\langle\hat{\mathrm{p}}\rangle = \int_{\text{lower limit}}^{\text{upper limit}} \{\mathrm{N}\cdot\cos(\mathrm{kx})\}^{*}\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\mathrm{x}}\{\mathrm{N}\cdot\cos(\mathrm{kx})\}\cdot\partial\mathrm{x}$$

$$\frac{-\hbar}{\mathrm{i}}\mathrm{N}^{2}\int_{-\infty}^{\infty}\cos(\mathrm{kx})\cdot\sin(\mathrm{kx})\cdot\partial\mathrm{x}$$

When we look up this integral off the internet, we find $\int_{-\infty}^{\infty}\cos(\mathrm{kx})\cdot\sin(\mathrm{kx})\cdot\partial\mathrm{x} = 0$. So, as we can see we got the right answer: $\langle\hat{\mathrm{p}}\rangle = 0$. While this problem is a bit difficult, notice how we were able to determine the momentum with this approach, while we couldn't do anything, at all, with the standard eigenvalue equation. So, we have that going for us, which is nice.

The expectation value approach also works with functions that are eigenfunctions. Let's do an example using the normalized "right wave" $\Phi = \mathrm{N}\cdot\mathrm{e}^{\mathrm{ikx}}$ eigenfunction of momentum, that being the:

$$\langle\hat{\mathrm{p}}\rangle = \int_{\text{lower limit}}^{\text{upper limit}} \left\{\mathrm{N}\cdot\mathrm{e}^{\mathrm{ikx}}\right\}^{*}\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\mathrm{x}}\left\{\mathrm{N}\cdot\mathrm{e}^{\mathrm{ikx}}\right\}\cdot\partial\mathrm{x} =$$

$$\langle\hat{\mathrm{p}}\rangle = \frac{\hbar}{\mathrm{i}}\int_{-\infty}^{\infty}\mathrm{N}^{*}\cdot\mathrm{e}^{-\mathrm{ikx}}\cdot\mathrm{ik}\cdot\mathrm{N}\cdot\mathrm{e}^{\mathrm{ikx}}\cdot\partial\mathrm{x} =$$

$$\langle\hat{\mathrm{p}}\rangle = \frac{\hbar\mathrm{ik}}{\mathrm{i}}\int_{-\infty}^{\infty}\mathrm{N}^{*}\cdot\mathrm{e}^{-\mathrm{ikx}}\cdot\mathrm{N}\cdot\mathrm{e}^{\mathrm{ikx}}\cdot\partial\mathrm{x} = \hbar\mathrm{k}\int_{-\infty}^{\infty}\Phi^{*}\Phi\cdot\partial\mathrm{x} = \hbar\mathrm{k}$$

where the complex conjugate $\left\{\mathrm{N}\cdot\mathrm{e}^{\mathrm{ikx}}\right\}^{*}$ is: $\mathrm{N}^{*}\cdot\mathrm{e}^{-\mathrm{ikx}}$, and we used the formula $\int\Phi^{*}\Phi\,\partial\mathrm{x} = \int|\Phi|^{2}\,\partial\mathrm{x} = 1$ in the last step which is the definition of normalization. While we determined the corrent momentum, you might ask, why not stick with $\widehat{\Omega}\Phi = \omega\cdot\Phi$ given that $\langle\hat{\mathrm{p}}\rangle$ was seemingly much more complicated to work with? You are correct, it is generally mathematically far more simple to work with the eigenvalue equation over the expectation value expression. However, the expectation value method always works, and also gives us a "clean" answer because we don't have to try to untangle the eigenvalue from the eigenfunction.

Now you might ask, why does the expectation value method work? For one, if we are working on eigenfunctions of the operator $\widehat{\Omega}$, the answer is seen in a simple derivation:

$$\langle\widehat{\Omega}\rangle = \int_{-\infty}^{\infty}\Phi^{*}\widehat{\Omega}\Phi\cdot\partial\tau = \int_{-\infty}^{\infty}\Phi^{*}\cdot\omega\cdot\Phi\cdot\partial\tau = \omega\cdot\int_{-\infty}^{\infty}\Phi^{*}\cdot\Phi\cdot\partial\tau = \omega$$

where we assume that Φ is normalized. However, this proof breaks down when we are not applying an eigenfunction of the operator, i.e. when $\hat{\Omega}\psi \neq \omega \cdot \psi$. What do we do in this case? Here is another important lesson, which is that wavefunctions can always be written as linear combinations of other wavefunctions. For example, let's say that the operator $\hat{\Omega}$ has two eigenfunctions Φ_1 and Φ_2, but ψ is not an eigenfunction of $\hat{\Omega}$. Upon further analysis you realize that ψ is a linear combination of the Φ's:

$$\psi = c_1 \cdot \Phi_1 + c_2 \cdot \Phi_2$$

where c_1 and c_2 are constants. When you apply the above to the expectation value expression:

$$\langle\hat{\Omega}\rangle = \int_{-\infty}^{\infty} \psi^* \hat{\Omega}\psi \cdot \partial\tau = \int_{-\infty}^{\infty} \{c_1 \cdot \Phi_1 + c_2 \cdot \Phi_2\}^* \hat{\Omega}\{c_1 \cdot \Phi_1 + c_2 \cdot \Phi_2\} \cdot \partial\tau$$

This problem has now turned into an algebraic mess which is a common occurrence. Fortunately, algebra is a middle school level of mathematics and as such we can deal with it:

$$\langle\hat{\Omega}\rangle = \int_{-\infty}^{\infty} \{c_1 \cdot \Phi_1 + c_2 \cdot \Phi_2\}^* \hat{\Omega}\{c_1 \cdot \Phi_1 + c_2 \cdot \Phi_2\} \cdot \partial\tau$$

$$= \int_{-\infty}^{\infty} \left\{c_1^*\Phi_1^*\hat{\Omega}c_1\Phi_1 + c_2^*\Phi_2^*\hat{\Omega}c_2\Phi_2 + c_1^*\Phi_1^*\hat{\Omega}c_2\Phi_2 + c_2^*\Phi_2^*\hat{\Omega}c_1\Phi_1\right\} \cdot \partial\tau$$

This can be broken up into four smaller integrals which is less scary.

$$\langle\hat{\Omega}\rangle = \int_{-\infty}^{\infty} c_1^*\Phi_1^*\hat{\Omega}c_1\Phi_1 \cdot \partial\tau + \int_{-\infty}^{\infty} c_2^*\Phi_2^*\hat{\Omega}c_2\Phi_2 \cdot \partial\tau + \int_{-\infty}^{\infty} c_1^*\Phi_1^*\hat{\Omega}c_2\Phi_2 \cdot \partial\tau + \int_{-\infty}^{\infty} c_2^*\Phi_2^*\hat{\Omega}c_1\Phi_1 \cdot \partial\tau$$

We can simplify this further using the relationships:

$$\hat{\Omega}c_1\Phi_1 = \omega_1 \cdot c_1\Phi_1, \qquad \hat{\Omega}c_2\Phi_2 = \omega_2 \cdot c_2\Phi_2, \qquad c_1^*c_1 = |c_1|^2, \qquad \text{and } \ c_2^*c_2 = |c_2|^2$$

to yield:

$$\langle\hat{\Omega}\rangle = |c_1|^2 \cdot \omega_1 \cdot \int_{-\infty}^{\infty} |\Phi_1|^2 \cdot \partial\tau + |c_2|^2 \cdot \omega_2 \cdot \int_{-\infty}^{\infty} |\Phi_2|^2 \cdot \partial\tau + c_1^*c_2 \cdot \omega_2 \int_{-\infty}^{\infty} \Phi_1^*\Phi_2 \cdot \partial\tau + c_2^*c_1 \cdot \omega_1 \int_{-\infty}^{\infty} \Phi_2^*\Phi_1 \cdot \partial\tau$$

Now the above monster can be solved using something that we know already, which is that eigenfunctions are normalized:

$$\int_{-\infty}^{\infty} |\Phi_1|^2 \cdot \partial\tau = \int_{-\infty}^{\infty} |\Phi_2|^2 \cdot \partial\tau = 1$$

Now we also must introduce a new concept called "orthonormality" for the 3rd and 4th expression above:

$$\int_{-\infty}^{\infty} \Phi_1^* \Phi_2 \cdot \partial\tau = \int_{-\infty}^{\infty} \Phi_2^* \Phi_1 \cdot \partial\tau = 0$$

What this means is that, for two eigenfunctions of the same operator, when you integrate them together you get 0. The proper language is that "they do not overlap", and we will explain this further in the next section on Hermitian operators. Regardless, the remainder of the proof is:

$$\langle\widehat{\Omega}\rangle = |c_1|^2 \cdot \omega_1 + |c_2|^2 \cdot \omega_2$$

Now you may have said to yourself, "I can't imagine when would I every run into an equation like: $\psi = c_1 \cdot \Phi_1 + c_2 \cdot \Phi_2$." Actually, you already have, with:

$$N \cdot \cos(kx) = \frac{N}{2} e^{ikx} + \frac{N}{2} e^{-ikx}$$

Here, $\psi = N \cdot \cos(kx)$, $c_1 = \frac{1}{2}$ and $c_2 = \frac{1}{2}$ and $\Phi_1 = e^{ikx}$ and $\Phi_2 = e^{-ikx}$. We have already shown that ψ is not the eigenfunction of the momentum operator $\hat{p}$, although Φ_1 and Φ_2 are since $\hat{p}\Phi_1 = \hbar k \cdot \Phi_1$ and $\hat{p}\Phi_2 = -\hbar k \cdot \Phi_2$. Since ψ can be expressed as a linear combination of that are eigenfunctions of $\hat{p}$ we can plug all this information into $\langle\hat{p}\rangle = |c_1|^2 \cdot \omega_1 + |c_2|^2 \cdot \omega_2$ to find:

$$\langle\hat{p}\rangle = \left|\frac{1}{2}\right|^2 \cdot \hbar k + \left|\frac{1}{2}\right|^2 \cdot (-\hbar k) = 0$$

Consequently, we not only see once again how the expectation value can allow us to figure out observables from difficult functions (ones that are not eigenfunctions), we also see how it works. We also see that $\psi = N \cdot \cos(kx)$ describes a particle that isn't moving. $\psi = N \cdot \sin(kx)$ would do the same thing.

12.4.3 Expectation Value examples: Position. We have already discussed how the position operator $\hat{x}$ is simply x. Consequently, let's apply the operator to our favorite wavefunction $\psi = N \cdot \cos(kx)$, and recall for the eigenvalue equation to work properly (for ψ to be an eigenfunction of $\widehat{\Omega}$) we need to see that $\widehat{\Omega}\psi = \omega \cdot \psi$:

$$\hat{x}\psi = x \cdot N \cdot \cos(kx)$$

Whups- this is a fail, the wavefunction on the right is supposed to be a number (ω) multiplying the original wavefunction. However, if $f(x) = \cos(kx)$ and $g(x) = x \cdot \cos(kx)$, then clearly $f(x) \neq g(x)$ since "x" is not a finite value like 5 or π. To be more plainspoken, you need to see $\omega = 5$ or $\omega = \pi$, not $\omega = x$. The example above is undoubtedly confusing; we have two explanations. For one, the application of an operator is akin to asking a question. The position operator is asking, "Where are you at?" However, this question is nonsensical when applied to $\psi = N \cdot \cos(kx)$, since technically this wave is somewhere everywhere from -∞ to ∞. Thus, the question itself is not sensible, and thus there is an uninterpretable result. Another, easier explanation is that ψ is not an eigenfunction of $\hat{x}$. And in these cases you need to apply the expectation value way of answering quantum mechanical questions. If you're interested in what is an eigenfunction of x, look up "Dirac Delta Functions".

12.4.4 Hermitian operators. One of the most important relationships in quantum mechanics is called orthonormality. This means that, if you have a few functions ψ_n that are eigenfunctions of the operator $\widehat{\Omega}$, then the following is true:

$$\int_{\text{lower limit}}^{\text{upper limit}} \psi_{n'}^{*}\psi_n \cdot \partial\tau = \delta_{n',n}$$

Where d is the Kronecker delta function:

$$\delta_{n',n} = \begin{cases} 1, \text{if } n'=n \\ 0, \text{if } n' \neq n \end{cases}$$

We saw this previously in our discussion on the proof of the expectation value equation. Where does this come from? It is assumed that the wavefunctions are eigenfunctions of an operator that is Hermitian. The definition of a Hermitian operator is:

$$\int \psi_{n'}^{*}\widehat{\Omega}\psi_n \cdot \partial\tau = \int \psi_n\left(\widehat{\Omega}\psi_{n'}\right)^{*} \cdot \partial\tau$$

Now while this seems very abstract, you're right, it is. However, it turns out that nearly all quantum mechanical operators (and most important the Hamiltonian operator) has this mathematical trait. The fact that the operator behaves this way has implications for the solutions to the operator, i.e. the wavefunctions. To see what we mean, first assume that the wavefunctions ψ_n and $\psi_{n'}$ are actually the exact same thing, meaning $n = n'$. Also $\widehat{\Omega}\psi_n = \omega_n\psi_n$. As a result:

$$\int \psi_n^{*}\widehat{\Omega}\psi_n \cdot \partial\tau = \int \psi_n^{*}\omega_n\psi_n \cdot \partial\tau = \omega_n \cdot \int \psi_n^{*}\psi_n \cdot \partial\tau$$

Also:

$$\int \psi_n\left(\widehat{\Omega}\psi_n\right)^* \cdot \partial\tau = \int \psi_n(\omega_n\psi_n)^* \cdot \partial\tau = \omega_n^* \cdot \int \psi_n\psi_n^* \cdot \partial\tau$$

Since, for a Hermitian operator $\int \psi_n^*\widehat{\Omega}\psi_n \cdot \partial\tau = \int \psi_n\left(\widehat{\Omega}\psi_n\right)^* \cdot \partial\tau$, then:

$$\omega_n \cdot \int \psi_n^*\psi_n \cdot \partial\tau = \omega_n^* \cdot \int \psi_n\psi_n^* \cdot \partial\tau$$

And thus:

$$\omega_n \cdot \int \psi_n^*\psi_n \cdot \partial\tau - \omega_n^* \cdot \int \psi_n\psi_n^* \cdot \partial\tau = (\omega_n - \omega_n^*) \int \psi_n^*\psi_n \cdot \partial\tau = 0$$

Where we used the fact that, through the associative axiom of multiplication: $\int \psi_n^*\psi_n \cdot \partial\tau = \int \psi_n\psi_n^* \cdot \partial\tau$. Now, there are only two ways for $(\omega_n - \omega_n^*) \int \psi_n^*\psi_n \cdot \partial\tau = 0$, either $\int \psi_n^*\psi_n \cdot \partial\tau = 0$ which we already know is false (its equal to 1) or $\omega_n - \omega_n^* = 0$, which means that $\omega_n = \omega_n^*$. When is a number equal to its complex conjugate? Only when that number is fully real. Thus, the eigenvalues of Hermitian operators have real eigenvalues.

Next assume that $n \neq n'$. The same analyses above yield:

$$\int \psi_{n'}^*\widehat{\Omega}\psi_n \cdot \partial\tau = \int \psi_{n'}^*\omega_n\psi_n \cdot \partial\tau = \omega_n \cdot \int \psi_{n'}^*\psi_n \cdot \partial\tau$$

Also:

$$\int \psi_n\left(\widehat{\Omega}\psi_{n'}\right)^* \cdot \partial\tau = \int \psi_n(\omega_{n'}\psi_{n'})^* \cdot \partial\tau = \omega_{n'}^* \cdot \int \psi_n\psi_{n'}^* \cdot \partial\tau$$

Since $\int \psi_{n'}^*\widehat{\Omega}\psi_n \cdot \partial\tau = \int \psi_n\left(\widehat{\Omega}\psi_{n'}\right)^* \cdot \partial\tau$ then:

$$\left(\omega_n - \omega_{n'}^*\right) \int \psi_{n'}^*\psi_n \cdot \partial\tau = 0$$

And we now have to figure out whether $\omega_n - \omega_{n'}^* = 0$ or if $\int \psi_{n'}^*\psi_n \cdot \partial\tau = 0$. Now, if ψ_n and $\psi_{n'}$ are different eigenfunctions of the operator then they must have different eigenvalues. If not, they would be the same. Thus, $\omega_n \neq \omega_{n'}$, and we have to conclude that different eigenfunctions of the same operator are orthonormal:

$$\int \psi_{n'}^*\psi_n \cdot \partial\tau = \begin{cases} 1, \text{if } n' = n \\ 0, \text{if } n' \neq n \end{cases}$$

12.5. The freewave potential. In the next few sections we will examine a few paradigms of systems that are good first examples. The first is called the "free wave" particle, which is a quantum mechanical object (let's just say its an electron), that lives in a single dimension without end. Also, there is nothing to interact with. As a result, the Hamiltonian: $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$ of that particle is simply:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

since V(x)=0 everywhere (no potential for interaction because there is nothing else to interact with). While this is a simple problem to work with, it has the unfortunate aspect of being highly unrealistic for describing the Universe with only one particle, and that the Universe doesn't end (fyi ours does, thanks to the Big Bang).

You may have already figured out that we have been working with the free wave system for this entire chapter. As a result we already know that there are four wavefunctions, and that $\psi = N \cdot e^{ikx}$ is for a particle moving right, $\psi = N \cdot e^{-ikx}$ is for a particle moving left, and $\psi = N \cdot \cos(kx)$ and $\psi = N \cdot \sin(kx)$ are for particles that have no net momenta. Great, but here is something you may have not noticed. Let's normalize the wavefunction by deriving the normalization constant that we already discussed is:

$$N = \frac{1}{\sqrt{\int \psi^2\, \partial\tau}}$$

And let's use an unnormalized wavefunction $\psi = e^{ikx}$ (recall, that our purpose here is to calculate what "N" is). First let's simply solve the integral

$$\int_{-\infty}^{\infty} \psi^2 \cdot \partial x = \int_{-\infty}^{\infty} \psi^*\psi \cdot \partial x = \int_{-\infty}^{\infty} e^{ikx^*}e^{ikx} \cdot \partial x = \int_{-\infty}^{\infty} e^{-ikx}e^{ikx} \cdot \partial x = \int_{-\infty}^{\infty} \partial x = \infty$$

To solve this we used the fact that $e^{-ikx}e^{ikx} = e^{-ikx+ikx} = e^0 = 1$. Thus, the normalized wavefunction is: $\psi = N \cdot e^{ikx} = \frac{1}{\sqrt{\infty}}e^{ikx}$. In case you are wondering, no this doesn't make sense. You can't have equations with ∞ in it, and the square root doesn't "save" it in some miraculous way. This normalized wavefunction is absurd, so you may be wondering how you fix it.

The answer is, you don't. You see, the problem itself is absurd, because this is a particle that is in an infinite universe and the particle may be found anywhere in it. Thus, the probability density for the normalized wavefunction $\psi^*\psi$ is:

$$\psi^*\psi = \frac{1}{\sqrt{\infty}}e^{-ikx}\frac{1}{\sqrt{\infty}}e^{ikx} = \frac{1}{\infty} = 0$$

And this is exactly what you should get. In an infinite universe, the probability for a particle to be at any particular point in space is 0 because the particle has an infinite number of other places to be. So, the result is fine, just weird.

Example problems, the "particle in a box". This paradigm is a bit more simple, which is that the free wave is in fact inside a finite universe. Inside the box there is no potential energy, so $\widehat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$. Outside the boundaries the potential energy is infinite, so the particle cannot leave the box. To make it interesting, we often make the particle have the mass of an electron and the box is 1×10^{-9} m (or 1 nm) big, which means that the electron displays quantum mechanical behavior. If the box was much bigger then the electron is just like a marble on a track, and we don't really need quantum mechanics to describe it. This is a lesson that there are size regimes over which you observe quantum mechanical effects, and bigger ones where you don't.

Shown on the right is the potential surface. Since the wavefunction $\psi(x)$ has to be $\psi(0) = 0$ at x=0, and $\psi(L) = 0$ at x=L, and have a double derivative that is equal to itself, the only mathematical entity that fits the bill for is $\psi = N \cdot \sin(?)$. Now, we must design the argument of the function "?" to sure that $\sin(x = L) = 0$. A sine wave always starts at 0, and it next crosses 0 at π. Thus, we know that:

$$\psi(x) = N \cdot \sin\left(\pi \frac{x}{L}\right)$$

works. Now, you might recall that we often found more than one solution to a problem; the free wave has four solutions for example. As you can see from the figure, the particle in a box also has more solutions because the sine wave has other 0's, the first one at p and the next one at 2p. Thus, another solution to the particle in a box is $\psi(x) = N \cdot \sin\left(2\pi \frac{x}{L}\right)$. And we can keep figuring out new solutions until we see that there is a general relationship

$\psi_n(x) = N \cdot \sin\left(n\pi \frac{x}{L}\right)$, where n=1, 2, 3…

While we have an infinite number of solutions for the particle in a box problem, how do we understand what they mean or represent? First, let's figure out how to normalize them. As we have already shown many times that the normalization constant is $N = \frac{1}{\sqrt{\int \psi^2 \, \partial\tau}}$, let's simply calculate the integral:

$$\int_0^L \psi^2 \cdot \partial x = \int_0^L \psi^*\psi \cdot \partial x = \int_0^L \sin\left(n\pi\frac{x}{L}\right)^* \sin\left(n\pi\frac{x}{L}\right) \cdot \partial x = \int_0^L \sin^2\left(n\pi\frac{x}{L}\right) \cdot \partial x$$

To solve this we simply look up a table of standard trigonometric integrals to find:

$$\int \sin^2(ax)\, \partial x = \frac{x}{2} - \frac{1}{4a}\sin(2ax)$$

and thus: $\int \sin^2\left(n\pi\frac{x}{L}\right) \partial x = \frac{x}{2} - \frac{L}{4n\pi}\sin\left(2n\pi\frac{x}{L}\right)$. When placed into a definite integral:

$$\int_0^L \sin^2\left(n\pi\frac{x}{L}\right) \cdot \partial x = \frac{x}{2} - \frac{L}{4n\pi}\sin\left(2n\pi\frac{x}{L}\right)\Big]_{x=0}^{x=L} = \frac{L}{2} - \frac{L}{4n\pi}\sin(2n\pi) = \frac{L}{2}$$

because $\sin(2n\pi) = 0$ since n is a whole number integer, i.e. since n=1, 2, 3… then $\sin(2n\pi) = \sin(4\pi) = \sin(6\pi) = 0$.

As a result, the proper normalized particle in a box wavefunctions are:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \cdot \sin\left(n\pi\frac{x}{L}\right)$$

Now for their interpretation, first we can calculate the energy. We will use the eigenvalue expression $\hat{H}\psi_n(x) = E \cdot \psi_n(x)$ since this is usually the fastest way if you know you are dealing with the eigenfunctions of the operator (here, the Hamiltonian).

$$\hat{H}\psi_n(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_n(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\sqrt{\frac{2}{L}} \cdot \sin\left(n\pi\frac{x}{L}\right) = \frac{n^2\pi^2}{2mL^2}\sqrt{\frac{2}{L}} \cdot \sin\left(n\pi\frac{x}{L}\right)$$

As a result we see that the energy is $E_n = \frac{n^2\pi^2}{2mL^2}$. Since n=1, 2, 3… then the n=1 state is the ground state and all the others are excited states, as these have higher energies than the ground state.

We can also figure out the average position of the particle in a box via the expectation value, which is always necessary when using the operator. Note that you must use normalized wavefunctions to properly evaluate expectation values.

$$\langle \hat{x} \rangle = \int_{lower}^{upper} \psi_{n'}^* \hat{x}\psi_n \cdot \partial\tau = \int_0^L \left(\sqrt{\frac{2}{L}} \cdot \sin\left(n\pi\frac{x}{L}\right)\right)^* \cdot x \cdot \sqrt{\frac{2}{L}} \cdot \sin\left(n\pi\frac{x}{L}\right) \cdot \partial x$$

Of course we know that sine functions are not complex, so $\sin(x)^* = \sin(x)$, and we can do some factoring to simplify the above into:

$$\langle\hat{x}\rangle = \frac{2}{L}\int_0^L x\cdot\sin^2\left(n\pi\frac{x}{L}\right)\cdot\partial x$$

Use of a table of trigonometric identities yields:

$$\langle\hat{x}\rangle = \frac{2}{L}\int x\cdot\sin^2\left(n\pi\frac{x}{L}\right)\cdot\partial x = \frac{2}{L}\left\{\frac{x^2}{2} - \frac{xL}{4n\pi}\sin\left(2n\pi\frac{x}{L}\right) - \frac{x^2}{4} - \frac{L^2}{8n^2\pi^2}\cos\left(2n\pi\frac{x}{L}\right)\right]_{x=0}^{x=L}\right\}$$

Inputting the limits and using the normalizer gives:

$$\langle\hat{x}\rangle = L - \frac{L}{2n\pi}\sin(2n\pi) - \frac{L}{2} - \frac{L}{4n^2\pi^2}\cos(2n\pi) + \frac{L}{4n^2\pi^2}$$

Since $\sin(2n\pi)$ and $\cos(2n\pi)$ are always 0 and 1, respectively, for n=1, 2, 3… then we are left with:

$$\langle\hat{x}\rangle = L - \frac{L}{2} = \frac{L}{2}$$

And thus $\langle\hat{x}\rangle = \frac{L}{2}$, the middle of the box, for every state of the particle in the box since there is no dependence on the quantum number n in the equation above.

Let’s do one last example, problem, which is the average momentum:

$$\langle\hat{p}\rangle = \int_{lower}^{upper}\psi_{n'}^{*}\hat{x}\psi_n\cdot\partial\tau = \int_0^L\left(\sqrt{\frac{2}{L}}\cdot\sin\left(n\pi\frac{x}{L}\right)\right)^{*}\cdot\frac{\hbar}{i}\frac{\partial}{\partial x}\sqrt{\frac{2}{L}}\cdot\sin\left(n\pi\frac{x}{L}\right)\cdot\partial x$$

Several steps of simplification yield:

$$\langle\hat{p}\rangle = \int_{lower}^{upper}\psi_{n'}^{*}\hat{x}\psi_n\cdot\partial\tau = \frac{2}{L}\frac{\hbar}{i}\frac{n\pi}{L}\int_0^L\cdot\sin\left(n\pi\frac{x}{L}\right)\cdot\cos\left(n\pi\frac{x}{L}\right)\cdot\partial x$$

Since $\int\sin(ax)\cdot\cos(ax)\,\partial x = -\frac{1}{4a}\cos(2ax)$ we find that:

$$\langle\hat{p}\rangle = \frac{2\hbar n\pi}{iL^2}\left\{-\frac{L}{4n\pi}\cos\left(2n\pi\frac{x}{L}\right)\right\}\Big]_{x=0}^{x=L} = -\frac{\hbar}{2iL}\cos(2n\pi) + \frac{\hbar}{2iL}$$

And since $\cos(2n\pi) = 0$ for n as a whole number we find that $\langle\hat{p}\rangle = 0$. Does this make sense? Very much so, because if the particle had some net momentum then it could escape the box. But, it can’t, so every time it starts to move left it must hit the wall and move right. The net of the left- and right- motion cancel out completely, so the particle is stuck.

Problems: Numerical

1. More on eigenvectors. A particle with some kinetic energy is created in an empty, infinite universe. You are 60% certain it is moving to the right (momentum= $+\hbar k$) and thus there is a 40% chance it is moving left (momentum= $-\hbar k$). If I write the wavefunction $\Psi(x)$ as a linear sum of normalized momentum eigenvectors: $N \cdot \Phi_n(x)$, where N is the normalization constant, the result is:

$$\Psi(x) = c_1 N\Phi_1(x) + c_2 N\Phi_2(x) = 0.7746 \cdot N \cdot e^{ikx} + 0.6325 \cdot N \cdot e^{-ikx}$$

a. How did I determine that c_1=0.7746 and c_2=0.6325? Does it have anything to do with the functions that they multiply (i.e $N \cdot e^{ikx}, N \cdot e^{-ikx}$)? (hint: square the numbers) **(2 pts)**

b. Please derive the expectation value $\langle p \rangle$ of momentum for this particle using the formula:

$$\langle p \rangle = \int_{-\infty}^{\infty} [c_1\Phi_1(x) + c_2\Phi_2(x)]^* \frac{\hbar}{i}\frac{\partial}{\partial x}[c_1\Phi_1(x) + c_2\Phi_2(x)]\,\partial x$$

Hint: $\int_{-\infty}^{\infty} N^2 e^{-ikx}e^{ikx} \cdot \partial x = 1$, $\int_{-\infty}^{\infty} N^2 e^{ikx}e^{ikx} \cdot \partial x = 0$ and $\int_{-\infty}^{\infty} N^2 e^{-ikx}e^{-ikx} \cdot \partial x = 0$ **(10 pts)**

2. More on eigenvectors. A particle with some kinetic energy is created in an empty, infinite universe. You are 75% certain it is moving to the right (momentum $=\hbar k$) and thus there is a 25% chance it is moving left (momentum= $-\hbar k$). If I write the wavefunction $\Psi(x)$ as a linear sum of normalized momentum eigenvectors: $N \cdot \Phi_n(x)$, where N is the normalization constant, the result is:

$$\Psi(x) = c_1 N\Phi_1(x) + c_2 N\Phi_2(x) = 0.866 \cdot N \cdot e^{ikx} + 0.500 \cdot N \cdot e^{-ikx}$$

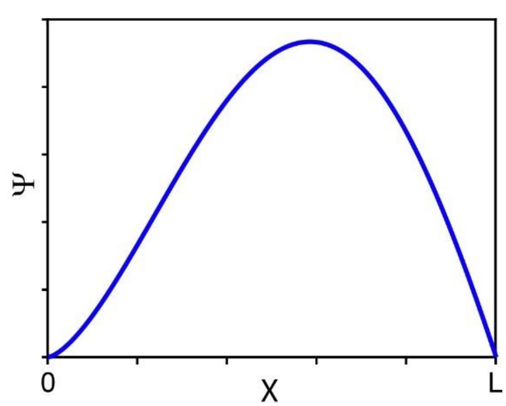
a. How did I determine that c_1=0.866 and c_2=0.500? Does it have anything to do with the functions that they multiply (i.e $N \cdot e^{ikx}, N \cdot e^{-ikx}$)? (hint: square the numbers) **(2 pts)**

b. Please derive the expectation value $\langle p \rangle$ of momentum for this particle using the formula:

$$\langle p \rangle = \int_{-\infty}^{\infty} [c_1\Phi_1(x) + c_2\Phi_2(x)]^* \frac{\hbar}{i}\frac{\partial}{\partial x}[c_1\Phi_1(x) + c_2\Phi_2(x)]\,\partial x$$

Hint: $\int_{-\infty}^{\infty} N^2 e^{-ikx}e^{ikx} \cdot \partial x = 1$, $\int_{-\infty}^{\infty} N^2 e^{ikx}e^{ikx} \cdot \partial x = 0$ and $\int_{-\infty}^{\infty} N^2 e^{-ikx}e^{-ikx} \cdot \partial x = 0$ **(10 pts)**

For the following questions, we will work with a particle wavefunction depicted here.



3. For a wavefunction of the form: $\Psi(x) = \frac{2}{L} \cdot \sqrt{x} \cdot \sin\left(\frac{\pi}{L}x\right)$, what is the variance in position: $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$?

a. First calculate $\langle x \rangle$ **(6 pts)**

b. Next calculate $\langle x^2 \rangle$ **(6 pts)**

c. And now determine $\langle x^2 \rangle - \langle x \rangle^2$ **(6 pts)**

Hint: $\frac{1}{2} - \frac{3}{2\pi^2} - \left(\frac{2}{3} - \frac{1}{\pi^2}\right)^2 \approx 0.0284$

Problems: Theoretical or Explain in Words

1. Math practice! Operate on $\Psi = r \cdot \sin(\theta)$ using the operator: **(10 pts)**

$$\left(\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\cos(\theta)\frac{\partial}{\partial r}r\right) - 2\frac{\cos^2(\theta)}{\sin^2(\theta)}$$

Hint: $\frac{\partial}{\partial\theta}\{\cos(\theta) \cdot \sin(\theta)\} = \cos^2(\theta) - \sin^2(\theta)$, and Ψ is an eigenfunction with an eigenvalue of -2.

2. Math practice! Operate on $\Psi = r \cdot \sin(\theta)$ using the operator:

$$\left(\frac{\partial}{\partial\theta}\tan(\theta)\frac{\partial}{\partial r}r\right) - 2\frac{\tan(\theta)\sec(\theta)}{\sin(\theta)}$$

Hint: $\frac{\partial}{\partial\theta}\{\tan(\theta) \cdot \sin(\theta)\} = \sin(\theta) + \tan(\theta)\sec(\theta)$, and Ψ is an eigenfunction with an eigenvalue of 2. **(10 pts)**

3. If I have a particle that does not experience any sort of potential energy (all energy is kinetic), then the Schrodinger equation is:

$$\frac{-\hbar^2}{2m}\frac{\partial^2\Psi(x)}{\partial x^2} = E \cdot \Psi(x)$$

which simplifies to:

$$\frac{\partial^2\Psi(x)}{\partial x^2} = -k^2 \cdot \Psi(x)$$

where $k^2 = \left[\frac{2m \cdot E}{\hbar^2}\right]$. Solutions include $\Psi(x) = e^{ik \cdot x}$ and $\Psi(x) = e^{-ik \cdot x}$, both of which have an energy of: $E = \frac{\hbar^2 k^2}{2m}$.

a. Please show that a linear combination of $e^{ik \cdot x}$ and $e^{-ik \cdot x}$, i.e. $\Psi(x) = e^{ik \cdot x} + e^{-ik \cdot x}$, is also eigenfunction of the Hamiltonian with the same energy $E = \frac{\hbar^2 k^2}{2m}$. **(5 pts)**

b. Please show that the wavefunction: $\Psi(x) = e^{ik \cdot x} - e^{-ik \cdot x}$ is also an eigenfunction of the Hamiltonian with energy $E = \frac{\hbar^2 k^2}{2m}$. **(5 pts)**

4. The eigenfunction of an operator $\Phi(x)$, such as $\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$, has the following property:

$$\hat{p}_x \Phi(x) = \omega \cdot \Phi(x)$$

where ω is just some constant(s). Which of the following functions are eigenfunctions of the momentum operator?

a. $k{\cdot}x^2$ **b.** $e^{k \cdot x^2}$ **c.** $\cos(k{\cdot}x)$ **d.** e^{ikx} **e.** $e^{ikx} + e^{-ikx}$ **(5 pts)**

5. The eigenfunction of an operator $\Phi(x)$, such as $\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$, has the following property:

$$\hat{p}_x \Phi(x) = \omega \cdot \Phi(x)$$

where ω is just some constant(s). Which of the following functions are eigenfunctions of the momentum operator?

a. $k{\cdot}x^2$ **b.** $e^{k \cdot x^2}$ **c.** $\sin(k{\cdot}x)$ **d.** e^{ikx} **e.** $e^{ikx} - e^{-ikx}$ **(5 pts)**

6. Which of the following are eigenfunctions of the kinetic energy operator $\frac{\hat{p}_x^2}{2m} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$?

a. $k{\cdot}x$ **b.** $k{\cdot}x^2$ **c.** $e^{k \cdot x^2}$ **d.** $\cos(k{\cdot}x)$ **(8 pts)**

e. Given the Schrodinger equation: $\frac{-\hbar^2}{2m}\frac{\partial^2 \Psi(x)}{\partial x^2} = E \cdot \Psi(x)$, and assume that we know that the energy is 0. In this case, is it acceptable for the wavefunction to be $\Psi(x)=k{\cdot}x$? **(5 pts)**

7. The "flux" operator: $\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x}$ tells you whether a wavefunction is moving left or right. If the answer is + or -, the wavefunction is moving either right or left. If you get 0, then the wavefunction is not moving.

Can you apply the flux operator on the following:

a. $\psi = e^{-ikx}$ **b.** $\psi = \sin(k \cdot x)$ **c.** $\psi = e^{-kx^2}$ **(9 pts)**

and tell me whether the wavefunction is moving left, right, or isn't moving.

8. The "flux" operator: $\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x}$ tells you whether a wavefunction is moving left or right. If the answer is + or -, the wavefunction is moving either right or left. If you apply the operator and get 0, then the wavefunction is not moving.

Can you apply the flux operator on the following:

a. $\psi = e^{ikx}$ **b.** $\psi = \cos(k \cdot x)$ **c.** $\psi = e^{-kx^2}$ **(9 pts)**

and tell me whether the wavefunction is moving left, right, or isn't moving.

9. Please normalize the wavefunction:

$$\Psi(x) = \sqrt{x} \cdot \sin\left(\frac{\pi}{L}x\right)$$

For this problem you will need to use the on-line definite integral calculator:

https://www.wolframalpha.com/widgets/view.jsp?id=8ab70731b1553f17c11a3bbc87e0b605

Hint: Hopefully you know that the normalization is: **(5 pts)**

$$N = \frac{1}{\sqrt{\int_0^L \Psi^* \cdot \Psi \cdot \partial x}}$$

10. Charles Hermite showed that wavefunctions have the property:

$$\int_{-\infty}^{\infty} \Psi_j^* \Psi_i \cdot \partial x = 0$$

for all i≠j; this is called orthonormality. All the operators we study are Hermitian. For a particle in a box, the ground state is:

$$\sqrt{\frac{2}{L}} \cdot \sin\left(\frac{\pi x}{L}\right)$$

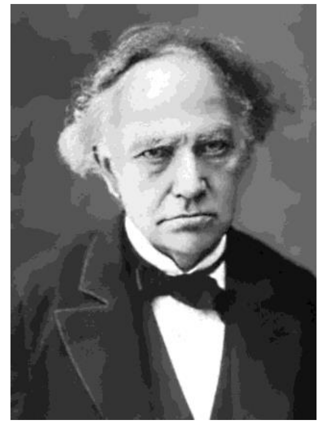
and all excited states are:

$$\sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n\pi x}{L}\right)$$

where n=2, 3, 4… Can you prove that $\int_0^L \Psi_j^* \Psi_i \cdot \partial x = 0$ where Ψ_i is the ground state and Ψ_j are the excited states? You should use an on-line integrator to show that $\int_0^L \Psi_j^* \Psi_i \cdot \partial x$ yields an expression that has "n" in it that is always 0 if n>1.

(5 pts)

Hint: The Wolfram web site often "hangs" on such calculations. To get it unstuck, hit the "=" on the lower right.



Top: Charles Hermite, 1901. Bottom: Charles Hermite, 2021.