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:$mathit{\Phi} = cos\left(\frac{2\pi}{\lambda}x\right)$ 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:

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

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:

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

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

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

Then you should know that the momentum of the state ***most definitely is not*** $\frac{-2\pi\hbar}{i\lambda}$. 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: $\psi = N \cdot cos\,(kx)$ where N is the normalization constant and $k = \frac{2\pi}{\lambda}$ is the wavevector. 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. $\hat{V} = 0$) Hamiltonian:

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

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

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

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

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

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

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 $\hat{H}\psi$ 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:

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

or:

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

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

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

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 $\hat{p}$:

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

Here we get a "pass" on the eigenvalue equation $\widehat{\Omega}\Phi = \omega \cdot \Phi$ because the wavefunction is present on both the right and left sides. Therefore, we do know that the momentum of a particle with this wavefunction is $p = \hbar k$ and it has an energy of $E = \frac{\hbar^2 k^2}{2m}$. Notice the consistency, as in the absence of potential the total energy is $E = \frac{p^2}{2m}$, and inserting p=$hslashk$ 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. Now we ask, is this electron moving to the right 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 $\widehat{\Omega}\Phi = \omega \cdot \Phi$ 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 $\hat{H}\psi = E\psi$. 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. Does this seem messy? It should, and it is, which is why we have to have multiple classes to discuss quantum mechanics.

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

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cosleft(kx\right)\ =\frac{N}{2}e^{ikx}+\frac{N}{2}e^{-ikx} \nonumber \]

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 $\widehat{\Omega}$:

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

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

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cosleft(kx\right)):

\[\langle \hat{p}\rangle =\int^{upper\ limit}_{lower\ limit}{}{\left\{N\cdot

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cosleft(kx\right)right\}}^*\frac\hslash{i}\frac{\partial }{\partial x}\left\{N\cdot

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cosleft(kx\right)right\}\cdot \partial x \nonumber \]

\[\frac{-\hslash }{i}N^2\int^{\infty }_{-\infty }{}

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cosleft(kx\right)cdot

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sinleft(kx\right)cdot \partial x \nonumber \]

When we look up this integral off the internet, we find \(\int^{\infty }_{-\infty }{}

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cosleft(kx\right)cdot

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sinleft(kx\right)cdot \partial x=0\). So, as we can see $\langle \hat{p} \rangle = 0$, in other words this quantum object has no net momentum. This is in fact the correct answer. While this problem is a bit difficult, notice how we were able to determine the momentum with this approach whereas the eigenvalue equation proved useless. 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" $\Phi = N \cdot e^{ikx}$ eigenfunction of momentum, that being the:

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

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

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

where the complex conjugate $\left\{ N \cdot e^{ikx} \right\}^*$ is: $N^* \cdot e^{-ikx}$, and we used the formula $\int \Phi^* \Phi \partial x = \int |\Phi|^2 \partial x = 1$ 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 $\langle \hat{p} \rangle$ was seemingly much more complicated to work with? You are correct, it is generally mathematically far simpler 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 $\widehat{\Omega} \psi \neq \omega \cdot \psi$. 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 $\widehat{\Omega}$ has two eigenfunctions Φ_1 and Φ_2, but ψ is not an eigenfunction of $\widehat{\Omega}$. Upon further analysis you realize that ψ is a linear combination of the $\Phi' s$:

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

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

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

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:

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

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

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

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

We can simplify this further using the relationships:

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

to yield:

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

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 3^{rd} and 4^{th} 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

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cosleft(kx\right)\ =\frac{N}{2}e^{ikx}+\frac{N}{2}e^{-ikx} \nonumber \]

Here, \(\psi =N\cdot

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cosleft(kx\right)), $c_1 = \frac{1}{2}$ 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

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cosleft(kx\right)) describes a particle that isn't moving. \(\psi =N\cdot

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sinleft(kx\right)) would do the same thing.

12.4.3 Schrödinger's Cat

In the previous example, it was found that a quantum particle described by the wavefunction $\psi = N \cdot cos\,(kx)$ or $\psi = N \cdot sin\,(kx)$ have $\langle \hat{p} \rangle = 0$. However, does this mean that $E = \frac{p^2}{2m} = 0$? Afterall, this is a particle with no potential energy. And now we ”””””””””have a conundrum because we already demonstrated that $E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$! The resolution lies in the fact that these trigonometric wavefunctions are composed of equal left- and right-travelling waves. Meaning that the particle has momentum, and thus kinetic energy, but since the momentum can be pointed either left or right they cancel each other out to yield a net $\langle \hat{p} \rangle = 0$! This is an example of quantum superposition, as exemplified by the famous Schrödinger's cat who is both alive and dead at the same time as explained in the box. It is important to note that the superposition is not because the particle is moving right and left at the same time, rather, the wavefunction is used because the experimentalist was not able (or wasn't told) about which direction the particle is travelling. Although it is true that the particle is moving either right or left, and an experimentalist was able to guess which direction and use the corresponding wavefunction for further analysis, the results would turn out to be incorrect. This seems like absolute nonsense, but this is true and has been confirmed multiple times. In fact, quantum superposition is the basis for quantum computing.

12.4.4 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

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cosleft(kx\right)), 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

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cosleft(kx\right)\ \nonumber \]

Whups- this is a fail, the wavefunction on the right is supposed to be a number (ω) multiplying the original wavefunction. However, if \(\left(kx\right)) and \(\left(kx\right)), then clearly $f(x) \neq g(x)$ since "x" is not a finite value like 5 or \piup. 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

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cosleft(kx\right)), 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".

12.4.5 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^{upper\ limit}_{lower\ limit}{}{}{\psi }^*_{n^'}\psi }_n\cdot \partial \tau ={\delta }_{n^',n} \nonumber

Where d is the Kronecker delta function:

{\delta }_{n^',n}={\{}^{1,\ if\ n^'=n\ }_{0,\ if\ n^'\neq n} \nonumber

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{\mathit{\Omega}}{\psi }_n\cdot \partial \tau =\int{}{\psi }_n{\left({\widehat{\mathit{\Omega}}\psi }_{n^'}\right)}^*\cdot \partial \tau \nonumber

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{\mathit{\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 \nonumber

Also:

\int{}{\psi }_n{\left({\widehat{\mathit{\Omega}}\psi }_{n^'}\right)}^*\cdot \partial \tau =\int{}{\psi }_n{\left({\omega }_{n^'}{\psi }_{n^'}\right)}^*\cdot \partial \tau ={\omega }^*_{n^'}\cdot \int{}{\psi }_n{\psi }^*_{r

Since \int{}{\psi }^*_{n^'}\widehat{\mathit{\Omega}}{\psi }_n\cdot \partial \tau =\int{}{\psi }_n{\left({\widehat{\mathit{\Omega}}\psi }_{n^'}\right)}^*\cdot \partial \tau then:

\left({\omega }_n-{\omega }^*_{n^'}\right)\int{}{\psi }^*_{n^'}{\psi }_n\cdot \partial \tau =0 \nonumber

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 ={\{}^{1,\ if\ n^'=n\ }_{0,\ if\ n^'\neq n} \nonumber

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