

Schrödinger's Equation: How can you have a matter wave without a wave equation?

Before we find out the equation for a matter wave, let's consider a normal classical wave – like one on a string.

$$y(x, t) = A \cos kx - \omega t \text{ where } k = \frac{2\pi}{\lambda}, \omega = 2\pi f \quad (1)$$

Satisfies the d'Alembert wave equation:

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2} \quad (2)$$

This is shown by:

$$y(x, t) \Rightarrow \begin{cases} \frac{\partial y}{\partial x} = -kA \sin kx - \omega t \\ \frac{\partial^2 y}{\partial x^2} = -k^2 A \cos kx - \omega t = -k^2 y(x, t) \\ \frac{\partial y}{\partial t} = \omega A \sin kx - \omega t \\ \frac{\partial^2 y}{\partial t^2} = -\omega^2 A \sin kx - \omega t = -\omega^2 y(x, t) \end{cases}$$

Plugging (1) and its respective 2nd spatial and temporal derivatives into (2), you show that:

$$-k^2 y = \frac{1}{v^2} \times -\omega^2 y \Rightarrow k = \frac{\omega}{v} \Rightarrow v = f\lambda$$

Which is the familiar frequency-wavelength relation we all know. The reason this works is ultimately because there is a factor of k^2 in the space derivative, and one of ω^2 in the time one. This shows that a specific wavefunction y is a solution to a wave equation (2) when the equation $v = f\lambda$ holds.

And this relationship between a wave function and wave equation is what Schrodinger considered when he wanted to find a wave equation. If particles do in fact have wave like behaviour, then they ought to have both a wave function, and a wave equation which that function satisfies. If so, then what form will this wave equation take?

Our first guess will be this; if a particle is to be described as a wave, then it makes sense that it should be described using a normal travelling wave, which as we saw before, was described by the function $\Psi(x, t) = A \cos kx - \omega t$. This would make sense, since it describes a wave with fixed frequency and wavelength, and as we know with the de Broglie-Einstein relations, for constant wavelength and frequency, momentum and energy must also be constant, which is what would be expected for a freely moving particle. The only problem is, if a force acts on a particle, then its momentum must change, therefore its wavelength associated with that particle must also change. This is a bit problematic, since the concept of a wavelength isn't actually defined if it changes quickly, since within one wave cycle, the wavelength will change. This basically means, if a force is acting on the particle, a function more complicated than Ψ is required to describe its motion. What Schrodinger really wanted to do was get a wave equation which would determine the wavefunction for any given situation! As we try to do that, we'll use the following assumptions:

1. Wave equation must agree with de Broglie-Einstein equations, $\lambda = \frac{h}{p}$ and $E = hf$
2. It must be consistent with the energy equation for a particle that states the total energy must be the sum of the kinetic and potential energies
i.e., $E_{tot} = E_k + E_p = \frac{p^2}{2m} + V(x, t)$. By using this equation for the potential energy, we're actually dictating the forces which are acting on the particle, since $F = -\frac{\partial V}{\partial x}$
3. It must be linear in $\Psi(x, t)$. This means if you have two solutions Ψ_1 and Ψ_2 , then any linear combination of these solutions is also required to be a solution i.e., $\Psi = c_1 \Psi_1 + c_2 \Psi_2$. This is pretty much just saying that you can add wavefunctions producing constructive and destructive interference – the same as superposition.
4. For constant potential energy, the equation should be sinusoidal – the same as a travelling wave of constant wavelength and frequency

So, using assumption number two – the energy statement, we have:

$$E_{tot} = \frac{p^2}{2m} + V(x, t) = hf$$

And using a load of definitions from earlier along with the reduced planks constant $\hbar = \frac{h}{2\pi}$:

$$\frac{\hbar^2 k^2}{2m} + V = \hbar\omega \quad (3)$$

In this equation, there is a factor of k^2 on the left, and ω on the right. As the 4th assumption said, for constant potential energy, the particle is freely moving, and the wave function should be sinusoidal as was said earlier in the assumptions.

Therefore, we can assume that the wave function is of the following form:

$$\Psi(x, t) = \cos(kx - \omega t)$$

Taking the derivatives as earlier:

$$\Psi(x, t) \Rightarrow \begin{cases} \frac{\partial^2 \Psi}{\partial x^2} = -k^2 \cos kx - \omega t = -k^2 \Psi \\ \frac{\partial \Psi}{\partial t} = \omega \sin kx - \omega t \end{cases}$$

Doing this, note taking the 2nd spatial derivative, you get a factor of k^2 and the first time derivative gives the required factor of ω .

Since the differential equation we're looking for needs to be consistent (3), which has both a factor of k^2 and ω in separate terms, we can conclude that the differential equation we seek probably has a factor of the second derivative with respect to x , and the first time derivative of the wavefunction. Furthermore, it also has a constant term in it – the potential energy, and in order to conserve linearity of the differential equation, this also needs to have a factor of the wavefunction.

Using all of these facts, we're led to the following differential equation where the α and β are constants to be determined. What we need to do, is fix these constants such that they make the proposed wave equation consistent with the de Broglie-Einstein postulates, and our earlier assumptions.

$$\alpha \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x, t) \Psi(x, t) = \beta \frac{\partial \Psi(x, t)}{\partial t} \quad (4)$$

Given at the moment we're only considering a particle moving freely in space, without being affected by any external forces, we can set the potential energy of the system to be a constant, so say $V(x, t) = V_0$. By substituting in the wavefunction which we proposed earlier into our guessed wave equation, we can compare the coefficients in order to determine the values of α and β

Doing this, we get:

$$\begin{aligned} -\alpha k^2 \cos kx - \omega t + V_0 \cos kx - \omega t &= \beta \sin kx - \omega t \\ \Rightarrow (\alpha k^2 - V_0) \cos kx - \omega t + \beta \omega \sin kx - \omega t &= 0 \end{aligned}$$

There is a clear problem with this. Given there is a mixture of sine and cosine terms, and we said that this expression must equal zero for all values of x and t , it's clear that the coefficients of the sines and cosines must respectively equal zero, therefore you get $\alpha = \frac{V_0}{k^2}$ and more problematically, $\beta = 0$. It's clear that we cannot have beta to equal zero, since that would remove the term involving the time derivative from our wave equation meaning there's no way of recovering the de Broglie-Einstein relation proposed in (3), which is definitely not what we wanted, so we're going to have to try and find another wavefunction which might satisfy the proposed wave equation.

Thankfully, however, it's relatively clear where this minor problem came from – the wavefunction we chose. We're simply borrowed it from a progressive wave, so it's pretty clear that it isn't going to work and requires a little adaptation to fit. The problem really is that trig functions oscillate between sines and cosines when you differentiate them, and since we have one first derivative, and one second, we're going to end up with one sine and one cosine term when we substitute our proposed wavefunction into the proposed wave equation. Therefore, this will clearly not lead to a nice solution. It's pretty simple to see that in order to resolve this problem, we must just add a mixture of sines and cosines into our wavefunction that we propose, therefore we will get a mixture of sines and cosines out! Therefore, next we will try:

$$\Psi(x, t) = \cos kx - \omega t + \gamma \sin kx - \omega t$$

Where the γ has just strategically been added to conveniently... make things work by providing some flexibility! No dodgy dealing going on here!

Doing the differentials again:

$$\Psi(x, t) \Rightarrow \begin{cases} \frac{\partial^2 \Psi}{\partial x^2} = -k^2 \cos kx - \omega t - k^2 \gamma \sin kx - \omega t = -k^2 \Psi \\ \frac{\partial \Psi}{\partial t} = \omega \sin kx - \omega t - \omega \gamma \cos kx - \omega t \end{cases}$$

Like earlier, we'll substitute these back into the wave equation, to get:

$$-\alpha k^2 \cos kx - \omega t - \alpha k^2 \gamma \sin kx - \omega t + V_0 \cos kx - \omega t + V_0 \gamma \sin kx - \omega t = \beta \omega \sin kx - \omega t - \beta \omega \gamma \cos kx - \omega t$$

Which can be rewritten by factorising out common factors:

$$-\alpha k^2 [\cos kx - \omega t + \gamma \sin kx - \omega t] + V_0 [\cos kx - \omega t + \gamma \sin kx - \omega t] = \beta \omega [-\gamma \cos kx - \omega t + \sin kx - \omega t]$$

Now, we will make a high quality factorisation thing, by factorising out a $\frac{1}{\gamma}$ from the expression in the brackets on the left hand side of the expression. This gives us the $\gamma \sin kx - \omega t$ term which is going to make everything dandy. i.e.,

$$(-\alpha k^2 + V_0) [\cos kx - \omega t + \gamma \sin kx - \omega t] = \frac{\beta \omega}{\gamma} [-\gamma^2 \cos kx - \omega t + \gamma \sin kx - \omega t]$$

When you do this, you see that the thing in the square brackets on the left exactly equals Ψ , and the part in brackets on the right is very close to it.

If we equate the things in the square brackets (which would clearly make things much easier to deal with), we achieve

$$-\gamma^2 \cos kx - \omega t + \gamma \sin kx - \omega t = \cos kx - \omega t + \gamma \sin kx - \omega t$$

The only thing preventing these two equations being equal is the multiple of $-\gamma^2$ on the cosine term on the right hand side. Wouldn't it be good if we could choose γ such that these two equations are the same (and coincidentally both equal Ψ) and can be cancelled from the equation? It would! So, let's!

Clearly, if you want to do this, it's required that:

$$-\gamma^2 = 1 \Rightarrow \gamma^2 = -1 \Rightarrow \gamma = \pm \sqrt{-1}$$

What's that I hear Velican say? Correct – you can't take the square root of a negative number! That wouldn't make any sense.... Right? Well, let's. (But we'll just ignore the minus sign...):

$$\gamma = i$$

Now when we look back at our original equation, it simplifies a load since you can cancel Ψ from each side of the equation until we're left with the simple expression:

$$-\alpha k^2 + V_0 = \frac{\beta \omega}{\gamma}$$

We can now compare this with the energy momentum relationship (3), and by comparing coefficients of k^2 and ω , you can clearly work out the values of α and β :

$$-\alpha = \frac{\hbar^2}{2m} \Rightarrow \alpha = -\frac{\hbar^2}{2m}$$

$$\frac{\beta}{\gamma} = \hbar \Rightarrow \beta = \gamma\hbar = i\hbar$$

Now we can substitute α and β back into our wave equation (4) to get it not in terms of the unknown variables, but in terms of constants which can be determined. Doing this, we arrive at the following presumably recognisable equation:

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

This differential equation is one which satisfies all of the four assumptions which were made at the start. One important thing to note is that this equation was derived in the special case of a free particle, not being acted upon by any external forces (the $V = V_0$ assumption), so we can only postulate that the quantum mechanical wave equation has the same form as in the general case when the potential energy of the particle varies. We (I) can't prove this mathematically, but I can be shown via empirical evidence to be true by comparing the implications of it with experiment.

This equation is the one that, in 1927, Erwin Schrodinger came up with (albeit in a much more esoteric and convoluted way) and remains one of the most important ones to ever be discovered.

This derivation, although looking pretty cool (?) doesn't really tell us much. The next question which we will ask is what is the significance of this equation, and what can it be used for?

When you want to use the Schrodinger equation to work out the wavefunction of a particle with mass m , the things you need to do are:

1. Determine the potential energy function, $V(x, t)$ – equivalent to specifying the forces acting on the particle.
2. Solve the Schrodinger for that specific potential energy function in order to find $\Psi(x, t)$

This does give rise to probably the most important question so far, which has been somewhat totally neglected, even though it's been used right from the start. What does the wavefunction represent?

Well, let's look at the wavefunction which we tried earlier as a solution to the equation:

$$\Psi(x, t) = \cos kx - \omega t + i \sin kx - \omega t$$

This is of course a complex function (since it contains the imaginary unit i). Given i also appears in the Schrodinger equation, this implies that the solution to that equation, much like our example of Ψ here, must also be complex.

Since it's complex, it shows that the quantum wavefunction is not a measurable quantity – it wouldn't make sense to measure an imaginary quantity, however you then ask yourself; what does the wavefunction represent if it's not a physical, measurable quantity – it would not make sense to not be measurable, after all, a particle is just by its nature localised at a point whereas a wavefunction is spread out over space.

Using knowledge of complex numbers, you can consider the modulus squared of the wave function. Maybe this will have a physical interpretation to be empirically determined:

$$|\Psi(x, t)|^2 = \Psi^* \Psi \in \mathbb{R}_{\geq 0}$$

The physicist Max Bourn suggested that the probability of finding a particle between a distance of x and $x + dx$ was represented by the modulus squared of the wavefunction. i.e., if a measurement was taken a time t , in order to locate a particle with wavefunction Ψ , then the probability a particle can be found between a distance of x and $x + dx$ is given by this expression:

$$P(x, t)dx = |\Psi(x, t)|^2 dx = \Psi^*(x, t)\Psi(x, t)dx$$

Therefore, to find the probability of a particle being located within a specific region of space, you just need to integrate the modulus squared of the wave function between the two limits x_1 and x_2 :

$$P(x, t) = \int_{x_1}^{x_2} |\Psi(x, t)|^2 dx$$

This statement is justified by saying that any wave – particle or normal wave must be associated to an area in space, therefore the particle must be at some location whereby the wave has a nonzero amplitude.

The great implication of this is that, if you know everything about the particle (its wavefunction), then you still are not able to predict with absolute certainty the outcome of any experiment. All that the quantum mechanical theory is able to offer is statistical information about the possible results of an observation.

So, after that abstract discussion, we still need try to work out how to actually solve the Schrodinger equation, then apply it to a problem. The technique which we will use is called separation of variables. We will search for solutions where the wavefunction is a product of two other functions – one in time and one in space. This only works, however if the potential energy is a function of only space (which is what we will consider) (or time) and not both, i.e., $V(x, t) = V(x)$. This isn't a particularly strenuous restriction, since most systems in physics are dictated by space dependant potential energy as opposed to time.

$$\Psi(x, t) = \psi(x)\phi(t)$$

Putting this expression for Ψ into the Schrodinger equation, you will get:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} [\psi(x)\phi(t)] + V(x)\psi(x)\phi(t) = i\hbar \frac{\partial}{\partial t} [\psi(x)\phi(t)]$$

Given that time is a constant with respect to space, and vice versa,

$$-\frac{\hbar^2}{2m} \phi(t) \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\phi(t) = i\hbar\psi(x) \frac{d\phi(t)}{dt}$$

Naturally, in order to separate the variables, we need to get all x terms on the left, and all t terms on the right hand side.

$$\frac{1}{\psi(x)} \left[-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) \right] = \frac{i\hbar}{\phi(t)} \frac{d\phi(t)}{dt}$$

Given that now neither sides variable is dependent on the other, it's clear that they must equal a constant which is not dependant on neither space nor time. Therefore, we can write these two equations to equal a constant, say K – called the separation constant. The two equations which we will form are called the space dependant equation (or time-independent) and equation in time (although not called the time dependant equation)

$$\text{Separation constant} \rightarrow \begin{cases} \frac{1}{\psi(x)} \left[-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) \right] = K \text{ (Space dependent equation)} \\ \frac{i\hbar}{\phi(t)} \frac{d\phi(t)}{dt} = K \text{ (Equation in time)} \end{cases}$$

Now let's look solely at the time dependant equation. Slightly rearranging to get the differential on its own, we achieve

$$\frac{d\phi(t)}{dt} = -\frac{iK}{\hbar} \phi(t)$$

This clearly has the solution

$$\phi(t) = e^{-\frac{iKt}{\hbar}} = \cos \frac{Kt}{\hbar} - i \sin \frac{Kt}{\hbar}$$

Since we're using \hbar in these expressions which has a convenient factor of 2π in it, when we remove that you get:

$$\phi(t) = \cos \frac{2\pi Kt}{h} - i \sin \frac{2\pi Kt}{h}$$

This solution is clearly an oscillatory function of time, and we know that they have angular frequency which can be found immediately – it's just the multiple of t in the sine and cosine functions:

$$\omega = \frac{2\pi K}{h} \Rightarrow K = \omega \frac{h}{2\pi} = \omega \hbar = E_{tot}$$

That's a pretty interesting result. We therefore can write our final solution for the time dependant Schrodinger equation:

$$\phi(t) = e^{-\frac{iEt}{\hbar}}$$

After that, we've solved the easy part of the Schrodinger equation – we know $\Psi(x, t) = \psi(x)e^{-\frac{iEt}{\hbar}}$. Next, we need to solve the space dependant Schrodinger equation. Substituting in $K = E$ and slightly rearranging, you achieve what is called the time-independent Schrodinger equation:

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

The solutions to this equation, $\psi(x)$ are called the eigenfunctions (German for characteristic function). When we've determined the eigenfunctions, time dependence can be reintroduced by multiplying by $\phi(t)$ to get our completed wavefunction $\Psi(x, t)$. Obviously, there is not one solution of ψ which works for all situations, so we will consider a very specific example called the infinite square well (which is quite possibly the simplest example there is)

Consider a box, with length a where the potential inside of the box is given by:

$$V(x) = \begin{cases} 0, & 0 \leq x \leq L \\ \infty, & x < 0, x > L \end{cases}$$

This is basically a statement saying that it's impossible for the particle to leave the box, since it would have to have infinite energy to overcome the potential barrier at the edges of the box. Furthermore, when inside of the box, since the potential is zero, the particle is under the influence of no forces between $0 \leq x \leq L$.

First, you can consider the larger case (the 2nd one, where the particle is outside of the box). Clearly, since the potential is infinite, the probability of finding the particle outside of the box must be zero, the wavefunction must be zero. That's half of the problem solved! (Albeit the easy half)

When the particle is inside of the box, we know $V(x) = 0$, therefore the TISE (time independent Schrodinger equation) simplifies to a normal 2nd order differential equation:

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

This can be rewritten in a much more... recognisable form, where k is a constant whose value is $k = \frac{\sqrt{2Em}}{\hbar}$

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

It's quite clear that the solution to this differential equation will be:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

The constants used, A and B can be fixed by using the boundary conditions of the problem. Namely, at $\psi(0) = \psi(L) = 0$. This condition is allowed since the wavefunction must be continuous (a smooth curve).

At $\psi(0) = 0$, you get $0 = A + B \Rightarrow A = -B$, therefore $\psi(x) = Ae^{ikx} - Ae^{-ikx} = A \sin kx$

At $\psi(L) = 0$, you get $0 = A \sin kx \Rightarrow k = \frac{n\pi}{L}$, $n \in \mathbb{Z}_{\geq 0}$, but $n = 0$ is the trivial solution ($\Psi = 0$), so ignore it. therefore, you get this (where interestingly, the wavefunctions look exactly the same as the standing waves of the harmonic frequencies on a string of length L):

$$\psi_n(x) = A_n \sin \frac{n\pi}{L} x, \quad n \in \mathbb{Z}_{>0}$$

Combining all of these results, you can achieve some form of energy quantisation. Using $k = n\pi/L$ and $k = \sqrt{2Em}/\hbar$ you get:

$$\frac{n\pi}{L} = \frac{\sqrt{2Em}}{\hbar} \Rightarrow E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}, \quad n \in \mathbb{Z}_{>0}$$

Things to note from this are that firstly, energy has become quantised, therefore can take only discrete values depending on n , with each different value of n corresponding to a different energy E_n and a different eigenfunction. Secondly, the lowest possible energy state (corresponding to $n = 1$) is not zero, rather slightly above zero – called the ground state, which is a consequence of Heisenberg's uncertainty principle (when a particle is confined to a finite region of space, there will always be uncertainty in its momentum, and in turn its energy).

After all of this, we can put these results together in order to find an expression in terms of n for the wavefunction:

$$\Psi_n(x, t) = A \sin \frac{n\pi x}{L} e^{-\frac{iE_n t}{\hbar}}$$

$$\text{And also } |\Psi(x, t)|^2 = \Psi^*(x, t)\Psi(x, t) = A^2 \sin^2 \frac{n\pi x}{L}$$

Now, we've managed to determine the wavefunction for our particle, although you might see a rather pesky A in there, which it would be nice to get rid of. What is the numerical value of A ? In order to calculate it, we can do something called normalising the wavefunction. This is basically saying that the probability of finding the particle somewhere in space must equal one, since we know the particle exists:

$$\int_{\mathbb{R}} |\Psi(x, t)|^2 dx = 1 = A^2 \int_0^L \sin^2 \frac{n\pi x}{L} dx = \frac{A^2}{2} \int_0^L 1 - \cos \frac{2n\pi x}{L} dx = \frac{A^2 L}{2} \Rightarrow A = \sqrt{\frac{2}{L}}$$

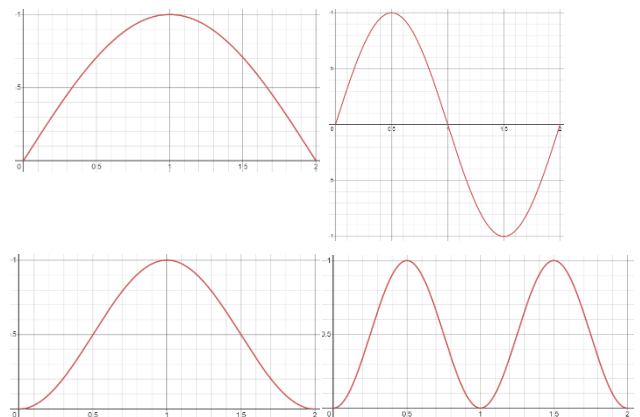
So, we can finally get an answer for the wavefunction inside the box:

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} e^{-\frac{iE_n t}{\hbar}}, \quad E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}, \quad n \in \mathbb{Z}_{>0}$$

Some things to note about this wave function are it's called a stationary state, since the modulus squared of the wave function $|\Psi(x, t)|^2 = \frac{2}{L} \sin^2 \frac{n\pi x}{L}$ is independent of time, so the probability is constant in time. Furthermore, every stationary state has a well-defined energy (which is quite important, but hard to explain without some further investigation).

And that's it (it's really not)! The last thing to do is plot this function on a graph. For a box of length 2, the two three wavefunctions and probability distributions look as follows:

These are quite obviously used to visualise where you are most likely to find the particle within the box for each different eigenstate. Furthermore, in the limit as $n \rightarrow \infty$, the waves become more and more compressed, to the point where no experiment would be able observe the oscillations, and the particle would have equal probability of being found anywhere in the box. Also, as n increases, the discreteness of energy can't be resolved, and it seems that the energy varies continuously – the quantum mechanical predictions approach those of classical.



Some non-finished work not included in my article:

Now, using all of the information we've worked out so far, we can use integration to calculate the probability of particle being within a given area for a given eigenfunction of energy. For example, let's try to calculate the probability of finding a particle in the first energy state (the ground state) within an area, say $\frac{L}{4} \leq x \leq \frac{L}{2}$ by just integrating the modulus squared of the normalised wavefunction:

$$P\left(\frac{L}{4} \leq x \leq \frac{L}{2}, t\right) = \int_{L/4}^{L/2} |\Psi_1(x, t)|^2 dx = \int_{L/4}^{L/2} \frac{2}{L} \sin^2 \frac{\pi x}{L} dx \stackrel{u=\frac{\pi x}{L}}{=} \frac{1}{4} + \frac{1}{2\pi} \approx 0.409$$

So, as you can see, after having normalised the wavefunction, it is simple to calculate the probability of finding the particle in any particular region of space, (irrespective of time)

Some simple probability theory:

- The total number of elements in a list $N = \sum_{x=0}^{\infty} N(x)$, where $N(x)$ is the number of elements with entry x
- The probability of a randomly selected element having entry x , denoted $P(x)$ is $P(x) = \frac{N(x)}{N}$
- The sum of all possible probabilities must equal 1: $\sum_{x=0}^{\infty} P(x) = 1$
- The mean entry in a list of elements can be calculated as follows: $\langle x \rangle = \frac{\sum x N(x)}{N} = \sum_{x=0}^{\infty} x P(x)$. Notice, there need not be an element with entry $\langle x \rangle$.
- In the context of quantum mechanics, the average is normally the quantity of interest, and is often called the expectation value, so that shall be the convention from now.
- Generally, the expectation value of a random function of x , $g(x)$ is given by $\langle g(x) \rangle = \sum_{x=0}^{\infty} g(x) P(x)$
- As an example, if you wanted to calculate the average of the square of all of the entries in a list, $\langle x^2 \rangle = \sum_{x=0}^{\infty} x^2 P(x)$
- Naturally, it's plausible that two data sets which have the same expectation value can have very different distributions. The obvious way to do this, would be (for every element) to calculate the difference between that entry and the expectation value, i.e., $\Delta x = x - \langle x \rangle$ and then compute the expectation value for $\Delta x = \sum (x - \langle x \rangle) P(x)$, however, this will clearly equal zero. To overcome this, you can just square the difference Δx and compute the expectation value of that. i.e., $\langle (\Delta x)^2 \rangle = \sigma^2 = \sum (x - \langle x \rangle)^2 P(x) = \langle x^2 \rangle - \langle x \rangle^2$. This value (denoted σ^2) is called the variance of a distribution and is a measure of the spread of said distribution. Taking the square root of the variance, you're left with the standard deviation of a data set $\sigma = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$. Note that this result implies that the expectation value of the square of the difference ($\sigma^2 = \langle (\Delta x)^2 \rangle$) is clearly non-negative, hence $\langle x^2 \rangle \geq \langle x \rangle^2$. Furthermore, the two are only equal when the standard deviation is zero, and the distribution has no spread at all. Note, the standard deviation in x is often called the uncertainty in x .
- Though all of the probability theory just covered applies to discrete data, it is relatively simple to extend the notion to a continuous distribution. This is done by considering that the probability of an element having an entry which lies between x and $x + dx$ is given by $p(x)dx$ where $p(x)$ is the probability density function. Just like earlier, the probability that some variable x lies within the interval $x_1 \leq x \leq x_2$ is given by the integral $P(x) = \int_{x_1}^{x_2} p(x)dx$, and the idea of an expected value can also be transferred to a continuous case; $\langle x \rangle = \int_{\mathbb{R}} x p(x)dx$.

From this, the relationship between probability theory and quantum mechanics seems pretty obvious. As we saw earlier, the probability of finding a particle in space is equal to the integral of the modulus squared, therefore the modulus squared of the wavefunction can be interpreted as the probability density of that function. Furthermore, the expectation value of a particle's position is given by:

$$\langle x \rangle = \int_{\mathbb{R}} x \Psi^* \Psi dx$$

Now, using this foundation in statistics, we can consider how it applies to the example of the position of a particle in the ground state of an infinite square well. If you look at a graph of $|\Psi_1(x, t)|^2$ against x , it's obvious the particle's most likely to be at the centre of the box, but let's confirm this using the probability theory we just developed.

$$\langle x \rangle = \int_{\mathbb{R}} x \Psi_1^* \Psi_1 dx = \frac{2}{L} \int_0^L x \sin^2 \frac{\pi x}{L} dx \stackrel{IBP}{=} \frac{1}{L} \left[\frac{1}{2} x^2 + \frac{x \sin \frac{2\pi x}{L}}{2\pi} + \frac{L \cos \frac{2\pi x}{L}}{4\pi^2} \right]_0^L = \frac{L}{2}$$

This result is exactly what we would have expected given the plot of $|\Psi_1(x, t)|^2$ against x , and what was predicted earlier. Furthermore, we see that the expectation value for position is time independent, which is also what was expected for our stationary state.

A second feature of stationary states is that they have a definite energy. Since the shape of the wavefunction, and by extension the modulus squared of the wave function is governed by the time independent Schrodinger equation

$H\psi(x) = E\psi(x)$, where in this example, the H is the Hamiltonian operator, $H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$. The equation the Hamiltonian operator and the energy is called the energy eigenvalue equation.

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