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: $\mathcal{E}\left(x,t\right) = \cos\left(\frac{2\pi}{\lambda}x - \omega t\right)$, 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.

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: $\mathcal{E}\left(x,t\right) = \cos\left(\frac{2\pi}{\lambda}x - \omega t\right)$, 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 $h\nu$ is the energy (E) of a photon (or any wave). Thus:$\psi\left(x,t\right) = \cos\left[\frac{1}{\hbar}(p\cdot x - E\cdot t)\right]$

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

$$Kinetic\ Energy + Potential\ Energy = Total\ Energy$$

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 hv of a wave:

$$mc^2 = hv$$

As the frequency of light v is related to the wavelength by: $\lambda v = c$, the energy of the wave can be converted into: $hv = h\frac{c}{\lambda}$. 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 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:

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

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 $\psi = \cos\left(\frac{\sqrt{2mE}}{\text{\hslashx}}\right)$. 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!