5.1: The Schrödinger Wave Equation

Comparing Matter Waves and Light Waves

The fact that we get the same results for the double slit for both matter and photons tells us that matter wave functions must look the same (have the same mathematical form), and behave the same (satisfy superposition). Nevertheless, there must be *something* different about these two cases, as they are very different quanta, physically. We will see that while these quanta have wave functions of the same form, their physical differences lead to different wave equations! Let's begin our exploration with a look at a plane wave with a wavelength λ and frequency f, and we will represent it with a cosine function.

$$f(x,t) = A\cos\left(\frac{2\pi}{\lambda}x \pm 2\pi ft\right) \tag{5.1.1}$$

We can make the link between the physical properties of photons and the wave function explicit by using Planck's and de Broglie's relations:

$$E = hf \;\text{ and }\; p = \frac{h}{\lambda} \quad \Rightarrow \quad A\cos\left(\frac{2\pi}{\lambda}x \pm 2\pi ft\right) = A\cos\left(\frac{2\pi p}{h}x \pm \frac{2\pi E}{h}t\right) = A\cos\left(\frac{p}{\hbar}x \pm \frac{E}{\hbar}t\right) \tag{5.1.2}$$

If we plug this wave function into the wave equation that we know so well, we get confirmation that it works for light:

$$\frac{\partial^2}{\partial x^2}A\cos\left(\frac{p}{\hbar}x \pm \frac{E}{\hbar}t\right) = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}A\cos\left(\frac{p}{\hbar}x \pm \frac{E}{\hbar}t\right) \quad \Rightarrow \quad -\frac{p^2}{\hbar^2}A\cos\left(\frac{p}{\hbar}x \pm \frac{E}{\hbar}t\right) = -\frac{1}{c^2}\frac{E^2}{\hbar^2}A\cos\left(\frac{p}{\hbar}x \pm \frac{E}{\hbar}t\right) \quad \Rightarrow \quad E = pc \tag{5.1.3}$$

We want to use the same wave function for matter, but this wave *equation* won't work, because it does not yield the proper relationship between energy and momentum for particles with mass.

Schrödinger's Equation for Free Particles

We technically should find a wave equation for matter that satisfies the energy/momentum relation for relativity, but this turns out to be tougher to do mathematically, and historically this was not done, either. Instead, we'll assume that the particle is moving at a speed that is not relativistic, and we'll use the Physics 9HA-level relationship between kinetic energy and momentum:

$$KE = \frac{p^2}{2m} \tag{5.1.4}$$

For a freely-moving electron (we'll deal with electrons under the influence of forces later), we need a wave equation that gives us the correct relation between energy and momentum, but still gives us a harmonic wave solution, from which we can build more general waves, and that interferes in the same way that a light wave does. Notice that if our wave function has the same coefficients for x and t as for light, then we need two derivatives with respect to x (to give us the p^2), but only one with respect to t (so that we get only one factor of E). Also, each derivative brings out a factor of $\hbar^{-1}$, so we need to multiply by a factor of $\hbar$ for each derivative. We no longer require the $\frac{1}{c^2}$ factor on the right side of the equation, but we do need a factor of $\frac{1}{2m}$ on the right hand side, to construct the kinetic energy/momentum relation. So let's try this:

$$\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) = \hbar\frac{\partial}{\partial t}\psi(x,t) \tag{5.1.5}$$

Does this produce a harmonic wave function like the one in Equation 5.1.2? The constants that come from the chain rule all work out nicely, but this wave equation falls short in the derivative itself – the single derivative of cosine on the right gives a (negative) sine function, which doesn't match the cosine that comes from two derivatives on the left side.

A guy named Erwin Schrödinger didn't give up when he got this close. He realized that just as light waves have two parts (electric and magnetic), so too should matter waves. Here's how he incorporated two parts to the wave function: He allowed it to be a *complex number*. The real part of the wave function would be one part of the matter wave, and the imaginary part another. And just like for EM waves where changing electric fields give rise to magnetic fields and vice-versa, the real and imaginary parts of this wave function also mix. His solution is now known as *Schrödinger's equation* (for a free particle):

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t) \tag{5.1.6}$$

Harmonic (plane wave) solutions to this differential equation look like:

$$\psi\left(x,t\right)=\psi_o\left[\cos\left(\frac{p}{\hbar}x\pm\frac{E}{\hbar}t\right)+i\sin\left(\frac{p}{\hbar}x\pm\frac{E}{\hbar}t\right)\right] \tag{5.1.7}$$

We can shorten the formula for the wave function using the Euler identity:

$$e^{i\theta}=\cos\theta\pm i\sin\theta \quad \Rightarrow \quad \psi\left(x,t\right)=\psi_oe^{i\left(\frac{p}{\hbar}x\pm\frac{E}{\hbar}t\right)} \tag{5.1.8}$$

As we saw in Section 4.5, a free particle does not automatically have a well-defined momentum. That is, while we have a plane wave solution to the free particle Schrödinger equation, that doesn't mean it is the only solution. Linear combinations of these plane waves can produce localized particles, the momentum (or kinetic energy) of which can be measured to be a wide range of values.

Wave Functions are Complex-Valued

Thanks to the work of Schrödinger, we now know that whatever it is that is "waving" in matter waves (we still don't have a good answer to that!), it is complex-valued. This leads to some complications that we have alluded-to before. first and foremost, we need the probability density to be positive-definite, and until now we have thought of the probability density as being the "square" of the probability amplitude, just like any wave's intensity is proportional to the square of its amplitude. But the square of a complex number is not positive in general, nor, for that matter, is it even a real number!

The solution to this is to insist that the probability density is the *magnitude-squared* of the probability amplitude (the wave function). The "magnitude-squared" operation is achieved by multiplying a complex number by its complex conjugate (the same number with the signs of all the imaginary i's switched):

$$\mathcal{P}\left(x\right)=\left|\psi\left(x\right)\right|^2=\psi^*\left(x\right)\psi\left(x\right) \tag{5.1.9}$$

An interesting consequence of this is that it leaves the wave function ambiguous. No matter how many boundary conditions we account for, we can never obtain an exact function for $\psi\left(x\right)$. In particular, we can always multiply it by a constant complex number with a magnitude of 1. This is because we can't *observe* the wave function, we can only see its probabilistic consequences, and these are unchanged by this *arbitrary quantum phase*:

$$\begin{aligned}\psi_2\left(x\right)=e^{i\delta}\psi_1\left(x\right) \quad \Rightarrow \quad \left|\psi_2\left(x\right)\right|^2=\left(e^{i\delta}\psi_1\left(x\right)\right)^*\left(e^{i\delta}\psi_1\left(x\right)\right)=\left(e^{-i\delta}\psi_1^*\left(x\right)\right)\left(e^{i\delta}\psi_1\left(x\right)\right)=e^0\psi_1^*\left(x\right)\psi_1\left(x\right)\\=\left|\psi_1\left(x\right)\right|^2\end{aligned} \tag{5.1.10}$$

Given that both of these wave functions $\psi_1\left(x\right)$ and $\psi_2\left(x\right)$ produce the same probability density, both will predict exactly the same probabilities of experimental results, and are therefore equally valid.

At this point it should also be noted how the complex-valued wave function is related to the Dirac bracket notation. When the bracket is closed, we have a complex number. If we reverse the order of the bracket, the value is changed to the complex conjugate:

$$\left<x\left|\psi\right.\right>=\psi\left(x\right) \quad \left<\psi\left|x\right.\right>=\psi^*\left(x\right) \tag{5.1.11}$$

If we wish to take the dot product of two state vectors $\left|\psi_1\right>$ and $\left|\psi_2\right>$ (this tells us how much they "overlap"), which we write most simply as $\left<\psi_1\left|\psi_2\right.\right>$, we can express this in terms of their wave functions. As with any dot product, it equals the sum (integral) of the products of their components (wave functions):

$$\left<\psi_1\left|\psi_2\right.\right>=\int\limits_{-\infty}^{+\infty}\left<\psi_1\left|x\right.\right>\left<x\left|\psi_2\right.\right>dx=\int\limits_{-\infty}^{+\infty}\psi_1^*\left(x\right)\psi_2\left(x\right)dx \tag{5.1.12}$$

What if the Particle is not "Free"?

It would be awfully boring if all we studied was particles that didn't interact with anything. So what does Schrödinger have to say about particles that experience forces? It turns out that the extension to such particles is a simple one. We have been assuming that the energy that appears in the argument of the harmonic wave function (Equation 5.1.2) is the kinetic energy, but what if it is just the *total* energy? Naturally these two values are one and the same in the case of a free particle, but a particle under the influence of a force also has some potential energy. So with this understanding that it is the total the energy of a particle that is cataloged in the wave function, we simply add a term to the left side of the Schrödinger equation, to go along with the kinetic energy term that is already there. Calling the potential energy (which depends only upon the position of the particle) $V\left(x\right)$, we have as the full Schrödinger equation:

$$
-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi\left(x,t\right)+V\left(x\right)\psi\left(x,t\right)=i\hbar\frac{\partial}{\partial t}\psi\left(x,t\right) \tag{5.1.13}
$$

The free particle case is obviously recovered when the potential energy is a constant zero value. We will spend the bulk of our remaining time deriving consequences for some especially-instructive functions for $V\left(x\right)$.

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