

Derivation of Schrodinger's Equation

The classical wave equation, given by

$$\frac{\partial^2}{\partial x^2}\Psi(x, t) - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}\Psi(x, t) = 0$$

has been successfully used to describe waves of all sorts—waves on strings, acoustic waves, and electromagnetic waves. However, we have seen that light also exhibits certain particle-like characteristics, and so we say that light is made up of photons whose propagation through space and time is governed by the wave equation. As we have seen in Compton's derivation of the Compton scattering equation, a photon's energy and momentum are given, respectively, by the two Einstein-deBroglie equations:

$$E = h\nu = \hbar\omega$$

$$p = h/\lambda = \hbar k$$

Recall that this last equation is derived from the relativistic energy equation

$$E^2 = p^2c^2 + m_0^2c^4$$

which, for massless photons becomes

$$E = pc \Rightarrow p = h\nu/c = h/\lambda$$

This last equation is often called the deBroglie relationship, since deBroglie suggested that particles such as electrons might exhibit wave-like characteristics whose wavelength would be described by this last equation.

The solution to the classical wave equation has the general form:

$$\Psi(x, t) = Ae^{i(kx - \omega t)}$$

where we find, upon plugging this solution back into the wave equation,

$$-k^2\Psi(x, t) - \frac{1}{c^2}(-\omega^2)\Psi(x, t) = 0$$

from which we find that the speed of the classical wave is given by

$$c = \pm \frac{\omega}{k} = \pm \frac{\hbar\omega}{\hbar k} = \pm \frac{E}{p} = \pm \frac{h\nu}{h/\lambda} = \pm \lambda\nu$$

Thus, we can have waves of different wavelength and frequency which will satisfy the wave equation. Typically, the solution to the wave equation must also satisfy certain boundary conditions which will serve to limit the allowed wavelengths and/or frequencies. The most general solution to the wave equation is actually a sum of all possible solutions consistent with the boundary conditions. Fourier analysis is based upon this fact and allows us to express any arbitrary waveform as a sum (or integral) of sines and cosines.

We can actually derive the classical wave equation starting from the Einstein, deBroglie relationships:

$$E = h\nu = \hbar\omega$$

and

$$p = h/\lambda = \hbar k$$

You will recall that deBroglie argued from this last equation that matter exhibits both a particle nature (momentum) and a wave nature (wavelength), and that this relationship was verified by Davisson and Germer's crystal diffraction experiments with electrons. For photons, with zero rest mass, the invariant energy equation from special relativity:

$$E^2 = p^2 c^2 + m_0^2 c^4$$

becomes

$$\begin{aligned} E &= pc \\ \hbar\omega &= c \hbar k \end{aligned}$$

Beginning with this energy equation, we can write this last equation in terms of differential operators, if we require that the solution to our equation be of the form

$$\Psi(x, t) = Ae^{i(kx - \omega t)}$$

since:

$$\begin{aligned} \frac{\partial}{\partial x} \Psi(x, t) &= ik \Psi(x, t) \\ \frac{\partial^2}{\partial x^2} \Psi(x, t) &= -k^2 \Psi(x, t) \\ \frac{\partial}{\partial t} \Psi(x, t) &= -i\omega \Psi(x, t) \\ \frac{\partial^2}{\partial t^2} \Psi(x, t) &= -\omega^2 \Psi(x, t) \end{aligned}$$

Thus, we note that we can write the energy equation in the form

$$\begin{aligned} \omega^2 \Psi(x, t) &= c^2 k^2 \Psi(x, t) \\ -\frac{\partial^2}{\partial t^2} \Psi(x, t) &= -c^2 \frac{\partial^2}{\partial x^2} \Psi(x, t) \end{aligned}$$

which can be rearranged to give the classical wave equation

$$\frac{\partial^2}{\partial x^2} \Psi(x, t) - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \Psi(x, t) = 0$$

This same procedure can be followed in an attempt to derive a wave equation that would be applicable to classical particles (i.e., particles moving with non-relativistic speeds).

For a “free” particle moving in space, the energy equation would be

$$E = \frac{p^2}{2m}$$

in the classical limit. Using the Einstein, deBroglie equations, this would become

$$\hbar\omega = \frac{\hbar^2 k^2}{2m}$$

Writing which in terms of differential operators operating on the known solution to the wave equation gives

$$\hbar\omega\Psi(x, t) = \frac{\hbar^2 k^2}{2m}\Psi(x, t)$$

or

$$\frac{\hbar}{-i} \frac{\partial}{\partial t} \Psi(x, t) = \frac{\hbar^2}{2m} \left[-\frac{\partial^2}{\partial x^2} \Psi(x, t) \right]$$

Upon rearranging this last equation can be expressed as

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

This is Schrodinger's equation for a free particle. For the case where the particle is moving in a potential energy field, we postulate that the equation for a particle with non-zero rest mass should be given by

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

It is this last equation that Schrodinger used to find the solution to the quantum mechanical hydrogen atom in 1925.