Wave Equations

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Photons and Electrons

We have seen that electrons and photons behave in a very similar fashion—both exhibit diffraction effects, as in the double slit experiment, both have particle like or quantum behavior. We can in fact give a complete analysis of photon behavior—we can figure out how the electromagnetic wave propagates, using Maxwell's equations, then find the probability that a photon is in a given small volume of space *dxdydz*, is proportional to $|E|^2 dxdydz$, the energy density. On the other hand, our analysis of the electron's behavior is incomplete—we know that it must also be described by a wave function $\psi(x,y,z,t)$ analogous to *E*, such that $|\psi(x,y,z,t)|^2\ dxdydz$ gives the probability of finding the electron in a small volume *dxdydz* around the point (x, y, z) at the time *t*. *However, we do not yet have the analog of Maxwell's equations to tell us how ψ varies in time and space.* The purpose of this section is to give a plausible derivation of such an equation by examining how the Maxwell wave equation works for a single-particle (photon) wave, and constructing parallel equations for particles which, unlike photons, have nonzero rest mass.

Maxwell's Wave Equation

Let us examine what Maxwell's equations tell us about the motion of the simplest type of electromagnetic wave—a monochromatic wave in empty space, with no currents or charges present. First, we briefly review the derivation of the wave equation from Maxwell's equations in empty space:

$$\begin{aligned}
&\text{div}\vec{B} = 0\\
&\text{div}\vec{E} = 0\\
&\text{curl}\vec{E} = -\frac{\partial \vec{B}}{\partial t}\\
&\text{curl}\vec{B} = \frac{1}{c^2}\frac{\partial \vec{E}}{\partial t}
\end{aligned}$$

To derive the wave equation, we take the curl of the third equation:

$$\text{curl curl}\vec{E} = -\frac{\partial}{\partial t}\text{curl}\vec{B} = -\frac{1}{c^2}\frac{\partial^2 \vec{E}}{\partial t^2}$$

together with the vector operator identity

$$\text{curl curl} = \text{grad(div)} - \nabla^2$$

to give

$$\nabla^2 \vec{E} - \frac{1}{c^2}\frac{\partial^2 \vec{E}}{\partial t^2} = 0\,.$$

For a plane wave moving in the *x*-direction this reduces to

$$\frac{\partial^2 \vec{E}}{\partial x^2} - \frac{1}{c^2}\frac{\partial^2 \vec{E}}{\partial t^2} = 0$$

The monochromatic solution to this wave equation has the form

$$\vec{E}(x,t) = \vec{E}_0 e^{i(kx-\omega t)}\,.$$

(Another possible solution is proportional to cos(kx - ωt). We shall find that the exponential form, although a complex number, proves more convenient. The physical electric field can be taken to be the real part of the exponential for the classical case.)

Applying the wave equation differential operator to our plane wave solution

$$\left(\frac{\partial^2}{\partial x^2} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\vec{E}_0 e^{i(kx-\omega t)} = \left(k^2 - \frac{\omega^2}{c^2}\right)\vec{E}_0 e^{i(kx-\omega t)} = 0\,.$$

If the plane wave is a solution to the wave equation, this must be true for all x and t, so we must have

$$\omega = ck\,.$$

This is just the familiar statement that the wave must travel at c.

What does the Wave Equation tell us about the *Photon*?

We know from the photoelectric effect and Compton scattering that the photon energy and momentum are related to the frequency and wavelength of the light by

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

$$p = \frac{h}{\lambda} = \hbar k$$

Notice, then, that the wave equation tells us that $\omega = ck$ and hence $E = cp$.

To put it another way, if we think of $e^{i(kx-\omega t)}$ as describing a particle (photon) it would be more natural to write the plane wave as

$$\vec{E}_0 e^{\frac{i}{\hbar}(px-Et)}$$

that is, in terms of the energy and momentum of the particle.

In these terms, applying the (Maxwell) wave equation operator to the plane wave yields

$$\left(\frac{\partial^2}{\partial x^2}-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\vec{E}_0 e^{\frac{i}{\hbar}(px-Et)}=\left(p^2-\frac{E^2}{c^2}\right)\vec{E}_0 e^{\frac{i}{\hbar}(px-Et)}=0$$

or

$$E^2=c^2p^2.$$

The wave equation operator applied to the plane wave describing the particle propagation yields the energy-momentum relationship for the particle.

Constructing a Wave Equation for a Particle with Mass

The discussion above suggests how we might extend the wave equation operator from the photon case (zero rest mass) to a particle having rest mass m_0. We need a wave equation operator that, when it operates on a plane wave, yields

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

Writing the plane wave function

$$\varphi(x,t)=Ae^{\frac{i}{\hbar}(px-Et)}$$

where A is a constant, we find we can get $E^2=c^2p^2+m_0^2c^4$ by adding a constant (mass) term to the differentiation terms in the wave operator:

$$\left(\frac{\partial^2}{\partial x^2}-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}-\frac{m_0^2c^2}{\hbar^2}\right)Ae^{\frac{i}{\hbar}(px-Et)}=-\frac{1}{\hbar^2}\left(p^2-\frac{E^2}{c^2}+m_0^2c^2\right)Ae^{\frac{i}{\hbar}(px-Et)}=0.$$

This wave equation is called the *Klein-Gordon* equation and correctly describes the propagation of relativistic particles of mass m_0. However, it's a bit inconvenient for nonrelativistic particles, like the electron in the hydrogen atom, just as $E^2 = m_0^2c^4 + c^2p^2$ is less useful than $E= p^2/2m$ for this case.

A Nonrelativistic Wave Equation

Continuing along the same lines, let us assume that a nonrelativistic electron in free space (no potentials, so no forces) is described by a plane wave:

$$\psi(x,t)=Ae^{\frac{i}{\hbar}(px-Et)}.$$

We need to construct a wave equation operator which, applied to this wave function, just gives us the ordinary nonrelativistic energy-momentum relationship, $E = p^2/2m$. The p^2 obviously comes as usual from differentiating twice with respect to x, but the only way we can get E is by having a *single* differentiation with respect to time, so this looks different from previous wave equations:

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

This is *Schrödinger's equation* for a free particle. It is easy to check that if $\psi(x,t)$ has the plane wave form given above, the condition for it to be a solution of this wave equation is just $E = p^2/2m$.

Notice one remarkable feature of the above equation—the i on the left means that ψ *cannot* be a real function.

How Does a Varying Potential Affect a de Broglie Wave?

The effect of a potential on a de Broglie wave was considered by Sommerfeld in an attempt to generalize the rather restrictive conditions in Bohr's model of the atom. Since the electron was orbiting in an inverse square force, just like the planets around the sun, Sommerfeld couldn't understand why Bohr's atom had only circular orbits, no Kepler-like ellipses. (Recall that all the observed spectral lines of hydrogen were accounted for by energy differences between these circular orbits.)

De Broglie's analysis of the allowed circular orbits can be formulated by assuming that at some instant in time the spatial variation of the wave function on going around the orbit includes a phase term of the form $e^{\frac{i}{\hbar}pq}$, where here the parameter q measures distance around the orbit. Now for an acceptable wave function, the total phase change on going around the orbit must be $2n\pi$, where n is an integer. For the usual Bohr circular orbit, p is constant on going around, q changes by $2\pi r$, where r is the radius of the orbit, giving

$$\frac{1}{\hbar} p 2\pi r = 2n\pi$$

so

$$pr = n\hbar,$$

the usual angular momentum quantization.

What Sommerfeld did was to consider a general Kepler ellipse orbit, and visualize the wave going around such an orbit. Assuming the usual relationship $p = h/\lambda$, the wavelength will vary as the particle moves around the orbit, being shortest where the particle moves fastest, at its closest approach to the nucleus. Nevertheless, the phase change on moving a short distance Δq should still be $\frac{1}{\hbar} p\Delta q$, and requiring the wave function to link up smoothly on going once around the orbit gives

$$\int pdq = nh$$

Thus only certain elliptical orbits are allowed. The mathematics is nontrivial, but it turns out that every allowed elliptical orbit has the same energy as one of the allowed circular orbits. This is why Bohr's theory gave all the energy levels. Actually, this whole analysis is old fashioned (it's called the "old quantum theory") but we've gone over it to introduce the idea of *a wave with variable wavelength, changing with the momentum as the particle moves through a varying potential*.

Schrödinger's Equation for a Particle in a Potential

Let us consider first the one-dimensional situation of a particle going in the x-direction subject to a "roller coaster" potential. What do we expect the wave function to look like? We would expect the wavelength to be shortest where the potential is lowest, in the valleys, because that's where the particle is going fastest—maximum momentum. Perhaps slightly less obvious is that the amplitude of the wave would be largest at the tops of the hills (provided the particle has enough energy to get there) because that's where the particle is moving slowest, and therefore is most likely to be found.

With a nonzero potential present, the energy-momentum relationship for the particle becomes the energy equation

$$E = \frac{p^2}{2m} + V(x).$$

We need to construct a wave equation which leads naturally to this relationship. In contrast to the free particle cases discussed above, the relevant wave function here will no longer be a plane wave, since the wavelength varies with the potential. However, at a given x, the momentum is determined by the "local wavelength", that is,

$$p = -i\hbar \frac{\partial \psi}{\partial x}.$$

It follows that the appropriate wave equation is:

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

This is the standard one-dimensional Schrödinger equation.

In three dimensions, the argument is precisely analogous. The only difference is that the square of the momentum is now a sum of three squared components, for the *x*, *y* and *z* directions, so $\frac{\partial^2}{\partial x^2}$ becomes $\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}=\nabla^2$, and the equation is:

$$i\hbar\frac{\partial\psi(x,y,z,t)}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z,t)+V(x,y,z)\psi(x,y,z,t).$$

This is the complete Schrödinger equation.