18.2: Quantized Energy - De Broglie's Hypothesis and the Schroedinger Equation

Subsequent to Planck's proposal that energy is quantized, the introduction of two further concepts led to the theory of quantum mechanics. The first was Einstein's relativity theory, and his deduction from it of the equivalence of matter and energy. The relativistic energy of a particle is given by

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

where p is the momentum and m_0 is the mass of the particle when it is at rest. The second was de Broglie's hypothesis that any particle of mass m moving at velocity v, behaves like a wave. De Broglie's hypothesis is an independent postulate about the structure of nature. In this respect, its status is the same as that of Newton's laws or the laws of thermodynamics. Nonetheless, we can construct a line of thought that is probably similar to de Broglie's, recognizing that these are heuristic arguments and not logical deductions.

We can suppose that de Broglie's thinking went something as follows: Planck and Einstein have proposed that electromagnetic radiation—a wave-like phenomenon—has the particle-like property that it comes in discrete lumps (photons). This means that things we think of as waves can behave like particles. Conversely, the lump-like photons behave like waves. Is it possible that other lump-like things can behave like waves? In particular is it possible that material particles might have wave-like properties? If a material particle behaves like a wave, what wave-like properties should it exhibit?

Well, if we are going to call something a wave, it must have a wavelength, λ, a frequency, ν, and a propagation velocity, v, and these must be related by the equation $v = \lambda\nu$. The velocity of propagation of light is conventionally given the symbol c, so $c = \lambda\nu$. The Planck-Einstein hypothesis says that the energy of a particle (photon) is $E = h\nu = hc/\lambda$. Einstein proposes that the energy of a particle is given by $E^2 = p^2c^2 + m_0^2c^4$. A photon travels at the speed of light. This is compatible with other relativistic equations only if the rest mass of a photon is zero. Therefore, for a photon, we must have $E = pc$. Equating these energy equations, we find that the momentum of a photon is

$$p = h/\lambda$$

Now in a further exercise of imagination, we can suppose that this equation applies also to any mass moving with any velocity. Then we can replace p with mv, and write

$$mv = h/\lambda$$

We interpret this to mean that any mass, m, moving with velocity, v, has a wavelength, λ, given by

$$\lambda = h/mv$$

This is ***de Broglie's hypothesis***. We have imagined that de Broglie found it by a series of imaginative—and not entirely logical—guesses and suppositions. The illogical parts are the reason we call the result a hypothesis rather than a derivation, and the originality of the guesses and suppositions is the reason de Broglie's hypothesis was new. It is important physics, because it turns out to be experimentally valid. Very small particles do exhibit wave-like properties, and de Broglie's hypothesis correctly predicts their wavelengths.

In a similar vein, we can imagine that Schrödinger followed a line of thought something like this: de Broglie proposes that any moving particle behaves like a wave whose wavelength depends on its mass and velocity. If a particle behaves as a wave, it should have another wave property; it should have an amplitude. In general, the amplitude of a wave depends on location and time, but we are thinking about a rather particular kind of wave, a wave that—so to speak—stays where we put it. That is, our wave is supposed to describe a particle, and particles do not dissipate themselves in all directions like the waves we get when we throw a rock in a pond. We call a wave that stays put a standing wave; it is distinguished by the fact that its amplitude depends on location but not on time.

Mathematically, the amplitude of any wave can be described as a sum of (possibly many) sine and cosine terms. A single sine term describes a simple wave. If it is a standing wave, its amplitude depends only on distance, and its amplitude is the same for any two points separated by one wavelength. Letting the amplitude be ψ, this standing wave is described by $\psi(x) = A\sin(ax)$, where x is the location, expressed as a distance from the origin at $x = 0$. In this wave equation, A and a are parameters that fix the maximum amplitude and the wavelength, respectively. Requiring the wavelength to be λ means that $a\lambda = 2\pi$. (Since ψ is a sine function, it repeats every time its argument increases by 2π radians. We require that ψ repeat every time its argument increases by $a\lambda$ radians, which requires that $a\lambda = 2\pi$.) Therefore, we have

$$a = 2\pi/\lambda$$

and the wave equation must be

$$\psi(x) = A\sin(2\pi x/\lambda)$$

Equations, ψ, that describe standing waves satisfy the differential equation

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

where C is a constant. In the present instance, we see that

$$\frac{d^2\psi}{dx^2} = -\left(\frac{2\pi}{\lambda}\right)^2 A\sin\left(\frac{2\pi x}{\lambda}\right) \quad = -\left(\frac{2\pi}{\lambda}\right)^2 \psi$$

From de Broglie's hypothesis, we have $\lambda = h/mv$, so that the constant C can be written as

$$C = \left(\frac{2\pi}{\lambda}\right)^2 = \left(\frac{2\pi mv}{h}\right)^2 = \left(\frac{2\pi}{h}\right)^2 (2m)\left(\frac{mv^2}{2}\right) = \left(\frac{8\pi^2 m}{h^2}\right)\left(\frac{mv^2}{2}\right)$$

Let T be the kinetic energy, $mv^2/2$, and let V be the potential energy of our wave-like particle. Then its energy is $E = T + V$, and we have $mv^2/2 = T = E - V$.

The constant C becomes

$$C = \left(\frac{8\pi^2 m}{h^2}\right) T = \left(\frac{8\pi^2 m}{h^2}\right)(E - V)$$

Making this substitution for C, we find a differential equation that describes a standing wave, whose wavelength satisfies the de Broglie equation. This is the time-independent ***Schrödinger equation*** in one dimension:

$$\frac{d^2\psi}{dx^2} = -\left(\frac{8\pi^2 m}{h^2}\right)(E - V)\psi$$

or

$$-\left(\frac{h^2}{8\pi^2 m}\right)\frac{d^2\psi}{dx^2} + V\psi = E\psi$$

Often the latter equation is written as

$$\left[-\left(\frac{h^2}{8\pi^2 m}\right)\frac{d^2}{dx^2} + V\right]\psi = E\psi$$

where the expression in square brackets is called the ***Hamiltonian operator*** and abbreviated to H, so that the Schrödinger equation becomes simply, if cryptically,

$$H\psi = E\psi$$

If we know how the potential energy of a particle, V, depends on its location, we can write down the Hamiltonian operator and the Schrödinger equation that describe the wave properties of the particle. Then we need to find the wave equations that satisfy this differential equation. This can be difficult even when the Schrödinger equation involves only one particle. When we write the Schrödinger equation for a system containing multiple particles that interact with one another, as for example an atom containing two or more electrons, analytical solutions become unattainable; only approximate solutions are possible. Fortunately, a great deal can be done with approximate solutions.

The Schrödinger equation identifies the value of the wavefunction, $\psi(x)$, with the amplitude of the particle wave at the location x. Unfortunately, there is no physical interpretation for $\psi(x)$; that is, no measurable quantity corresponds to the value of $\psi(x)$. There is, however, a physical interpretation for the product $\psi(x)\psi(x)$ or $\psi^2(x)$. [More accurately, the product $\psi(x)\psi^*(x)$, where

$\psi^* \left(x\right)$ is the complex conjugate of $\psi \left(x\right)$. In general, x is a complex variable.] $\psi^2 \left(x\right)$ is the probability density function for the particle whose wavefunction is $\psi \left(x\right)$. That is, the product $\psi^2 \left(x\right) dx$ is the probability of finding the particle within a small distance, dx, of the location x. Since the particle must be somewhere, we also have

$$1=\int^{+\infty}_{-\infty}{\psi^2\left(x\right)dx}$$