Introduction to the quantum theory of matter and Schrödinger's equation

The quantum theory of matter assumes that matter has two natures: a particle nature and a wave nature. The particle nature is described by classical physics (Newton's laws), and the wave nature is described by quantum physics. This is similar to light, which has both a wave and particle nature. The wave nature is described by the classical Maxwell's equations, whereas the particle nature is described by the quantum physics.

Relativistic relationships between mass, energy, and momentum

One of the centerpieces of Einstein's theory of special relativity is that the mass of a particle increases as its velocity increases:

$$\boxed{m = \frac{m_o}{\sqrt{1-(\mathrm{v}/c)^2}}} \qquad [1]$$

where m_o is the rest mass of the particle.

To derive the equation for the kinetic energy T of a particle in terms of its velocity, we start by applying Newton's second law of motion: the force F acting on a particle equals the time-derivative of the particle momentum p:

$$F = \frac{dp}{dt} = \frac{d(m\mathrm{v})}{dt}$$

The kinetic energy T of a particle can then be found by:

$$T = \int F d\mathrm{s} = \int \frac{dp}{dt} d\mathrm{s} = \int \frac{ds}{dt} dp = \int \mathrm{v} d(m\mathrm{v})$$

integrating by parts, this becomes

$$T = \left[m\mathrm{v}^2\right]_0^{\mathrm{v}} - \int_0^{\mathrm{v}} m\mathrm{v} d\mathrm{v} = \left[m\mathrm{v}^2\right]_0^{\mathrm{v}} - \int_0^{\mathrm{v}} \frac{m_o \mathrm{v}}{\sqrt{1-(\mathrm{v}/c)^2}} d\mathrm{v}$$

$$= \left[m\mathrm{v}^2 + m_o c^2 \sqrt{1-(\mathrm{v}/c)^2}\right]_{\mathrm{v}=0}^{\mathrm{v}=\mathrm{v}} = m\mathrm{v}^2 + c^2 m_o^2 \sqrt{1-(\mathrm{v}/c)^2} - m_o c^2$$

or

$$T = mc^2 - m_o c^2 \qquad \text{(matter)}$$

For small velocities, the kinetic energy T becomes:

$$T = mc^2 - m_o c^2 = \frac{m_o c^2}{\sqrt{1-(\mathrm{v}/c)^2}} - m_o c^2 \approx \frac{1}{2} m_o \mathrm{v}^2 \qquad (\text{for } \mathrm{v} << c)\ , \qquad [2]$$

Einstein interpreted the terms $m_o c^2$ and mc^2 as the *rest energy* and *total relativistic energy* of the particle, respectively. Hence we have Einstein's famous statement:

$$\boxed{E = mc^2 \qquad \text{(matter)}} \qquad [3]$$

Another form of this expression can by found by squaring both sides and replacing m with its velocity-dependent formula:

$$E^2 = \frac{m_o^{\ 2}}{1-\left(\mathrm{v}/c\right)^2} c^4 \quad ,$$

which can be rearranged to read:

$$E^2 = m_o^{\ 2} c^4 + c^2 \frac{m_o^{\ 2}}{1-\left(\mathrm{v}/c\right)^2} \mathrm{v}^2$$

but the last term is simply c^2p^2, so we have

$$\boxed{E^2 = m_o^2 c^4 + c^2 p^2 \quad \text{(matter)}} \qquad [4]$$

The Dual Nature of Light

Wave (classical) nature

The classical theory of light is that it is a wave, described in terms of electric and magnetic fields. Maxwell's equations describe the relationship between these fields and their sources (charges and currents). The wave equation electromagnetic waves in free space is for the electric field $\mathcal{E}\,(t,x)$ is:

$$\frac{\partial^2 \mathcal{E}}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 \mathcal{E}}{\partial t^2} \quad . \quad \text{(light waves)} \qquad [5]$$

which admits plane-wave solutions at a frequency ν (in Hz) of the form:

$$\mathcal{E}(t,x) = \mathcal{E}_+ e^{j(-\omega t + kx)} + \mathcal{E}_- e^{j(-\omega t - kx)} \qquad \text{(light waves)} \qquad [6]$$

Here, $\omega = 2\pi\nu$ is the radian frequency, $k = \omega / c$ is the *wavenumber* of the medium, and $\mathcal{E}_+$ and $\mathcal{E}_-$ are arbitrary constants. The $\mathcal{E}_+$ and $\mathcal{E}_-$ terms represent waves propagating in the + and – directions, respectively. Both waves repeat themselves spatially over a distance $\lambda = \ 2\pi / k \ = \ c / \nu$, called a *wavelength*.

Another common way to represent plane waves is in the frequency (phasor) domain, where time is suppressed:

$$\mathcal{E}(x) = \mathcal{E}_+ e^{jkx} + \mathcal{E}_- e^{-jkx} \qquad \text{(light waves)} \qquad [7]$$

(Note here, the physics time-convention $e^{-j\omega t}$ is used, unlike the $e^{j\omega t}$ convention typically used in engineering).

Particle (quantum) nature

The quantum theory of light, proposed by Einstein, states that light consists of energy packets, called photons, that travel at the speed of light. Photons have momentum, but no rest mass. This theory was able to explain the puzzling results of photoelectric experiments. Einstein proposed that the energy of a photon is determined by its frequency ν,

$$\boxed{E = h\nu \quad \text{(photons)} \;,} \qquad [8]$$

where h is Plank's constant.

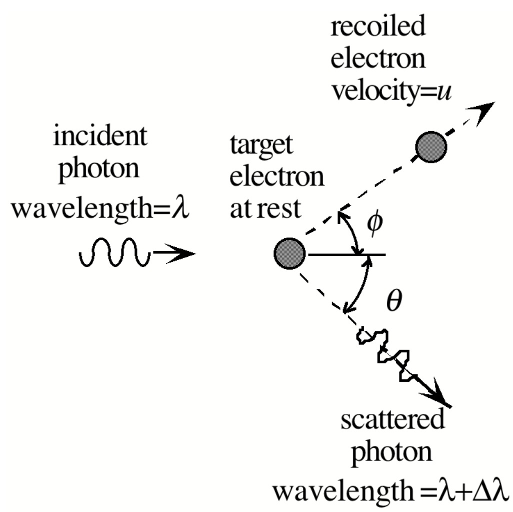
Einstein also proposed that photons have momentum. To see how this could be so, we first remember (equation 4) the relativistic relationship between energy E and momentum p of a mass particle is:

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

However, since the rest mass m_o of a photon is zero, this would imply from [4] that for photons:

$$\boxed{p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda} \qquad \text{(photons)}} \qquad [9]$$

These assumptions about the photon energy and momentum were validated by Compton's famous Scattering experiment, whereby electrons were bombarded with x-ray photons.



In this experiment, photons of wavelength λ bombard an electron initially at rest. After the collision, the electron would recoil at some angle ϕ and a new, downshifted, photon would be emitted at an angle θ. Equating the electron+photon energy and momentum before and after the collision, the following relationship can be derived between the wavelength shift $\Delta\lambda$ and the angle shift θ of the photon:

$$\Delta\lambda = \frac{h}{m_e c^2}(1 - \cos\theta) \quad . \qquad [10]$$

This relation was verified experimentally by Compton in 1923.

Wave (quantum) Nature of Matter

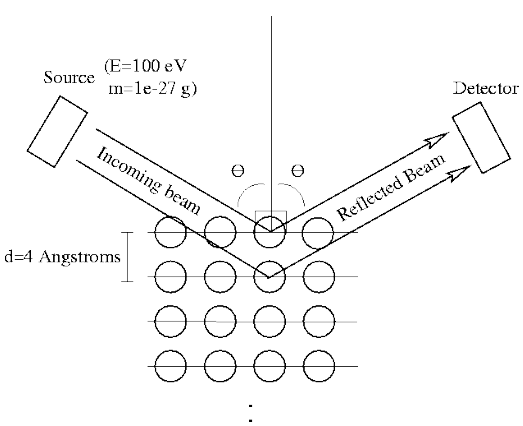
deBroglie proposed that just as light has both a particle and wave nature, so too might matter have both natures. This would mean that matter has a wavelength and frequency. de Broglie proposed that a mass particle has frequency ν, and its relationship to its kinetic plus potential energy E is the same as for a light wave (equation 8):

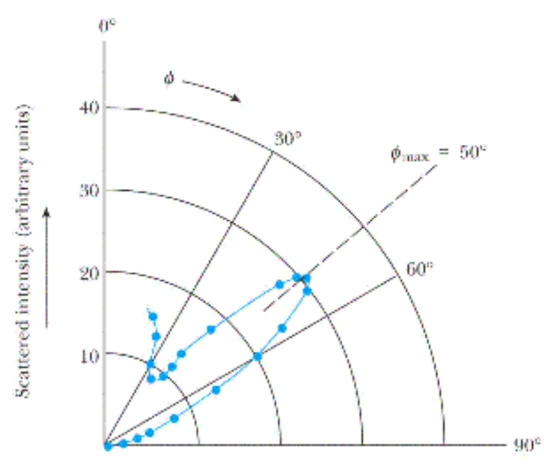
$$\boxed{E = h\nu \quad \text{(matter)}} \qquad [11]$$

deBroglie also proposed that mass particles have wavelength λ, and, when the particle is free (i.e., not in a potential field), this wavelength is related to the particle's momentum p just the same as for a photon (equation 9):

$$\boxed{p = \frac{h}{\lambda} \quad \text{(matter)} \ .} \qquad [12]$$

(Note here that deBroglie did *not* say that p is equal to either E/c or $h\nu/c$, as in the case of photons, since the equations for nonrelativistic particles should not have c in them.) This prediction of wavelength was validated experimentally by the Davisson-Germer experiment, where electrons incident on a nickel sheet scattered off at an angle that corresponded to the Bragg scattering of X-rays off of crystals.





The classical and quantum theories of light and matter can now be summarized:

	Light	Matter
Classical Theory	Nature: wave Description: Maxwell's equations $\lambda = c/\nu$	Nature: corpuscular Description: $E = \frac{1}{2}m\text{v}^2$ (when $\text{v} << c$) $p = m\text{v}$
Quantum Theory	Nature: corpuscular Description: $E = h\nu$ $p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda}$	Nature: wave Description: $E = h\nu$ $\lambda = \frac{h}{p} \approx \sqrt{\frac{h}{2m\nu}}$ (when $\text{v} << c$)

The Schrödinger Wave Equation

Once the concepts of mass frequency and wavelength were accepted, the next question was: what sort of wave equation would a mass wave satisfy? The electromagnetic wave equation cannot work for mass waves, since the relationship between wavelength and frequency for mass waves is *not* $\lambda = c/\nu$, as it is for light waves.

As a starting point, we expect a mass wavefunction to have the same general form (equation 6) as for a light wave:

$$\Psi(t,x) = \Psi_+ e^{j(-\omega t + kx)} + \Psi_- e^{j(-\omega t - kx)} , \qquad [13]$$

except that the radian frequency $\omega = 2\pi\nu$ and the wavenumber $k = 2\pi/\lambda$ will have a different relationship than they do for light waves. Next, consider an electron traveling in a force-free environment at a constant, nonrelativistic, speed v<<c. We will let $E = \frac{1}{2}m\text{v}^2$ represent the particle's energy above its rest energy, and $p = m\text{v}$ its momentum. Using equations 11 and 12, the frequency and wavelength of the electron are:

$$\nu = E/h$$

and

$$\lambda = \frac{h}{m\text{v}} = \frac{h}{\sqrt{2mE}} . \qquad [15]$$

Substituting equation 14 into equation 15, we find that the relationship between the frequency ν and wavelength λ of a mass wave is:

$$\nu = \frac{h}{2m\lambda^2} \quad \text{(mass waves)} \qquad [16]$$

A wavefunction that has these time and position characteristics is:

$$\Psi(x,t) = \Psi_{+} e^{\frac{jx\sqrt{2mE}}{\hbar}} e^{\frac{-jE}{\hbar}t} + \Psi_{-} e^{\frac{-jx\sqrt{2mE}}{\hbar}} e^{\frac{-jE}{\hbar}t} \qquad [17]$$

where Ψ_{+} and Ψ_{-} are constants and $\hbar = h/2\pi$. The first and second terms in this expression represent forward and backward traveling electrons, respectively. A wave equation that yields this solution is:

$$\frac{-\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} = j\hbar\frac{\partial \Psi}{\partial t} \quad . \qquad [18]$$

This wave equation was proposed by Schrödinger in 1926. Substituting the wave function into the right-hand side of Schrödinger's equation yields:

$$\begin{aligned} j\hbar\frac{\partial \Psi}{\partial t} &= j\hbar\frac{\partial}{\partial t}\left[\Psi_{+} e^{\frac{jx\sqrt{2mE}}{\hbar}} e^{\frac{-jE}{\hbar}t} + \Psi_{-} e^{\frac{-jx\sqrt{2mE}}{\hbar}} e^{\frac{-jE}{\hbar}t}\right] \\ &= j\hbar\frac{-jE}{\hbar}\left[\Psi_{+} e^{\frac{jx\sqrt{2mE}}{\hbar}} e^{\frac{-jE}{\hbar}t} + \Psi_{-} e^{\frac{-jx\sqrt{2mE}}{\hbar}} e^{\frac{-jE}{\hbar}t}\right] = E\Psi \end{aligned} \qquad [19]$$

This means that the Schrödinger equation for a single energy particle can be written as:

$$\frac{-\hbar^2}{2m}\frac{1}{\Psi}\frac{\partial^2 \Psi}{\partial x^2} = E \qquad [20]$$

Since we have assumed that the particle is traveling in a force-free environment, its only energy E above the particle's rest energy is kinetic energy, so the term $\frac{-\hbar^2}{2m}\frac{1}{\Psi}\frac{\partial^2 \Psi}{\partial x^2}$ represents the kinetic energy of the particle. If the particle is also in a potential field with potential $V(x)$, the total energy E becomes the sum of the kinetic plus the potential energy, so Schrödinger's equation becomes:

$$\frac{-\hbar^2}{2m}\frac{1}{\Psi}\frac{\partial^2 \Psi}{\partial x^2} + V(x) = E$$

which is Schrödinger equation for particles with constant energy E , often called the time-independent Schrödinger equation.

Finally, particles with uncertain energy can be expressed as the sum particles of constant energy particles, each with a different energy. This is often called the superposition principle of quantum mechanics. Using [13], such a particle can be expressed as:

$$\Psi(x,t) = \int p(E) e^{\frac{jx\sqrt{2mE}}{\hbar}} e^{\frac{-jE}{\hbar}t} dE$$

where $p(E)$ is the probability that the particle has energy between E and $E+dE$