Introduction to quantum mechanics

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Quantum mechanics is the body of scientific principles that explains the behavior of matter and its interactions with energy on the scale of atoms and subatomic particles and how these phenomena could be related to everyday life (see Schrodinger's cat).

Classical physics explains matter and energy at the macroscopic level of the scale familiar to human experience, including the behavior of astronomical bodies. It remains the key to measurement for much of modern science and technology; but at the end of the 19th Century observers discovered phenomena in both the large (macro) and the small (micro) worlds that classical physics could not explain. Coming to terms with these limitations led to the development of quantum mechanics, a major revolution in physics. This article describes how physicists discovered the limitations of classical physics and developed the main concepts of the quantum theory that replaced them in the early decades of the 20th century. These concepts are described in roughly the order they were first discovered; for a more complete history of the subject, see History of quantum mechanics.

Some aspects of quantum mechanics can seem counter-intuitive or even paradoxical, because they describe behavior quite different than that seen at larger length scales, where classical physics is an excellent approximation. In the words of Richard Feynman, quantum mechanics deals with "nature as She is — absurd." [2]

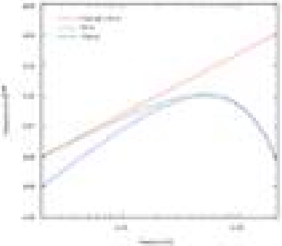
Many types of energy, such as photons (discrete units of light), behave in some respects like particles and in other respects like waves. Radiators of photons (such as neon lights) have emission spectra that are discontinuous, in that only certain frequencies of light are present. Quantum mechanics predicts the energies, the colours, and the spectral intensities of all forms of electromagnetic radiation.

Quantum mechanics ordains that the more closely one pins down one measure (such as the position of a particle), the less precise another measurement pertaining to the same particle (such as its momentum) must become.Put another way, measuring position first and then measuring momentum does not have the same outcome as measuring momentum first and then measuring position; the act of measuring the first property necessarily introduces additional energy into the micro-system being studied, thereby perturbing that system.

Even more disconcerting, pairs of particles can be created as "entangled twins." As is described in more detail in the article on Quantum entanglement, entangled particles seem to exhibit what Einstein called "spooky action at a distance," matches between states that classical physics would insist must be random even when distance and the speed of light ensure that no physical causation could account for these correlations.[3]

The first quantum theory: Max Planck and black body radiation

Thermal radiation is electromagnetic radiation emitted from the surface of an object due to the object's temperature. If an object is heated sufficiently, it starts to emit light at the red end of the spectrum — it is *red hot*. Heating it further causes the colour to change from red to yellow to blue to white, as light at shorter wavelengths (higher frequencies) begins to be emitted. It turns out that a perfect emitter is also a perfect absorber. When it is cold, such an object looks perfectly black, because it absorbs all the light that falls on it and emits none. Consequently, an ideal thermal emitter is known as a black body, and the radiation it emits is called black body radiIn the late 19th century, thermal radiation had been fairly well-characterized experimentally. How the wavelength at which the radiation is strongest changes with temperature is given by Wien's displacement law, and the overall power emitted per unit area is given by the Stefan–Boltzmann law. However, classical physics was unable to explain the relationship between temperatures and predominant frequencies of radiation. In fact, at short wavelengths, classical physics predicted that energy will be emitted by a hot body at an infinite rate. This result, which is clearly wrong, is known as the ultraviolet catastrophe. Physicists were searching for a single theory that explained why they got the experimental results that they did.



Correct values (green) contrasted against the classical values (Rayleigh-Jeans law; red and Wien approximation, blue).

The first model that was able to explain the full spectrum of thermal radiation was put forward by Max Planck in 1900.[4] He modeled the thermal radiation as being in equilibrium, using a set of harmonic oscillators. To reproduce the experimental results he had to assume that each oscillator produced an integer number of units of energy at its single characteristic frequency, rather than being able to emit any arbitrary amount of energy. In other words, the energy of each oscillator was "quantized."[note 2] The quantum of energy for each oscillator, according to Planck, was proportional to the frequency of the oscillator; the constant of proportionality is now known as the Planck constant. The Planck constant, usually written as *h*, has the value 6.63×10^{-34} J s, and so the energy

E of an oscillator of frequency *f* is given by

$$E = nhf, \quad \text{where} \quad n = 1, 2, 3, \ldots$$

Planck's law was the first quantum theory in physics, and Planck won the Nobel Prize in 1918 "in recognition of the services he rendered to the advancement of Physics by his discovery of energy quanta."[8] At the time, however, Planck's view was that quantization was purely a mathematical trick, rather than (as we now know) a fundamental change in our understanding of the world.

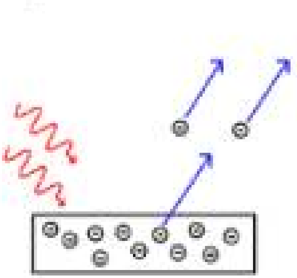
Photons: the quantization of light

In 1905, Albert Einstein took an extra step. He suggested that quantization was not just a mathematical trick: the energy in a beam of light occurs in individual packets, which are now called photons.[3] The energy of a single photon is given by its frequency multiplied by Planck's constant:

$$E = hf.$$

For centuries, scientists had debated between two possible theories of light: was it a wave or did it instead comprise a stream of tiny particles? By the 19th century, the debate was generally considered to have been settled in favour of the wave theory, as it was able to explain observed effects such as refraction, diffraction and polarization. James Clerk Maxwell had shown that electricity, magnetism and light are all manifestations of the same phenomenon: the electromagnetic field. Maxwell's equations, which are the complete set of laws of classical electromagnetism, describe light as waves: a combination of oscillating electric and magnetic fields. Because of the preponderance of evidence in favour of the wave theory, Einstein's ideas were met initially with great skepticism. Eventually, however, the photon model became favoured; one of the most significant pieces of evidence in its favour was its ability to explain several puzzling properties of the photoelectric effect, described in the following section. Nonetheless, the wave analogy remained indispensable for helping to understand other characteristics of light, such as diffraction.

The photoelectric effect



Light (red arrows, left) is shone upon a metal. If the light is of sufficient frequency (i.e. sufficient energy), electrons are ejected (blue arrows, right).

Main article: Photoelectric effect

In 1887 Heinrich Hertz observed that light can eject electrons from metal.[9] In 1902 Philipp Lenard discovered that the maximum possible energy of an ejected electron is related to the frequency of the light, not to its *intensity*; if the frequency is too low, no electrons are ejected regardless of the intensity. The lowest frequency of light that causes electrons to be emitted, called the threshold frequency, is different for every metal. This observation is at odds with classical electromagnetism, which predicts that the electron's energy should be proportional to the *intensity* of the radiation.[10]:24

Einstein explained the effect by postulating that a beam of light is a stream of particles (*photons*), and that if the beam is of frequency *f* then each photon has an energy equal to *hf*.[9] An electron is likely to be struck only by a single photon, which imparts at most an energy *hf* to the electron.[9] Therefore, the intensity of the beam has no effect; only its frequency determines the maximum energy that can be imparted to the electron.

To explain the threshold effect, Einstein argued that it takes a certain amount of energy, called the *work function*, denoted by φ, to remove an electron from the metal.[9] This amount of energy is different for each metal. If the energy of the photon is less than the work function then it does not carry sufficient energy to remove the electron from the metal. The threshold frequency, *f0*, is the frequency of a photon whose energy is equal to the work function:

$$\varphi = h f_0.$$

If *f* is greater than *f0*, the energy *hf* is enough to remove an electron. The ejected electron has a kinetic energy *EK* which is, at most, equal to the photon's energy minus the energy needed to dislodge the electron from the metal:

$$E_K = hf - \varphi = h(f - f_0).$$

Einstein's description of light as being composed of particles *extended* Planck's notion of quantised energy: a single photon of a given frequency *f* delivers an invariant amount of energy *hf*. In other words, individual photons can deliver more or less energy, but only depending on their frequencies. However, although the photon is a *particle* it was still being described as having the wave-like property of frequency. Once again, the particle account of light was being "compromised".[11][note 4]

The relationship between the frequency of electromagnetic radiation and the energy of each individual photon is why ultraviolet light can cause sunburn, but visible or infrared light cannot. A photon of ultraviolet light will deliver a high amount of energy—enough to contribute to cellular damage such as occurs in a sunburn. A photon of infrared light will deliver a lower amount of energy—only enough to warm one's skin. So an infrared lamp can warm a large surface, perhaps large enough to keep people comfortable in a cold room, but it cannot give anyone a sunburn.

If each individual photon had identical energy, it would not be correct to talk of a "high energy" photon. Light of high frequency could carry more energy only because of flooding a surface with more photons arriving *per second*. Light of low frequency could carry more energy only for the same reason. If it were true that all photons carry the same energy, then if you doubled the rate of photon delivery, you would double the number of energy units arriving each second. Einstein rejected that wave-dependent classical approach in favour of a particle-based analysis where the energy of the particle must be absolute and varies with frequency in discrete steps (i.e. is quantised). All photons of the same frequency have identical energy, and all photons of different frequencies have proportionally different energies.

In nature, single photons are rarely encountered. The sun emits photons continuously at all electromagnetic frequencies, so

they appear to propagate as a continuous wave, not as discrete units. The emission sources available to Hertz and Lennard in the 19th century shared that characteristic. A sun that radiates red light, or a piece of iron in a forge that glows red, may both be said to contain a great deal of energy. It might be surmised that adding continuously to the total energy of some radiating body would make it radiate red light, orange light, yellow light, green light, blue light, violet light, and so on in that order. But that is not so, as larger suns and larger pieces of iron in a forge would glow with colours more toward the violet end of the spectrum. To change the color of such a radiating body it is necessary to change its temperature. An increase in temperature changes the quanta of energy available to excite individual atoms to higher levels, enabling them to emit photons of higher frequencies.

The total energy emitted per unit of time by a sun (or by a piece of iron in a forge) depends on both the number of photons emitted per unit of time, as well as the amount of energy carried by each of the photons involved. In other words, the characteristic frequency of a radiating body is dependent on its temperature. When physicists were looking only at beams of light containing huge numbers of individual and virtually indistinguishable photons, it was difficult to understand the importance of the energy levels of individual photons. So when physicists first discovered devices exhibiting the photoelectric effect, they initially expected that a higher intensity of light would produce a higher voltage from the photoelectric device. Conversely, they discovered that strong beams of light toward the red end of the spectrum might produce no electrical potential at all, and that weak beams of light toward the violet end of the spectrum would produce higher and higher voltages. Einstein's idea that individual units of light may contain different amounts of energy, depending on their frequency, made it possible to explain such experimental results that had hitherto seemed quite

counter-intuitive.

Although the energy imparted by photons is invariant at any given frequency, the initial energy state of the electrons in a photoelectric device prior to absorption of light is not necessarily uniform. Anomalous results may occur in the case of individual electrons. For instance, an electron that was already excited above the equilibrium level of the photoelectric device might be ejected when it absorbed uncharacteristically low frequency illumination. Statistically, however, the characteristic behavior of a photoelectric device will reflect the behavior of the vast majority of its electrons, which will be at their equilibrium level. This point is helpful in comprehending the distinction between the study of individual particles in quantum dynamics and the study of massed particles in classical physics.

The quantization of matter: the Bohr model of the atom

By the dawn of the 20th century, it was known that atoms comprise a diffuse cloud of negatively-charged electrons surrounding a small, dense, positively-charged nucleus. This understanding suggested a model in which the electrons circle around the nucleus like planets orbiting a sun.[note 2] However, it was also known that the atom in this model would be unstable: according to classical theory orbiting electrons are undergoing centripetal acceleration, and should therefore give off electromagnetic radiation, the loss of energy also causing them to spiral toward the nucleus, colliding with it in a fraction of a second.

A second, related, puzzle was the emission spectrum of atoms. When a gas is heated, it gives off light only at discrete frequencies. For example, the visible light given off by hydrogen consists of four different colours, as shown in the picture below. By contrast, white light consists of a continuous emission across the whole range of visible frequencies.

In 1885 the Swiss mathematician Johann Balmer discovered that each wavelength λ (lambda) in the visible spectrum of hydrogen is related to some integer n by the equation

$$\lambda = B\left(\frac{n^2}{n^2-4}\right) \qquad n = 3, 4, 5, 6$$

where B is a constant which Balmer determined to be equal to 364.56 nm. Thus Balmer's constant was the basis of a system of discrete, i.e. quantised, integers.

In 1888 Johannes Rydberg generalized and greatly increased the explanatory utility of Balmer's formula. He predicted that λ is related to two integers n and m according to what is now known as the Rydberg formula:[11]

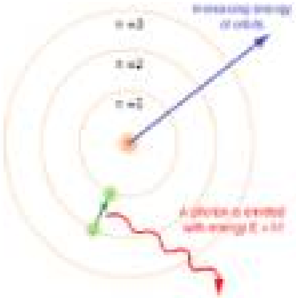
$$\frac{1}{\lambda} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right),$$

where R is the Rydberg constant, equal to 0.0110 nm−1, and n must be greater than m.

Rydberg's formula accounts for the four visible wavelengths of hydrogen by setting $m = 2$ and $n = 3, 4, 5, 6$. It also predicts additional wavelengths in the emission spectrum: for $m = 1$ and for $n > 1$, the emission spectrum should contain certain ultraviolet wavelengths, and for $m = 3$ and $n > 3$, it should also contain certain infrared wavelengths. Experimental observation of these wavelengths came two decades later: in 1908 Louis Paschen found some of the predicted infrared wavelengths, and in 1914 Theodore Lyman found some of the predicted ultraviolet wavelengths.

Bohr's model

Main article: Bohr model



The Bohr model of the atom, showing an electron quantum jumping to ground state $n = 1$.

In 1913 Niels Bohr proposed a new model of the atom that included quantized electron orbits.[14] In Bohr's model, electrons could inhabit only certain orbits around the atomic nucleus. When an atom emitted (or absorbed) energy, the electron did not move in a continuous trajectory from one orbit around the nucleus to another, as might be expected classically. Instead, the electron would jump instantaneously from one orbit to another, giving off the emitted light in the form of a photon.[15] The possible energies of photons given off by each element were determined by the differences in energy between the orbits, and so the emission spectrum for each element would contain a number of lines.[16]

Bohr theorised that the angular momentum, L, of an electron is quantised:

$$L = n\frac{h}{2\pi},$$

where n is an integer and h is the Planck constant. Starting from this assumption, Coulomb's law and the equations of circular motion show that an electron with n units of angular momentum will orbit a proton at a distance r given by

$$r = \frac{n^2 h^2}{4\pi^2 k_e m e^2}$$

,

where *ke* is the Coulomb constant, m is the mass of an electron, and e is the charge on an electron. For simplicity this is written as

$$r = n^2 a_0,$$

where *a0*, called the Bohr radius, is equal to 0.0529 nm. The Bohr radius is the radius of the smallest allowed orbit.

The energy of the electron[note 5] can also be calculated, and is given by

$$E = -\frac{k_e e^2}{2a_0}\frac{1}{n^2}$$

.

Thus Bohr's assumption that angular momentum is quantised means that an electron can only inhabit certain orbits around the nucleus, and that it can have only certain energies. A consequence of these constraints is that the electron will not crash into the nucleus: it cannot continuously emit energy, and it cannot come closer to the nucleus than *a0* (the Bohr radius).

An electron loses energy by jumping instantaneously from its original orbit to a lower orbit; the extra energy is emitted in the form of a photon. Conversely, an electron that absorbs a photon gains energy, hence it jumps to an orbit that is farther from the nucleus.

Each photon from glowing atomic hydrogen is due to an electron moving from a higher orbit, with radius r_n, to a lower orbit, r_m. The energy E_γ of this photon is the difference in the energies E_n and E_m of the electron:

$$E_\gamma = E_n - E_m = \frac{k_e e^2}{2a_0}\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

Since Planck's equation shows that the photon's energy is related to its wavelength by $E_\gamma = hc/\lambda$, the wavelengths of light that can be emitted are given by

$$\frac{1}{\lambda} = \frac{k_e e^2}{2a_0 hc}\left(\frac{1}{m^2} - \frac{1}{n^2}\right).$$

This equation has the same form as the Rydberg formula, and predicts that the constant R should be given by

$$R = \frac{k_e e^2}{2a_0 hc}.$$

Therefore the Bohr model of the atom can predict the emission spectrum of hydrogen in terms of fundamental constants.[note 7] However, it was not able to make accurate predictions for multi-electron atoms, or to explain why some spectral lines are brighter than others.

Wave-particle duality

In 1924, Louis de Broglie proposed the idea that just as light has both wave-like and particle-like properties, matter also has wave-like properties.[17] The wavelength, λ, associated with a particle is related to its momentum, p through the Planck constant h:[15][16]

$$p = \frac{h}{\lambda}.$$

The relationship, called the de Broglie hypothesis, holds for all types of matter. Thus all matter exhibits properties of both particles and waves.

Three years later, the wave-like nature of electrons was demonstrated by showing that a beam of electrons could exhibit diffraction, just like a beam of light. At the University of Aberdeen, George Thomson passed a beam of electrons through a thin metal film and observed the predicted diffraction patterns. At Bell Labs, Davisson and Germer guided their beam through a crystalline grid. Similar wave-like phenomena were later shown for atoms and even small molecules. De Broglie was awarded the Nobel Prize for Physics in 1929 for his hypothesis; Thomson and Davisson shared the Nobel Prize for Physics in 1937 for their experimental work.

The concept of wave-particle duality says that neither the classical concept of "particle" nor of "wave" can fully describe the behavior of quantum-scale objects, either photons or matter. Indeed, astrophysicist A.S. Eddington proposed in 1927 that "We can scarcely describe such an entity as a wave or as a particle; perhaps as a compromise we had better call it a 'wavicle' ".[20] (This term was later popularised by mathematician Banesh Hoffmann.)[21]:172 Wave-particle duality is an example of the principle of complementarity in quantum physics. An elegant example of wave-particle duality, the double slit experiment, is discussed in the section below.

De Broglie's treatment of quantum events served as a jumping off point for Schrödinger when he set about to construct a wave equation to describe quantum theoretical events.

The double-slit experiment

Main article: Double-slit experiment

Light from one slit interferes with light from the other, producing an interference pattern (the 3 fringes shown at the right).

In the double-slit experiment as originally performed by Thomas Young and Augustin Fresnel in 1827, a beam of light is directed through two narrow, closely spaced slits, producing an interference pattern of light and dark bands on a screen. If one of the slits is covered up, one might naively expect that the intensity of the fringes due to interference would be halved everywhere. In fact, a much simpler pattern is seen, a simple diffraction pattern. Closing one slit results in a much simpler pattern diametrically opposite the open slit. Exactly the same behaviour can be demonstrated in water waves, and so the double-slit experiment was seen as a demonstration of the wave nature of light.

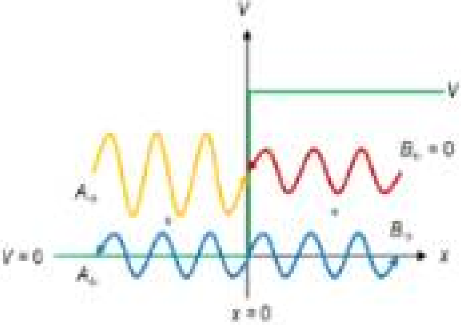
The diffraction pattern produced when light is shone through one slit (top) and the interference pattern produced by two slits (bottom). The interference pattern from two slits is much more complex, demonstrating the wave-like propagation of light.

The double-slit experiment has also been performed using electrons, atoms, and even molecules, and the same type of interference pattern is seen. Thus it has been demonstrated that all matter possesses both particle and wave characteristics.

Even if the source intensity is turned down so that only one particle (e.g. photon or electron) is passing through the apparatus at a time, the same interference pattern develops over time. The quantum particle acts as a wave when passing through the double slits, but as a particle when it is detected. This is a typical feature of quantum complementarity: a quantum particle will act as a wave when we do an experiment to measure its wave-like properties, and like a particle when we do an experiment to measure its particle-like properties. Where on the detector screen any individual particle shows up will be the result of an entirely random process

Solution of Schrödinger equation for a step potential

In quantum mechanics and scattering theory, the one dimensional step potential is an idealized system used to model incident, reflected and transmitted matter waves. The problem consists of solving the time-independent Schrödinger equation for a particle with a step-like potential in one dimension. Typically, the potential is modelled as a Heaviside step fuSchrödinger equation and potential function



Scattering at a finite potential step of height V_0, shown in green. The amplitudes and direction of left and right moving waves are indicated. Yellow is the incident wave, blue are reflected and transmitted, red does not occur. $E > V_0$ for this figure

The time-independent Schrödinger equation for the wave function

$$\psi(x)$$

is:

$$H\psi(x) = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x),$$

where *H* is the Hamiltonian, ħ is the reduced Planck constant, *m* is the mass, *E* the energy of the particle. The step potential is simply the Heaviside step function:

$$V(x) = \Theta(x) = \begin{cases} 0 & x < 0 \\ 1 & x > 0 \end{cases}$$

where *V*0 is the height of the barrier.

The barrier is positioned at *x* = 0, though any position *x*0 may be chosen without changing the results, simply by shifting position of the step by −*x*0.

The first term in the Hamiltonian,

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi$$

is the kinetic energy of the particle.

Solution

The step divides space in two parts: *x* < 0 and *x* > 0. In any of these parts the potential is constant, meaning the particle is quasi-free, and the solution of the Schrödinger equation can be written as a superposition of left and right moving waves (see free particle)

$$\psi_1(x) = \frac{1}{\sqrt{k_1}}\left(A_{\rightarrow}e^{ik_1x} + A_{\leftarrow}e^{-ik_1x}\right) \quad x < 0$$

,

$$\psi_2(x) = \frac{1}{\sqrt{k_2}}\left(B_{\rightarrow}e^{ik_2x} + B_{\leftarrow}e^{-ik_2x}\right) \quad x > 0$$

where subscripts 1 and 2 denote the regions *x* < 0 and *x* > 0 respectively, the subscripts (→) and (←) on the amplitudes *A* and *B* denote the direction of the particle's velocity vector: right and left respectively.

The coefficients 1/√k1 and 1/√k2 are normalization constants. The wave vectors related to the energy by

$$k_1 = \sqrt{2mE/\hbar^2}$$

,

$$k_2 = \sqrt{2m(E - V_0)/\hbar^2}$$

both of which have the same form as the De Broglie relation (in one dimension)

$$p = \hbar k$$

.

Boundary conditions

The coefficients *A*, *B* have to be found from the boundary conditions of the wave function at *x* = 0. The wave function and its derivative have to be continuous everywhere, so:

$$\psi_1(0) = \psi_2(0)$$

,

$$\frac{d}{dx}\psi_1(0) = \frac{d}{dx}\psi_2(0)$$

.

Inserting the wave functions, the boundary conditions give the following restrictions on the coefficients

$$\sqrt{k_2}(A_{\rightarrow} + A_{\leftarrow}) = \sqrt{k_1}(B_{\rightarrow} + B_{\leftarrow})$$

$$\sqrt{k_1}(A_{\rightarrow} - A_{\leftarrow}) = \sqrt{k_2}(B_{\rightarrow} - B_{\leftarrow})$$

Transmission and reflection

It is useful to compare the situation to the classical case. In both cases, the particle behaves as a free particle outside of the barrier region. A classical particle with energy *E* larger than the barrier height *V0* will be slowed down but never reflected by the barrier, while a classical particle with $E < V0$ incident on the barrier from the left would always be reflected.

To study the quantum case, let us consider the following situation: a particle incident on the barrier from the left side $A\rightarrow$. It may be reflected ($A\leftarrow$) or transmitted $B\rightarrow$. Here and in the following assume $E > V0$.

To find the amplitudes for reflection and transmission for incidence from the left, we set in the above equations $A\rightarrow = 1$ (incoming particle), $A\leftarrow = R$ (reflection), $B\leftarrow = 0$ (no incoming particle from the right) and $B\rightarrow = T$ (transmission). We then solve for T and R.

The result is:

$$\sqrt{T} = \frac{2\sqrt{k_1 k_2}}{k_1 + k_2}$$

$$\sqrt{R} = \frac{k_1 - k_2}{k_1 + k_2}.$$

The model is symmetric with respect to a parity transformation and at the same time interchange $k1$ and $k2$. For incidence from the right we have therefore the amplitudes for transmission and reflection

$$\sqrt{T'} = \sqrt{T} = \frac{2\sqrt{k_1 k_2}}{k_1 + k_2}$$

$$\sqrt{R'} = -\sqrt{R} = \frac{k_2 - k_1}{k_1 + k_2}.$$

Potential well

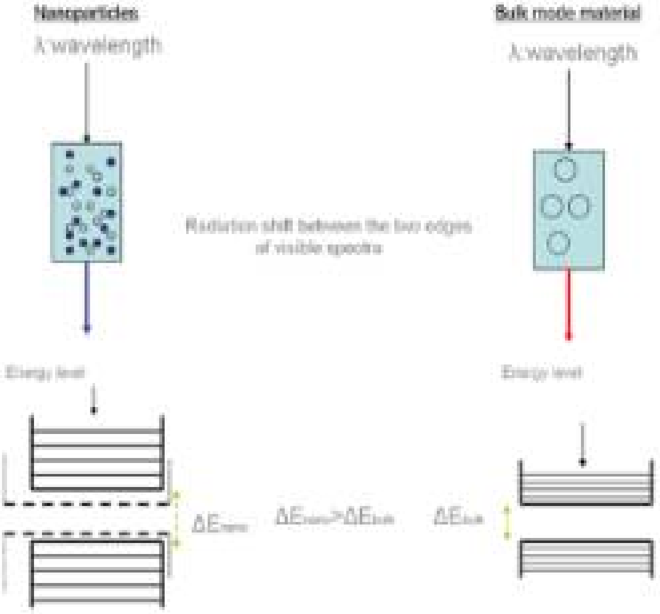
A **potential well** is the region surrounding a local minimum of potential energy. Energy captured in a potential well is unable to convert to another type of energy (kinetic energy in the case of a gravitational potential well) because it is captured in the local minimum of a potential well. Therefore, a body may not proceed to the global minimum of potential energy, as it would naturally tend to due to entropy.

energy may be released from a potential well if sufficient energy is added to the system such that the local maximum is surmounted. In quantum physics, potential energy may escape a potential well without added energy due to the probabilistic characteristics of quantum particles; in these cases a particle may be imagined to tunnel *through* the walls of a potential well.

The graph of a 2D potential energy function is a potential energy surface that can be imagined as the Earth's surface in a landscape of hills and valleys. Then a *potential well* would be a valley surrounded on all sides with higher terrain, which thus could be filled with water (e.g., be a lake) without any water flowing away toward another, lower minimum (e.g. sea level).

In the case of gravity, the region around a mass is a gravitational potential well, unless the density of the mass is so low that tidal forces from other masses are greater than the gravity of the body itself.

A potential hill is the opposite of a potential well, and is the region surrounding a local maximum.



Quantum confinement is responsible for the increase of energy difference between energy states and band gap. A phenomenon tightly related with the optical and electronic properties of the materials.

The quantum confinement effect can be observed once the diameter of the particle is of the same magnitude as the wavelength of the electron wave function.[1] When materials are this small, their electronic and optical properties deviate substantially from those of bulk materials.[2]

A particle behaves as if it were free when the confining dimension is large compared to the wavelength of the particle. During this state, the bandgap remains at its original energy due to a continuous energy state. However, as the confining dimension decreases and reaches a certain limit, *typically in nanoscale*, the energy spectrum turns to discrete. As a result, the bandgap becomes size dependent. This ultimately results in a blue shift in optical illumination as the size of the particles decreases.

Specifically, the effect describes the phenomenon resulting from electrons and electron holes being squeezed into a dimension that approaches a critical quantum measurement, called the exciton Bohr radius. In current application, a quantum dot such as a small sphere confines in three dimensions, a quantum wire confines in two dimensions, and a quantum well confines only in one dimension. These are also known as zero-, one- and two-dimensional potential wells, respectively. In these cases they refer to the number of dimensions in which a confined particle can act as a free carrier. See *external links*, below, for application examples in biotechnology and solar cell technology.

Quantum mechanics view

See also: Particle in a box

The electronic and optical properties of materials are affected by size and shape. Well-established technical achievements including quantum dots were derived from size manipulation and investigation for their theoretical corroboration on quantum confinement effect.[3] The major part of the theory is the behaviour of the exciton ensembles more like an atom as its surrounding space shortens. A rather good approximation of an exciton's behaviour is the 3-D model of a particle in a box.[4] The solution of this problem provides a sole mathematical connection between energy states and the dimension of space. It is obvious that decreasing the volume or the dimensions of the available space, the energy of the states increase. Shown in the diagram is the change in electron energy level and bandgap between nanomaterial and its bulk state.

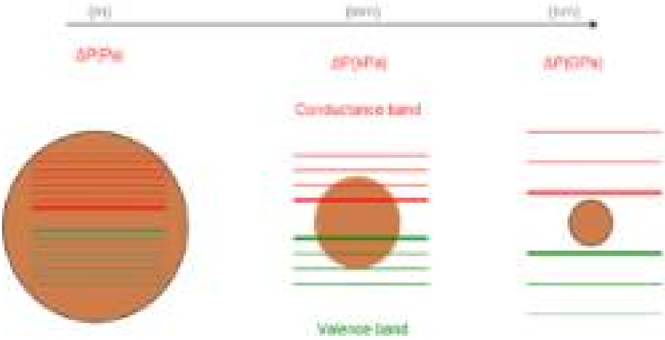
The following equation shows the relationship between energy level and dimension spacing:

$$\psi_{n_x,n_y,n_z} = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

$$E_{n_x,n_y,n_z} = \frac{\hbar^2 \pi^2}{2m} \left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 + \left(\frac{n_z}{L_z}\right)^2\right]$$

Research results[3] provide an alternative explanation of the shift of properties at nanoscale. In the bulk phase, the surfaces appear to control some of the macroscopically observed properties. However in nanoparticles, surface molecules do not obey the expected configuration in space. As a result, surface tension changes tremendously.

Classical mechanics view



The classical mechanic explanation employs Young-Laplace law to provide evidence on how Pressure drop advances from scale to scale.

The Young-Laplace equation can give a background on the investigation of the scale of forces applied to the surface molecules:

$$
\begin{aligned}
\Delta p &= \gamma \nabla \cdot \hat{n} \\
&= 2\gamma H \\
&= \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)
\end{aligned}
$$

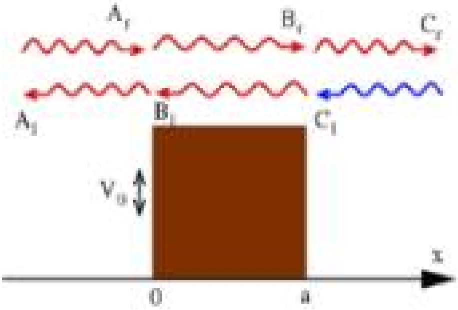
Under the assumption of spherical shape R1=R2=R and resolving Young Laplace equation for the new radii R(nm) we estimate the new ΔP(GPa). The smaller the R, the greater the pressure it is. The increase in pressure at the nanoscale results in strong forces toward the interior of the particle. Consequently, the molecular structure of the particle appears to be different from the bulk mode, especially at the surface. These abnormalities at the surface are responsible for changes of inter-atomic interactions and bandgap.[6][7]

Rectangular potential barrier

In quantum mechanics, the rectangular (or, at times, square) potential barrier is a standard one-dimensional problem that demonstrates the phenomena of wave-mechanical tunneling (also called "quantum tunneling") and wave-mechanical reflection. The problem consists of solving the one-dimensional time-independent Schrödinger equation for a particle encountering a rectangular potential energy barrier. It is usually assumed, as here, that a free particle impinges on the barrier from the left.

Although a particle hypothetically behaving as a point mass would be reflected, a particle actually behaving as a matter wave has a finite probability that it will penetrate the barrier and continue its travel as a wave on the other side. In classical wave-physics, this effect is known as evanescent wave coupling. The likelihood that the particle will pass through the barrier is given by the transmission coefficient, whereas the likelihood that it is reflected is given by the reflection coefficient. Schrödinger's wave-equation allows these coefficients to be calculated.

Calculation



The time-independent Schrödinger equation for the wave function

$\psi(x)$

reads

$$H\psi(x) = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x)$$

where

H

is the Hamiltonian,

$\hbar$

is the (reduced) Planck constant,

m

is the mass,

E

the energy of the particle and

$$V(x) = V_0[\Theta(x) - \Theta(x-a)]$$

is the barrier potential with height

$V_0 > 0$

and width

a

.

$$\Theta(x) = 0,\ x < 0;\ \Theta(x) = 1,\ x > 0$$

is the Heaviside step function.

The barrier is positioned between

$x = 0$

and

$x = a$

. The barrier can be shifted to any

x

position without changing the results. The first term in the Hamiltonian,

$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi$

is the kinetic energy.

The barrier divides the space in three parts (

$x < 0, 0 < x < a, x > a$

). In any of these parts, the potential is constant, meaning that the particle is quasi-free, and the solution of the Schrödinger equation can be written as a superposition of left and right moving waves (see free particle). If

$E < V_0$

$$\psi_L(x) = A_r e^{ik_0 x} + A_l e^{-ik_0 x} \quad x < 0$$

$$\psi_C(x) = B_r e^{ik_1 x} + B_l e^{-ik_1 x} \quad 0 < x < a$$

$$\psi_R(x) = C_r e^{ik_0 x} + C_l e^{-ik_0 x} \quad x > a$$

where the wave numbers are related to the energy via

$$k_0 = \sqrt{2mE/\hbar^2} \qquad x < 0 \quad or \quad x > a$$

$$k_1 = \sqrt{2m(E - V_0)/\hbar^2} \quad 0 < x < a$$

.

The index r/l on the coefficients A and B denotes the direction of the velocity vector. Note that, if the energy of the particle is below the barrier height,

k_1

becomes imaginary and the wave function is exponentially decaying within the barrier. Nevertheless, we keep the notation r/l even though the waves are not propagating anymore in this case. Here we assumed

$E \neq V_0$

. The case

$E = V_0$

is treated below.

The coefficients

A, B, C

have to be found from the boundary conditions of the wave function at

$x = 0$

and

$x = a$

. The wave function and its derivative have to be continuous everywhere, so.

$$\psi_L(0) = \psi_C(0)$$

$$\frac{d}{dx}\psi_L(0) = \frac{d}{dx}\psi_C(0)$$

$$\psi_C(a) = \psi_R(a)$$

$$\frac{d}{dx}\psi_C(a) = \frac{d}{dx}\psi_R(a)$$

Inserting the wave functions, the boundary conditions give the following restrictions on the coefficients

$$A_r + A_l = B_r + B_l$$

$$ik_0(A_r - A_l) = ik_1(B_r - B_l)$$

$$B_r e^{iak_1} + B_l e^{-iak_1} = C_r e^{iak_0} + C_l e^{-iak_0}$$

$$ik_1(B_r e^{iak_1} - B_l e^{-iak_1}) = ik_0(C_r e^{iak_0} - C_l e^{-iak_0})$$

E = V0

If the energy equals the barrier height, the solutions of the Schrödinger equation in the barrier region are not exponentials anymore but linear functions of the space coordinate

$$\psi_C(x) = B_1 + B_2 x \quad 0 < x < a.$$

The complete solution of the Schrödinger equation is found in the same way as above by matching wave functions and their derivatives at

$x = 0$

and

$x = a$

. That results in the following restrictions on the coefficients:

$$A_r + A_l = B_1$$

$$ik_0(A_r - A_l) = B_2$$

$$B_1 + B_2 a = C_r e^{iak_0} + C_l e^{-iak_0}$$

$$B_2 = ik_0(C_r e^{iak_0} - C_l e^{-iak_0})$$

.

Transmission and reflection

At this point, it is instructive to compare the situation to the classical case. In both cases, the particle behaves as a free particle outside of the barrier region. A classical particle with energy

E

larger than the barrier height

V_0

would *always* pass the barrier, and a classical particle with

$E < V_0$

incident on the barrier would *always* get reflected.

To study the quantum case, consider the following situation: a particle incident on the barrier from the left side (

A_r

). It may be reflected (

A_l

) or transmitted (

C_r

).

To find the amplitudes for reflection and transmission for incidence from the left, we put in the above equations

$A_r = 1$

(incoming particle),

$A_l = r$

(reflection),

C_l

=0 (no incoming particle from the right), and

$C_r = t$

(transmission). We then eliminate the coefficients

B_l, B_r

from the equation and solve for

r

and

t

.

The result is

$$t = \frac{4k_0k_1e^{-ia(k_0-k_1)}}{(k_0+k_1)^2 - e^{2iak_1}(k_0-k_1)^2}$$

$$r = \frac{(k_0^2-k_1^2)\sin(ak_1)}{2ik_0k_1\cos(ak_1) + (k_0^2+k_1^2)\sin(ak_1)}.$$

Due to the mirror symmetry of the model, the amplitudes for incidence from the right are the same as those from the left. Note that these expressions hold for any energy

$E > 0$


Thank you