Principles of quantum mechanics

In order to understand the behavior of individual atoms and molecules and how they interact with radiation (atomic and molecular spectroscopy), one needs to know how particles move in response to the forces acting to them.

Laws of **classical mechanics** – Isaac Newton, 17th century – explain the motion of everyday objects and planets.

Can the motion of atomic and subatomic particles be expressed using the laws of classical mechanics? **NO!!!**

By the end of 19th century – experimental evidence accumulated – **classical mechanics failed** when it was applied to **very small particles**.

1926 – appropriate concepts were discovered and equations describing the motion of small particles were derived – **quantum mechanics**.

Equations of classical mechanics

$E = E_k + V$ total energy of a particle $\quad E_k \quad$ kinetic energy

$V \qquad$ potential energy $\qquad E_k = \frac{1}{2} mv^2, \qquad E = \frac{1}{2} mv^2 + V$

$p = mv \qquad$ linear momentum $\qquad E = \frac{p^2}{2m} + V \quad v = dx/dt,\ x - \text{coordinate}$

$$\frac{dx}{dt} = \left(\frac{2(E-V)}{m} \right)^{1/2}$$ differential equation for coordinate as function of time

The solution for a given total energy gives the position of the particle as a function of time. If we know V as a function of x, we can calculate the speed and the momentum of the particle.

The equation allows us to predict the trajectory of the particle exactly.

Let V a uniform constant potential independent of x and p

For $V = 0$ $\qquad \dfrac{dx}{dt} = \left(\dfrac{2E}{m}\right)^{1/2}$ $\qquad\qquad x(t) = x(0) + \left(\dfrac{2E}{m}\right)^{1/2} t$

For the constant energy E, $E = \dfrac{p(0)^2}{2m}$, $\quad x(t) = x(0) + \dfrac{p(0)t}{m}$ $\qquad\qquad p(t) = m\dfrac{dx}{dt} = p(0)$

Newton's second law of motion:

$$\frac{dp}{dt} = F \qquad\qquad m\frac{d^2x}{dt^2} = F$$

If we know the force acting everywhere at all times, we can solve the above equations and to obtain the trajectory.

Example: a particle is subjected to a force F for a time period τ, and is then allowed to travel freely.

$$\frac{dp}{dt} = F, \quad \text{constant for } 0 < t < \tau \qquad \frac{dp}{dt} = 0, \quad \text{for } t \geq \tau \qquad p(t) = p(0) + Ft \quad \text{for } 0 < t < \tau$$

$$p(\tau) = p(0) + F\tau \qquad\qquad\qquad \text{For } p = 0 \qquad\qquad\qquad E = \frac{F^2\tau^2}{2m}$$

The total energy of the accelerated particle is increased by E by the force. Since the applied force and time for which it acts may take any value, the energy may be increased by any value.

Rotational motion

$J = I\omega$ **angular momentum** of the particle

ω angular velocity, I moment of inertia, $I = mr^2$, T torque

$$\frac{dJ}{dt} = T \qquad\qquad\qquad E = \frac{T^2 \tau^2}{2I}$$

Harmonic oscillator

A particle that experiences a restoring force proportional to its displacement: a spring or two atoms connected with a bond, etc.

$F = -kx,$ k **force constant**

$$m\frac{d^2 x}{dt^2} = -kx \qquad x = A\sin\omega t \qquad p = m\omega A\cos\omega t \qquad\qquad \omega = \left(\frac{k}{m}\right)^{1/2}$$

Position of the particle varies **harmonically** (as $\sin\omega t$)

$\upsilon = \dfrac{\omega}{2\pi}$ - frequency; A - amplitude (maximal displacement)

Total energy of harmonic oscillator

$$F = \frac{-dV}{dx} \qquad V = \frac{1}{2}kx^2 \qquad \text{if } V = 0 \text{ at } x = 0 \qquad E = \frac{p^2}{2m} + V = \frac{p^2}{2m} + \frac{1}{2}kx^2 = \frac{1}{2}kA^2$$

The energy of the oscillating particle can be raised to any value by a suitably controlled impulse that knocks it to amplitude A. The frequency of the motion depends only on the structure of oscillator (force constant k and mass m) and is independent of the energy.

The amplitude defines the energy, $E = \dfrac{1}{2}kA^2$, and is independent of the frequency.

Classical physics:

1) predicts a precise trajectory, $x(t)$ and $p(t)$;
2) allows the translational, rotational, and vibrational modes of motion to be excited to *any* energy simply by controlling the forces, torques, and impulses we apply.

Failures of classical physics

Classical mechanics provides only an approximate description of the motion of particles, and fails when small masses, small moments of inertia, and small transfers of energy are involved.

Examples of failures: 1. **Black-body radiation**

A hot object emits light (electromagnetic radiation). At high temperatures, a significant portion of the radiation is in the visible region and, as the temperature is raised, a higher proportion of short-wavelength blue light is generated.

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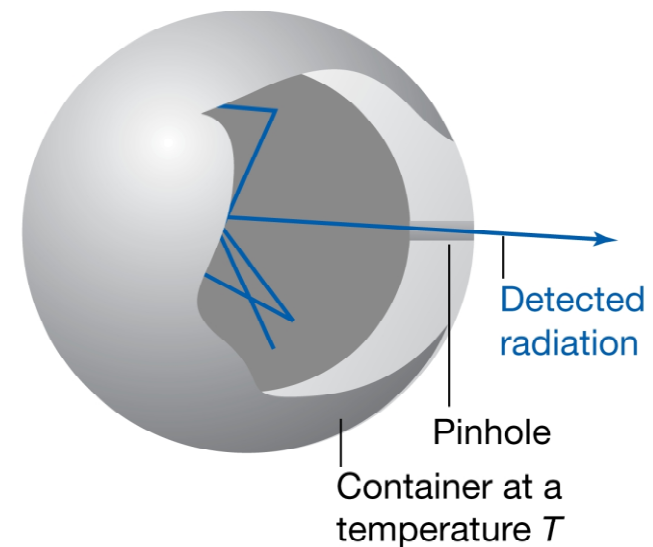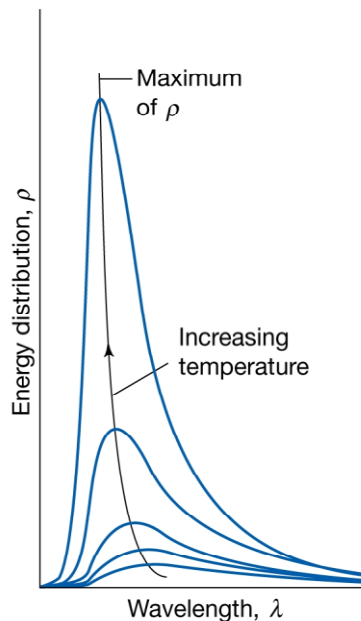
A **black body** – an object capable of emitting and adsorbing all frequencies of radiation uniformly. A pinhole in an empty container at constant temperature. Any radiation leaking out of the hole has been absorbed and re-emitted inside so many times that it has come to thermal equilibrium with the walls.

Wien's displacement law (1893): $\qquad\qquad T\lambda_{max} = \text{constant}$

Stefan's law (1879): $\qquad\qquad\qquad\qquad E = aT^4$

E – the total energy density, the total energy per unit volume in the electromagnetic field.

     Rayleigh (1900): electromagnetic field is a collection of harmonic oscillators. The presence of light at a certain frequency ν (and therefore of wavelength $\lambda = c/\nu$) is due to the excitation of the electromagnetic oscillator of that frequency. Rayleigh's calculations consisted of two parts:

1)   He calculated the number of oscillators in an enclosure that corresponds to a wavelength λ.

$$N_\lambda = \frac{8\pi}{\lambda^4}$$

2)   According to the **classical equipartition principle**, each oscillator is associated with an energy kT. $\qquad dE = \rho d\lambda \qquad \rho = \dfrac{8\pi kT}{\lambda^4} \qquad \rho$ - the energy per unit volume per unit wavelength.

The Rayleigh-Jeans law thus predicts that oscillators of extremely small wavelengths (high frequency, corresponding to ultraviolet light, X-rays, and even γ-rays) should be strongly excited even at room temperature. Absurd!!! – according to classical physics, objects should glow in the dark: there should in fact be no darkness.
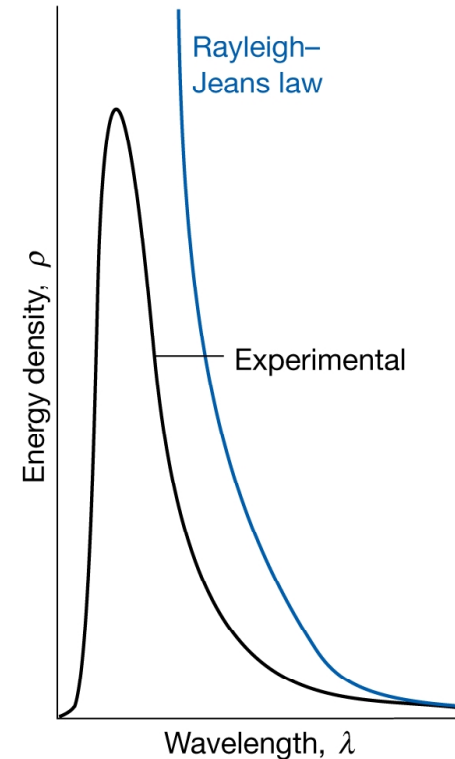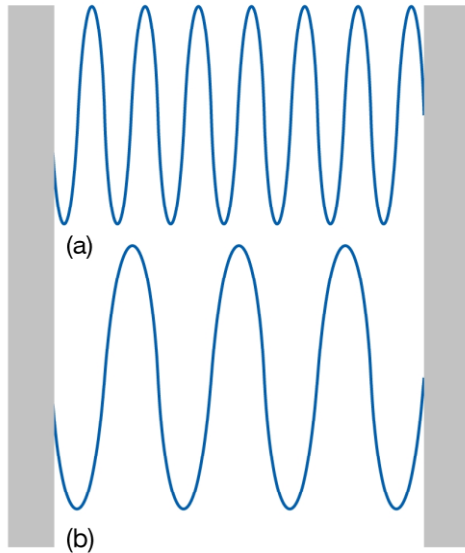
Max Planck (1900) found that he could account for experimental observations by proposing that the energy of each electromagnetic oscillator is limited to **discrete** values and cannot be varied arbitrarily. The limitation of energy to discrete values is called the **quantization** of energy (Latin word *quantum*, amount). Planck proposed that the permitted energies of an oscillator of frequency ν are integral multiplies of $h\nu$. h is fundamental constant now known as **Planck's constant**. $\qquad E = nh\nu \qquad\qquad h = 6.626 \times 10^{-34}$ J s

Since an oscillator of frequency ν can possess only the energies 0, $h\nu$, $2h\nu$, ..., a ray of light of that frequency can be thought of as consisting of 0, 1, 2, ... particles, where each particle has an energy $h\nu$. These particles are called **photons**. If the electromagnetic field of frequency ν has an energy E in some region, the number of photons of that frequency in the region is $E/h\nu$.

Why Planck's hypothesis was successful? The atoms in the walls of the black body are in the thermal motion, and this motion excites the oscillators of the electromagnetic field.

Classical mechanics: all the oscillators of the field share equally in the energy supplied by the walls, and so even the highest frequencies are excited. **Quantum mechanics**: the oscillators are excited only if they can acquire an energy of at least $h\nu$. This is too large for the walls to supply in the case of the high-frequency oscillators, and so the latter remains unexcited. The effect of quantization is to eliminate the contribution from high-frequency oscillators, for they cannot be excited with the energy available.

According to detailed calculations (Physical Chemistry, Chapter 19), the energy density in the range λ to $\lambda+d\lambda$ is given by the **Planck distribution**: $dE = \rho d\lambda$ $\rho = \dfrac{8\pi hc}{\lambda^5}\left\{\dfrac{1}{e^{hc/\lambda kT}-1}\right\}$

The value of h was obtained as adjustable parameter in the theory, through a best fit of experimental data. $\rho \to 0$ as $\lambda \to 0$ or $\nu \to \infty$

Rayleigh-Jeans law: for long wavelengths, $hc/\lambda kT \ll 1$, $e^{hc/\lambda kT}-1 = 1+\dfrac{hc}{\lambda kT}+...-1 \approx \dfrac{hc}{\lambda kT}$,

$\rho \to \dfrac{8\pi kT}{\lambda^4}$ as $\lambda \to \infty$ or $\nu \to 0$ Also, $\rho \to \dfrac{8\pi kT}{\lambda^4}$ as $h \to 0$

The Planck distribution also accounts for the Stefan and Wien laws:

$E = \int \rho d\lambda = aT^4$ with $a = \dfrac{4\sigma}{c}$ and $\sigma = \dfrac{\pi^2 k^4}{60c^2 h^3}$

The Wien law is obtained by looking for the wavelength at which $dE/d\lambda = 0$ $\lambda_{max}T = \dfrac{hc}{5k}$

Accounting for black body radiation involves understanding how energy is taken up by the electromagnetic field. On the other hand, accounting for the heat capacities of solids involves examining how energy is taken up by the vibrations of atoms.

Heat capacities

If classical physics were valid, the mean energy of vibration of each atom in one dimension in a solid would be kT. Since the N atoms in a block are free to vibrate in three dimensions, the total vibrational energy of a block is expected to be $3NkT$. Therefore, the contribution of the vibrational energy to the molar internal energy is $$U_m = 3N_A kT = 3RT$$

Since the heat capacity at constant volume is $C_V = (\partial U_m / \partial T)_V$, classical physics predicts that $C_V = 3R$

Dulong and Petit's law: molar heat capacities of all monoatomic solids are the same (~25 kJ K^{-1} mol^{-1}).

All metals were found to have molar heat capacities lower than $3R$ at low temperatures and the values approach zero as the $T \to 0$. Einstein assumed that each atom oscillated about its equilibrium position with a single frequency v, and invoked Planck's hypothesis that the energy of any oscillation is nhv with integer n.

Molar vibrational energy of the metal: $$U_m = \frac{3N_A hv}{e^{hv/kT-1}}$$

Einstein formula: $C_V = 3R \left(\frac{hv}{kT}\right)^2 \left\{\frac{e^{hv/2kT}}{e^{hv/kT}-1}\right\}^2$. For $kT \gg hv$, $C_V = 3R \left(\frac{hv}{kT}\right)^2 \left\{\frac{1+hv/2kT+...}{1+hv/kT...-1}\right\}^2 = 3R$

At low temperatures, $e^{hv/kT} \to \infty$ implying that $C_V \to 0$.

Physical reason: at low temperatures only a few oscillators possess enough energy to begin oscillating. At higher temperatures, there is enough energy available for all oscillators to become active: all 3N oscillators contribute, and the heat of capacity approaches its classical value. **Quantization must be introduced in order to explain thermal properties of solids.**

Photoelectric effect

Electrons are ejected from metals when they are exposed to ultraviolet radiation:
1) No electrons are ejected, regardless of the intensity of the radiation, unless its frequency exceeds a certain threshold value characteristic of the metal.
2) The kinetic energy of the ejected electrons is linearly proportional to the frequency of the incident radiation but independent of its intensity.
3) Even at low light intensity, electrons are ejected immediately if the frequency is above threshold.

If the photon energy is $h\nu$, the kinetic energy of the ejected electron $\qquad \dfrac{1}{2}m_e v^2 = h\nu - \Phi$

where Φ is the work function of the metal, the energy required to remove the electron.

The expression predicts that the kinetic energy of an ejected electron should be proportional to the frequency. It therefore provides another route to measure h, since a plot of kinetic energy of the photoelectron should give a straight line of slope h.

The photoelectric effect indicates a corpuscular nature of light – the wave theory of light has to be modified.

Compton effect

A. Compton (1923): when X-rays are scattered from electrons, their wavelength is slightly increased. According to classical physics, the electron to be accelerated by the electric field, and many different wavelengths are to be expected in the scattered ray. In fact, the wavelength is increased by a single definite amount that depends only on the angle through which the light is scattered and is independent of the wavelength of the incident radiation:

$$\delta\lambda = \lambda_C (1 - \cos\theta) \qquad\qquad \lambda_C = 2.43 \text{ pm - Compton wavelength of the electron}$$

The maximum wavelength shift, 4.86 pm, occurs for 180°. The photon theory can explain these observations if we suppose that, as well as having an energy, a photon of light of frequency ν and wavelength λ also has a linear momentum

$$p = \frac{h\nu}{c} \qquad\qquad p = \frac{h}{\lambda}$$

If the photon has a momentum, its scattering can be treated as a collision between a particle of momentum h/λ and another of mass m_e. From conservation of energy and linear momentum, one obtains

$$\lambda_C = \frac{h}{m_e c} = 2.246 \text{pm}$$

Diffraction of electrons

The photoelectric effect and the Compton effect both show that the light has the attributes of particles. On the other hand experiments carried out in 1925 forced people to think that **matter is wavelike**.

Davidson and Germer: diffraction of electrons by a crystal.
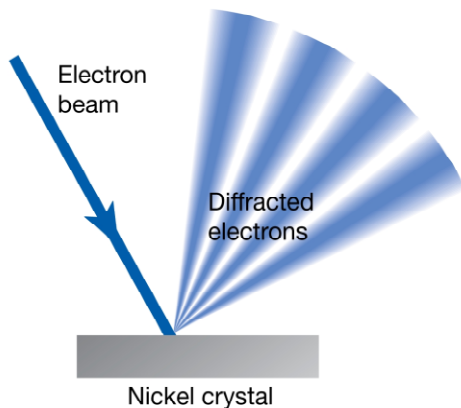
Depending on whether the interference is constructive or destructive, the result is a region of enhanced or diminished intensity.

Diffraction is a characteristic property of waves because it occurs when there is interference between their peaks and troughs.

Since then, similar experiments have been repeated for other particles (including molecular hydrogen) and showed clearly that particles have wavelike properties. When examined on an atomic scale, the concepts of particle and wave melt together, particles taking on the characteristics of waves, and waves the characteristics of particles.

de Broglie suggested that any particle, not only photons, traveling with a momentum p should have in some sense a wavelength given by the **de Broglie relation**:

$$\lambda = \frac{h}{p}$$
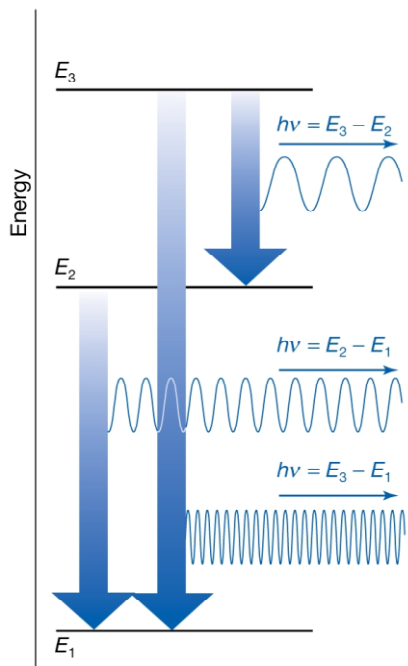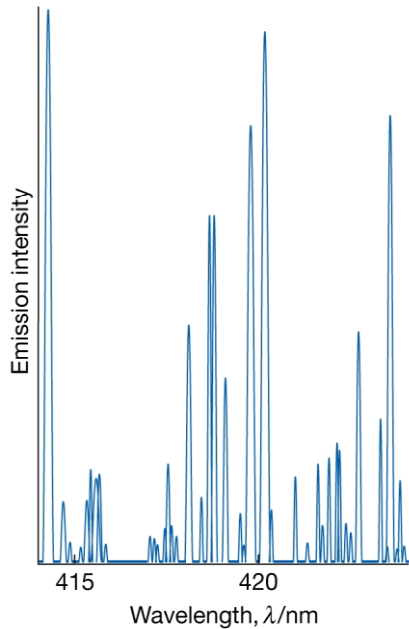
Atomic and molecular spectra

The mostly directly compelling evidence for the quantization of energy comes from the observation of the frequencies of radiation absorbed and emitted by atoms and molecules.
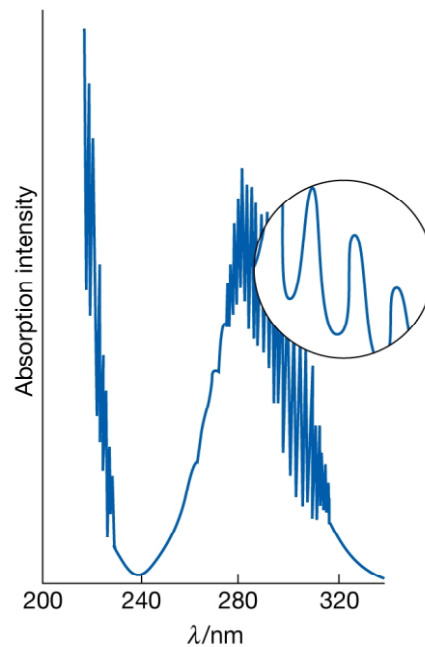
The spectrum of light emitted by excited mercury atoms consists of radiation at a series of discrete frequencies (spectral lines). A part of the ultraviolet absorption spectrum of SO_2. When a molecule changes its state, it does so by absorbing light at definite frequencies. This suggests that it can possess only discrete energies, not an arbitrary energy. Radiation is emitted and absorbed at a series of discrete frequencies. Therefore, the energy of the atoms and molecules is also confined to discrete values, for then energy can be discarded or absorbed only in discrete amounts. If the energy of an atom decreases by ΔE, the energy is carried away as a photon of frequency $\nu = \Delta E/h$, and a line appears in the spectrum. Classical mechanics failed in its attempts to account for the appearance of spectra and other phenomena.

The basic concepts of classical mechanics are false. A new mechanics, **quantum mechanics**, had to be devised to take its place.

We shall take the de Broglie relation $p = h/\lambda$ as a starting point and abandon the classical concept of particles moving on trajectories. We suppose that the position of a particle is distributed through space like the amplitude of wave. In order to describe this distribution, we introduce the concept of wavefunction ψ in place of the trajectory, and then set up the scheme for calculating and interpreting ψ.

Schrödinger equation

In 1926, the Austrian physicist Erwin Schrödinger proposed an equation for finding the wavefunction of any system. The Schrödinger equation for a particle of mass m moving in one dimension with energy E is

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

V is the potential energy of the particle,

$$\hbar=\frac{h}{2\pi}=1.055\times10^{-34}\text{ Js}$$

$$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}(E-V)\psi=0$$

For a free particle, $V = 0$ (or a constant), for a harmonic oscillator, $V=\frac{1}{2}kx^2$.

For three-dimensional systems:

$$-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi=E\psi \qquad \text{where} \quad \nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

In the general case, the Schrödinger equation is written as $H\psi = E\psi$

where H is the hamiltonian operator of the system, $H = -\dfrac{\hbar^2}{2m}\nabla^2 + V$

For the evolution of a system with time, we solve time-dependent Schrödinger equation: $H\psi = i\hbar\dfrac{\partial\psi}{\partial t}$

The justification of the Schrödinger equation

Let's consider the case of motion in a region where the potential energy is zero.

Then $-\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2} = E\psi$ and a solution is $\psi = e^{ikx} = \cos kx + i\sin kx$ $k = \left(\dfrac{2mE}{\hbar^2}\right)^{1/2}$

$\cos kx$ (or $\sin kx$) is a wave of wavelength $\lambda = 2\pi/k$. The energy of the particle is entirely kinetic.

Therefore $E = p^2/2m$ and, because $E = \dfrac{k^2\hbar^2}{2m}$, $p = k\hbar$.

The linear momentum is related to the wavelength of the wavefunction as $p = \dfrac{2\pi}{\lambda} \times \dfrac{h}{2\pi} = \dfrac{h}{\lambda}$

de Broigle relation

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The kinetic energy and the wavefunction

If the potential energy is uniform but non-zero, the Schrödinger equation is $-\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2}=(E-V)\psi$

The solutions are the same as before but with

$$E-V=\frac{k^2\hbar^2}{2m}$$

From the relation $\lambda = 2\pi/k$ one obtains

$$\lambda = \frac{h}{\{2m(E-V)\}^{1/2}}$$

The greater the difference between the total energy and the potential energy, the smaller the wavelength of the wavefunction. The greater the kinetic energy, the smaller the wavelength. A stationary particle (with zero kinetic energy) has infinite wavelength, meaning that its wavefunction has the same value everywhere. That is, for a particle at rest, ψ = constant.

In terms of curvature of wavefunction, i.e. its second derivative $d^2\psi/dx^2$, when the wavefunction is sharply curved (when it has a short wavelength), the kinetic energy is large. When the wavefunction is not sharply curved (when its wavelength is long), the kinetic energy is low.

$|\psi|^2$

dx

Probability $= |\psi|^2 dx$

x x + dx


z

$d\tau$

r

y

x
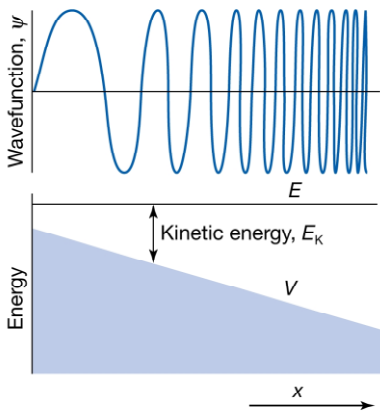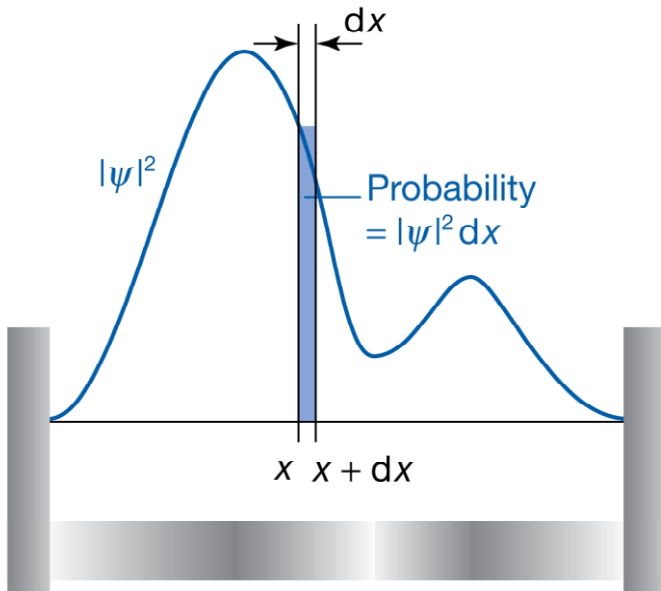
The Born interpretation of the wavefunction

Max Born made use of an analogy with the wave theory of light, in which the square of the amplitude of an electromagnetic wave is interpreted as its intensity and therefore (in quantum terms) as the number of photons present. The square of the wavefunction (or $\psi^*\psi$ if ψ is complex) is proportional to the probability of finding the particle at each point in space. For a one dimensional system:

If the amplitude of wavefunction of a particle is ψ at some point x, then the probability of finding the particle between x and $x + dx$ is proportional to $\psi^*\psi dx$.

$\psi^*\psi$ is a **probability density**; ψ itself is called **probability amplitude**. For a particle moving in three dimensions (e.g. an electron near a nucleus in an atom), the wavefunction depends on the point r with coordinates x, y, and z, and the interpretation of $\psi(r)$ is:

If the wavefunction of a particle is ψ at some point r, then the probability of finding the particle in an infinitesimal volume $d\tau = dxdydz$ at the point r is proportional to $\psi^*\psi d\tau$.
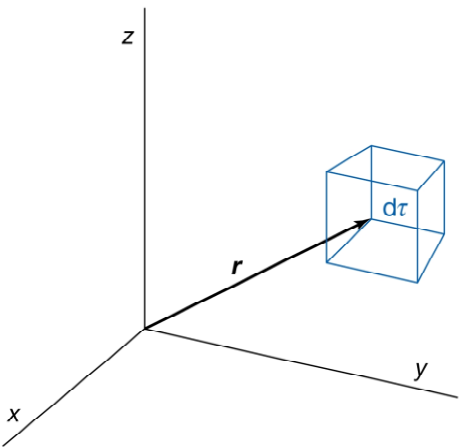
If ψ is a solution of the Schrödinger equation, then so is $N\psi$, where N is any constant. Hence, we can always find a factor, the **normalization constant**, such that the proportionality of the Born interpretation becomes an equality. The sum over all space of the individual probabilities must be 1 (the probability of the particle being somewhere in the system is 1)

$$N^2 \int \psi\psi^* \, dx = 1 \qquad\qquad N = \left\{ \frac{1}{\int \psi\psi^* \, dx} \right\}^{1/2}$$

This procedure is called normalizing the wavefunction. Assuming that we always use normalized wavefunctions; that is, from now on we assume that ψ already includes the normalization factor, i.e.
$$\int \psi\psi^* \, dx = 1 \qquad \int \psi\psi^* \, dxdydz = 1 \qquad \int \psi\psi^* \, d\tau = 1$$
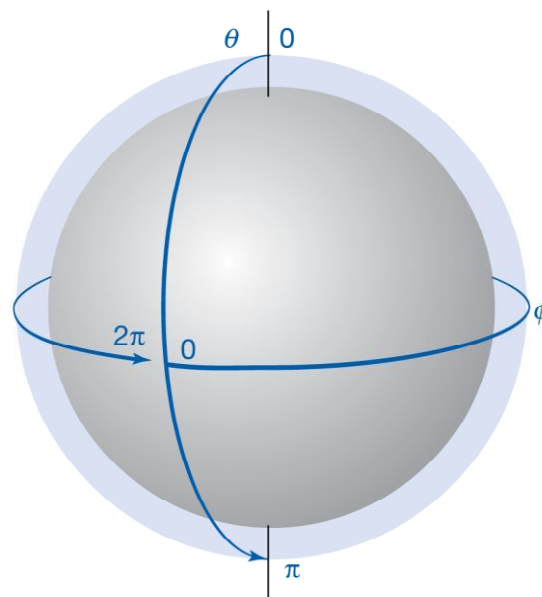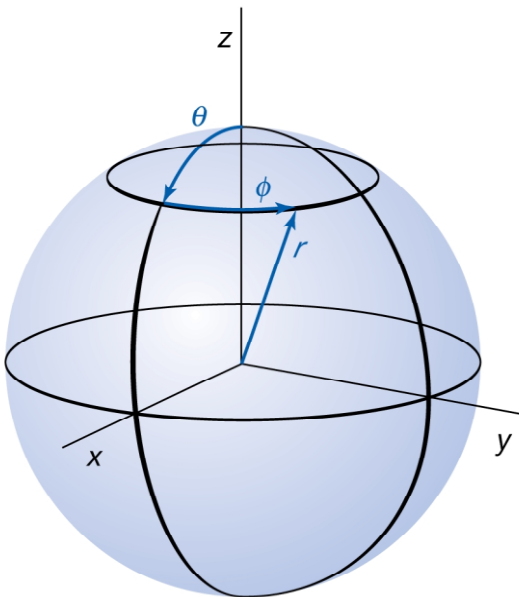
For spherical polar coordinates:
$$x = r\sin\theta\cos\varphi \qquad y = r\sin\theta\sin\varphi \qquad z = r\cos\theta$$
the volume element $\qquad d\tau = r^2 \sin\theta \, dr d\theta d\varphi$
The radius r can range from 0 to ∞, the colatitude θ ranging from 0 to π, and the azimuth φ from 0 to 2π.
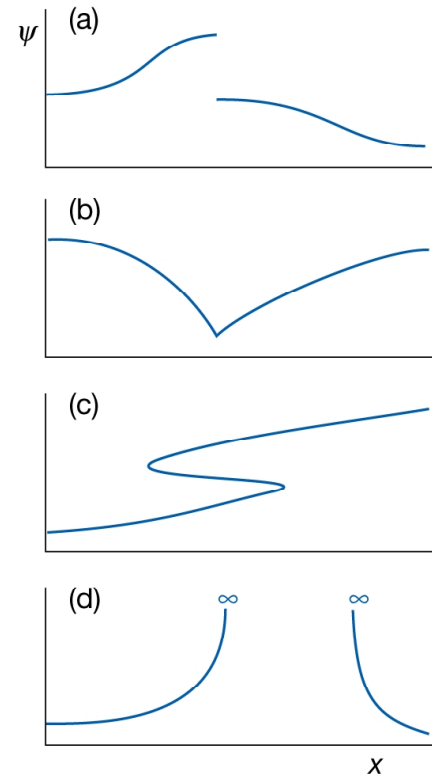
Example. Normalizing a wavefunction

Normalize the wavefunction of an electron in the lowest energy state of a hydrogen atom, which is proportional to e^{-r/a_0}, with a_0 a constant and r the distance from the nucleus.

A useful integral for calculations: $\int_0^\infty x^n e^{-ax} dx = \dfrac{n!}{a^{n+1}}$

$$\int \psi^* \psi d\tau = N^2 \int_0^\infty r^2 e^{-2r/a_0} dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\varphi = N^2 \times \frac{1}{4} a_0^3 \times 2 \times 2\pi = \pi a_0^3 N^2$$

$$N = \left(\frac{1}{\pi a_0^3}\right)^{1/2} \qquad\qquad \psi = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

(a)

ψ

(b)

(c)

(d)

x

Quantization

The Born interpretation puts severe restriction on wavefunctions:

1) to be continuous;
2) to have a continuous slope;
3) to be single-valued;
4) to be finite almost everywhere.

These are such severe restrictions that acceptable solutions of the Schrödinger equation do not in general exist for arbitrary values of energy E. A particle may possess only certain energies, for otherwise its wavefunction would be physically unacceptable. That is, the energy of a particle is quantized. The acceptable energies can be found by solving the Schrödinger equation for motion of various kinds, and selecting the solutions that conform to the above restrictions.

Quantum mechanical principles

Operators and observables

$$H\psi = E\psi \qquad\qquad H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V$$

H is an **operator**, something that operates on the function ψ. It takes the second derivative of ψ, multiplies it by $-\hbar^2/2m$ and adds the result to the result of multiplying ψ by V. H is hamiltonian operator playing a special role in quantum mechanics.

The Schrödinger equation is an **eigenvalue equation**, an equation of the form

(Operator)(function) = (Numerical factor) x (same function) $\qquad\qquad \hat{\Omega}f = \omega f$

The numerical factor ω is called the **eigenvalue** of the operator $\hat{\Omega}$. In the Schrödinger equation, the eigenvalue is the energy. The function f (which must be the same on each side in an eigenvalue equation) is the **eigenfunction** corresponding to that eigenvalue. In the Schrödinger equation, the eigenfunction is the wavefunction corresponding to the energy E.

(Energy operator)(wavefunction) = (energy)(wavefunction)

The importance of eigenvalue equations is that the above pattern exemplified by the Schrödinger equation itself is repeated for other properties, which in quantum mechanics are called **observables**. In general:

(Operator)(wavefunction) = (observable)(wavefunction) $\qquad\qquad \hat{\Omega}\psi = \omega\psi$

where $\hat{\Omega}$ is the operator (e.g. the hamiltonian H) corresponding to the observable ω (e.g. the energy E). Therefore, if we know both the wavefunction ψ and the operator corresponding to the observable of interest, we can predict the outcome of an observation of that property (e.g. an atom's energy) by picking out the factor ω in the corresponding eigenvalue equation.

Quantum mechanical calculations are often simplified by using the orthogonality property. Two functions are called orthogonal if $\int \psi_i {}^* \psi_j d\tau = 0$

Eigenfunctions corresponding to different eigenvalues of the same operator are orthogonal.

For example, if ψ_1 corresponds to one energy and ψ_2 corresponds to a different energy, then the two functions should be orthogonal and the integral of their product is zero.

Consider $\sin x$ and $\sin 2x$, both eigenfunctions of the operator d^2/dx^2, with eigenvalues -1 and -4, respectively.
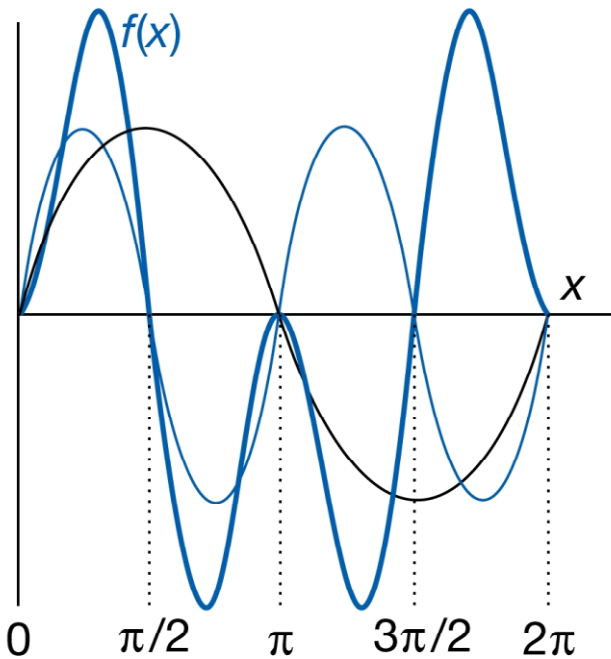
$$\int \sin ax \sin bx\, dx = \frac{\sin(a-b)x}{2(a-b)} - \frac{\sin(a+b)x}{2(a+b)} + const$$

For $a = 1$ and $b = 2$, $\int \sin ax \sin bx\, dx = 0$

Operators

Linear momentum $\qquad \hat{p} = \dfrac{\hbar}{i}\dfrac{d}{dx} \qquad \dfrac{\hbar}{i}\dfrac{d\psi}{dx} = p\psi$

The operator for position $\qquad \hat{x} = x \times$

Example: a general solution for free translational motion:

$$\psi = Ae^{ikx} + Be^{-ikx} \qquad\qquad E = \frac{k^2\hbar^2}{2m}$$

Let's select $B = 0$, then $\quad \psi = Ae^{ikx}$ and

$$\frac{\hbar}{i}\frac{d\psi}{dx} = \frac{\hbar}{i}A\frac{de^{ikx}}{dx} = \frac{\hbar}{i}A \times ike^{ikx} = \hbar k Ae^{ikx} = k\hbar\psi$$

Hence, $p = k\hbar$, as we already knew. Now suppose instead that we chose the wavefunction with $A = 0$, then by the same reasoning $p = -k\hbar$, which shows that a particle described by the wavefunction e^{-ikx} has the same magnitude of momentum (and the same kinetic energy) but directed towards $-x$ (the momentum is a vector quantity, and the sign gives the direction).

Superpositions and expectation values

Suppose now that that the wavefunction of the free particle has $A = B$. What is the linear momentum of the particle? The wavefunction is

$$\psi = A\left(e^{ikx} + e^{-ikx}\right) = 2A\cos kx$$

However, when we apply the linear momentum operator, we find

$$\frac{\hbar}{i}\frac{d\psi}{dx} = \frac{2A\hbar}{i}\frac{d}{dx}\cos x = -\frac{2kA\hbar}{i}\sin kx$$

This is not an eigenvalue equation because the function on the right differs from that on the left.

Linear superposition of wavefunctions

When the wavefunction of a particle is not an eigenfunction of an operator, the property (observable) corresponding to this operator is indefinite. However, in the current example the momentum is not completely indefinite because the cosine wavefunction is a **linear superposition**, or sum, of e^{ikx} and e^{-ikx}, and these individually correspond to definite momentum states. We can write the superposition as $\qquad \psi = \psi_{\rightarrow} + \psi_{\leftarrow}$

The interpretation of this wavefunction is that if the momentum of the particle is measured, its magnitude will be found to be $k\hbar$, but half the measurements will show that it is moving to the right, and half the measurements will show that it is moving to the left.

The same interpretation applies to any wavefunction written as a superposition. Suppose the wavefunction is a sum of many different linear momentum eigenfunctions:

$$\psi = c_1 \psi_1 + c_2 \psi_2 + ... = \sum_n c_n \psi_n$$

where c_n are numerical coefficients and the various ψ_n correspond to different momentum states. Then quantum mechanics tells us:

1) When the momentum is measured, one of the values corresponding to the ψ_n that contribute to the superposition will be found.

2) Which of these possible values will be found is unpredictable, but the probability of measuring a particular value in a series of observations is proportional to the square of its coefficient in the superposition.

3) The average value of a large number of observations is given by the expectation value $\langle \Omega \rangle$ of the observable Ω:

$$\langle \Omega \rangle = \int \psi * \hat{\Omega} \psi d\tau$$

The uncertainty principle

If the particle's wavefunction is Ae^{ikx}, it corresponds to a definite state of linear momentum $k\hbar$. But what is the position of the particle?

$$\psi^* \psi = \left(Ae^{-ikx}\right)^* \left(Ae^{ikx}\right) = A^2 \left(e^{-ikx}\right)\left(e^{ikx}\right) = A^2$$

The probability density is a constant independent of x. Therefore, the particle has an equal probability to be found anywhere. If the moment is specified precisely, it is impossible to predict the location of the particle.
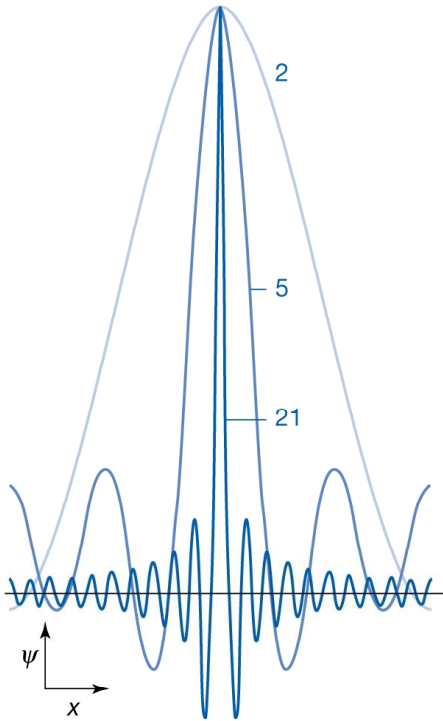
Heisenberg uncertainty principle: It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle.

Werner Heisenberg at a quantitative version of this result by considering expectation values of position and momentum: $\Delta p \Delta q \geq \dfrac{1}{2}\hbar$

Δp is the uncertainty in the linear momentum (the root mean square deviation of the momentum from its mean value) and Δq is the uncertainty in position (the r.m.s. deviation of the position from the mean position).

If we know that the particle is at a definite location, its wavefunction must be large there and zero everywhere else. Such a wavefunction can be created by superimposing a large number of harmonic (sine and cosine, or e^{ikx}) functions to a **wave packet** – a linear combination of wavefunctions that correspond to many different linear momenta. When an infinite number of components is used, the wave packet is a sharp, infinitely narrow spike – perfect localization of the particle.

Example. Using the uncertainty principle

The speed of a projectile of mass 1.0 g is known to within 1 μm s^{-1}. Calculate the minimum uncertainty in its position.

We estimate Δp from $m\Delta v$, where Δv is the uncertainty in the speed and then use the Heisenberg relation to estimate the minimum uncertainty in its position, Δq.

$$\Delta q = \frac{\hbar}{2m\Delta v} = \frac{1.055 \times 10^{-34}\, Js}{2 \times \left(1.0 \times 10^{-3}\, kg\right) \times \left(1 \times 10^{-6}\, ms^{-1}\right)} = 5 \times 10^{-26}\, m$$

The uncertainty is completely negligible for all practical purposes concerning macroscopic objects.

The Heisenberg uncertainty relation applies to a number of pairs of observables called **complementary observables**, which are defined by the properties of their operators. Other than position and momentum, they include properties related to angular momentum.

The heart of the difference between classical and quantum mechanics – some observables are complementary. Quantum mechanics shows that position and moment are complementary, and that we would have to make a choice: we can specify position at the expense of momentum, or momentum at the expense of position.

Two observables Ω_1 and Ω_2 are complementary when their corresponding operators do not **commute**, i.e., the effect of the two operators depends on their order:

$$\hat{\Omega}_1\left(\hat{\Omega}_2\,\psi\right) \neq \hat{\Omega}_2\left(\hat{\Omega}_1\,\psi\right)$$

We can illustrate this property for position and momentum:

$$\hat{x}\hat{p}_x \psi = x \times \frac{\hbar}{i}\frac{d\psi}{dx} \qquad \hat{p}_x\hat{x}\psi = \frac{\hbar}{i}\frac{d}{dx}(x\psi) = \frac{\hbar}{i}\left(\psi + x\frac{d\psi}{dx}\right)$$

The different outcomes of the effect of applying $\hat{\Omega}_1$ and $\hat{\Omega}_2$ in a different order are expressed by introducing the **commutator** of the two operators: $\qquad [\hat{\Omega}_1,\hat{\Omega}_2] = \hat{\Omega}_1\hat{\Omega}_2 - \hat{\Omega}_2\hat{\Omega}_1$

The commutator of the operators for position and linear momentum is $\qquad [\hat{x},\hat{p}_x] = -\hbar/i = i\hbar$

This commutator is of such vital significance for quantum mechanics that it is taken as a fundamental distinction between classical mechanics and quantum mechanics. Actually, this commutator is taken as a postulate of quantum mechanics and is used to justify the choice of operators for position and linear momentum.

Now, we can give the Heisenberg uncertainty principle in its most general form. For any two pairs of observables, Ω_1 and Ω_2, the uncertainties (the root mean square deviations of their values from the mean) in simultaneous determination are related by $\qquad \Delta\Omega_1\Delta\Omega_2 \geq \frac{1}{2}\left|\left\langle[\hat{\Omega}_1,\hat{\Omega}_2]\right\rangle\right|$