

3. Basic Principles of Quantum Mechanics

As mentioned in the previous Chapter, all chemical reactions consist of changes of the electron cloud that surrounds the nuclei. It is therefore, of central importance that we are able to describe the properties and behaviour of the electrons in chemical systems. It turns out that **classical mechanics** (as developed by e.g. [Kepler](#), [Galilei](#), and [Newton](#)) succeeds in describing the motion of macroscopic bodies very accurately but fails to capture the behaviour of the electrons that can only be represented via a **quantum mechanical** description. It is for this reason that we will discuss the basic principles that characterize quantum mechanics in this chapter.

Quantum mechanics is a relatively new field of physics that was developed at the beginning of the last century as the common effort of different scientists ([Heisenberg](#), [Planck](#), [de Broglie](#), [Bohr](#), [Schrödinger](#), [Born](#), [Dirac](#) and others). Up to that time, it was possible to describe all known physical phenomena with the laws of classical physics as either **particles** (classical mechanics, kinematics) or **waves** (optics, classical electro-magnetism). The discovery of new phenomena such as e.g. the **photoelectric effect** has led to the development of a new physics that has revolutionized the way we look at the world around us. Many insights from quantum mechanics are at first sight counterintuitive (i.e. they differ substantially from what we would expect in a classical picture!) which makes this field one of the most fascinating areas of modern physics.

The main goal of this chapter is an introduction to the basic concepts of quantum mechanics so that we can understand in what way a quantum mechanical picture differs from its classical counterpart. This will give us the basis for an understanding of the electronic structure of atoms that is introduced in Chapter 4.

3.1 Useful Mathematical Notions

As a first introduction, you can find here a very short optional summary of some of the mathematical notions that are useful for an understanding of Chapter 3 (and many other fields of chemistry!). This is not directly part of the material of the exam but is meant for you as a possibility to check and refresh your knowledge in mathematics. With the exception of '**operators**', all of the basic mathematical concepts mentioned here are part of the contents defined for the Swiss maturity exams. Click here if you want to access the [summary of useful mathematical notions](#).

3.2 Classical Mechanics: Particles and Waves

All phenomena in classical physics can be described either as a *particle* or a *wave*. The two following chapters give you a short summary as a reminder of the characteristic features of classical particle motion and wave phenomena.

3.2.1 The motion of point particles

In classical mechanics, the motion of a point particle with mass m , position r_o , and velocity v_o is completely determined at any instant in time t if we know the total force f that acts on the particle.

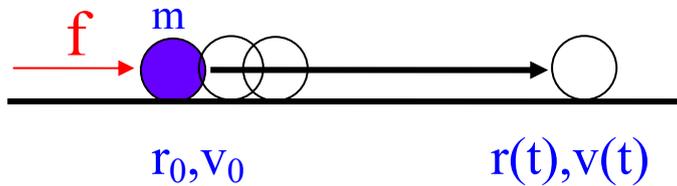


Fig. 3.1 Motion of a classical point particle with mass m under the action of the force f .

The motion of the particle can be described using **Newton's law** that relates the force f acting on the particle to the acceleration a it experiences:

$$\boxed{\vec{f} = m\vec{a}} \quad \vec{a} = \frac{d\vec{v}}{dt} = \frac{d^2\vec{r}}{dt^2} \quad \vec{v} = \frac{d\vec{r}}{dt}$$

From this we get the equations of motion, i.e. the time evolution of the particle position and its velocity as

$$\boxed{\vec{r}(t) = \vec{r}_o + \vec{v}_o t + \frac{1}{2}\vec{a}t^2} \quad \boxed{\vec{v}(t) = \vec{v}_o + \vec{a}t}$$

The particle possess the kinetic energy given by

$$\boxed{E_{kin} = \frac{1}{2}mv^2}$$

E_{kin} can take any positive value $E_{kin} \geq 0$. We say, the particle's kinetic energy is *continuous*.

This leads us to the important finding that:

The position and the velocity of any classical particle are exactly determined at any given time. Its energy is a continuous function of the particle velocity.

3.2.2 Wave Phenomena



Not all phenomena of classical physics are describable in a particle picture. A second large class of physical events can be described as **waves**. A **wave** is a disturbance that propagates through space or space and time, often transferring energy.

Fig. 3.2 Surface waves in water (from wikipedia) with highs and lows.

From every day live, you are already familiar with many wave phenomena, such as for instance **water waves** shown in Fig.3.2 (periodical variations of the quantity of water molecules) or **sound waves** (periodical compressions of air that travel through space and can be detected by a mechanosensitive device in your inner ear). Water waves and sound waves are examples for **mechanical waves** that exist in a medium (which on deformation is capable of producing elastic restoring forces). On the other hand, **electromagnetic radiations** such as visible light are waves that are characterized by periodic oscillation of the electromagnetic field (see. Fig.3.3) that can travel through vacuum without the need of a transmitting medium.

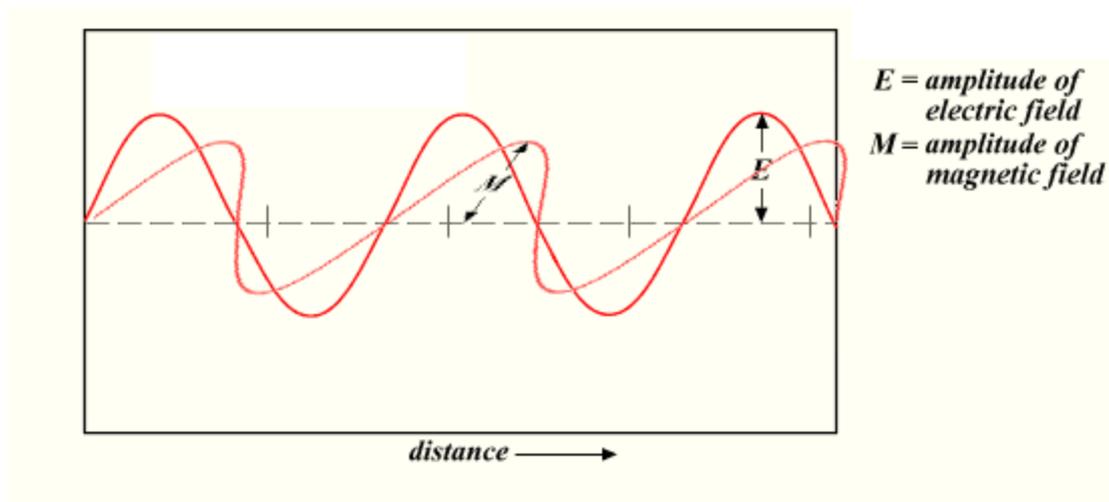


Fig. 3.3 Electromagnetic wave. The electric field and the magnetic field oscillate at right angles to each other and to the direction of propagation (from wikipedia).

Electromagnetic waves are classified according to how many periodic oscillations they have per second (i.e. their frequency). Fig. 3.4 shows the entire span of electromagnetic waves that range from high-frequency [γ-rays](#) that we have already encountered in chapter 2.5 on radioactivity, to x-rays, ultraviolet (UV) radiation, the visible spectrum, infrared (IR), microwave, to radiowaves (FM and QM) and long radio waves.

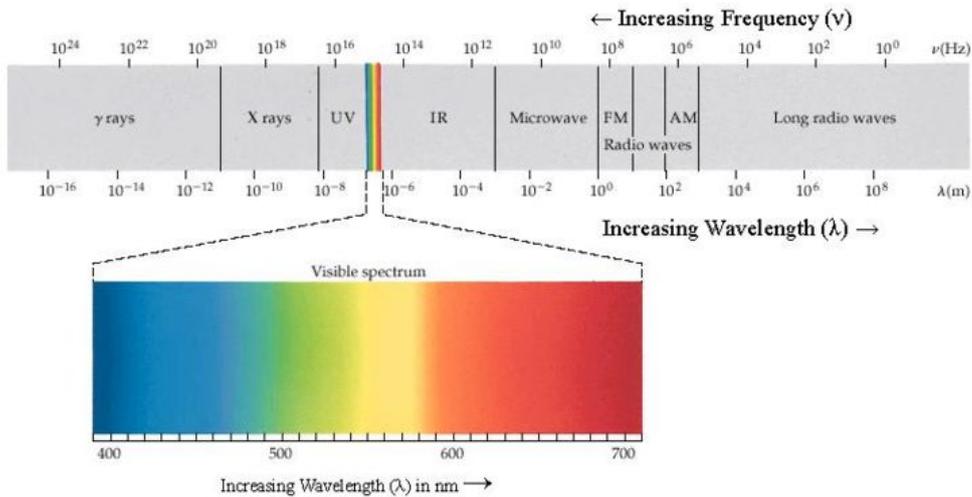


Fig. 3.4 Spectrum of electromagnetic waves (from wikipedia).

Mathematical description of the simplest wave: the harmonic oscillation

If we attach a mass m to a harmonic spring with spring constant k , the spring is elongated to an equilibrium length x_0 for which the gravitational force that acts on the mass is exactly compensated by the elastic force of the spring

$$-mg = kx_0$$

If we pull on the mass and elongate the spring further, the restoring force of the spring is proportional to the elongation $\Delta x = x - x_0$

$$f = -k\Delta x$$

If we release the mass, the spring starts to oscillate around the equilibrium length x_0 by periodic elongations and compressions. If we record the instantaneous displacement $\Delta x(t)$ of the spring as a function of time we find the form shown in Fig. 3.5.

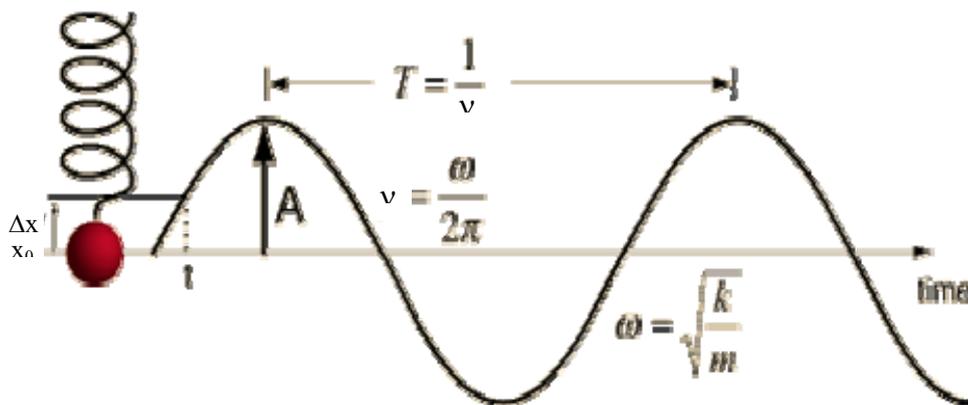


Fig. 3.5 Harmonic oscillation of a mass on a spring.

We can use Newton's law

$$f = ma$$

to find the differential equation that determines $\Delta x(t)$

$$m \frac{d^2 \Delta x(t)}{dt^2} = -k \Delta x(t)$$

A possible function $\Delta x(t)$ that fulfils this equation is for instance a simple trigonometric function

$$\Delta x(t) = A \sin(\omega t + \delta)$$

If we insert this function in the differential equation above, we obtain

$$-mA\omega^2 \sin(\omega t) = -kA \sin(\omega t)$$

$$\omega = \sqrt{\frac{k}{m}}$$

ω is the **angular velocity** (i.e. the change of angle [radians] as a function of time) of the oscillation,

$$\omega = \frac{\delta \varphi}{\delta t}$$

A is the **amplitude** (i.e. the maximal displacement from the equilibrium length), δ is called the **phase** (the phase determines at which point the oscillation starts, e.g. in a minimum or at half a period etc...) and $\Delta x(t)$ is called the **wavefunction**. Other characteristic quantities of a harmonic wave are its **period T [s]** (the time it takes between two equivalent points, e.g. maxima or minima, of the oscillation). The **frequency ν** of the oscillation is the number of oscillation per second measured in Hertz (**1 Hertz = 1 s⁻¹**). The frequency ν is related to the period T by

$$\nu = \frac{1}{T}$$

The **wavelength $\lambda [m]$** of the oscillation is the length between two equivalent points. The wave travels with the **velocity (also called 'group velocity') c**

$$c = \frac{\lambda}{T} = \lambda \nu$$

For mechanical waves, c (and λ and ν) are a function of the medium in which the wave travels, e.g. the **velocity of sound in air at 20°C is 344 m/s**, at the same temperature, the speed of sound in helium is $c = 927$ m/s. Electromagnetic waves can travel in vacuum (without the help of any medium) with the **speed of light $c = 3 \times 10^8$ m/s**.

Wave Phenomena: Interference and diffraction

Waves can exhibit phenomena that cannot be explained in a classical particle pictures. Typical such wave phenomena are **interference** and **diffraction**. Two or more waves can superimpose and form a new wave, this effect is called **interference**. When two sinusoidal waves superimpose, the resulting waveform depends on the frequency, the amplitude and in particular on the relative difference in phase (the **phase shift**) of the two waves. If the two waves have the same amplitude A and wavelength the resultant waveform will have an amplitude between 0 and $2A$ depending on whether the two waves are **in phase** (i.e. both waves have their minima and maxima at exactly the same time) or **out of phase** (i.e. one wave has a maximum when the other one has a minimum). Consider two waves that are in phase, with amplitudes A_1 and A_2 . Their troughs and peaks line up and the resultant wave will have an amplitude $A = A_1 + A_2$. This is known as **constructive interference**.

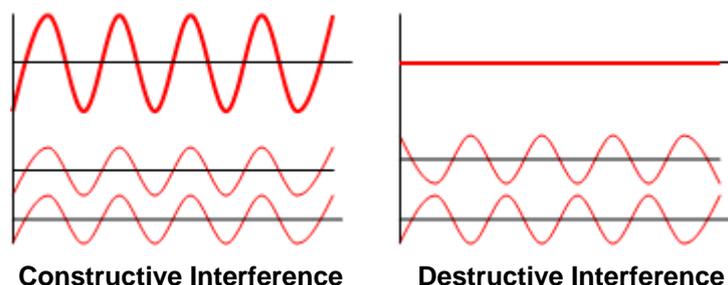


Fig. 3.6 Constructive and destructive interference of two waves.

If the two waves are π radians, or 180° , out of phase, then one wave's crests will coincide with another wave's troughs and so will tend to cancel out. The resultant amplitude is $A = |A_1 - A_2|$. If $A_1 = A_2$, the resultant amplitude will be zero. This is known as **destructive interference**.

Light or other waves such as sound waves can bend when they pass around an edge or through a slit. This bending is called **diffraction**. The characteristic pattern of high and low intensity areas shown in Fig. 3.7 is called **diffraction pattern**. While diffraction always occurs, its effects are generally only noticeable for waves where the wavelength is on the order of the feature size of the diffracting objects or apertures.

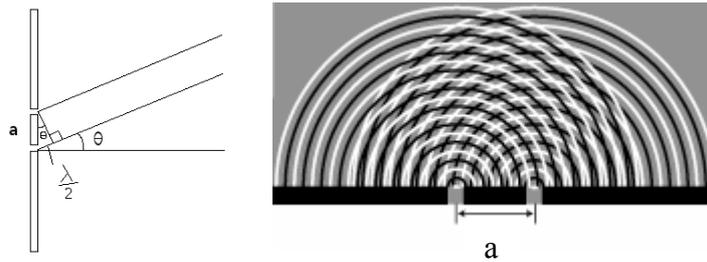


Fig. 3.7 Double slit diffraction and interference pattern (from wikipedia).

If we have two apertures, a parallel wave front that is arriving at these two slides will create two circular waves that as a function of the phase shift will superimpose constructively or destructively. The angular positions of the intensity minima correspond to path length differences of an odd number of half wavelengths

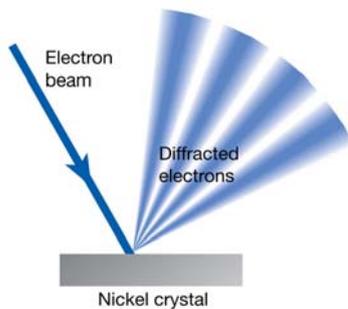
$$a \sin \theta = \frac{\lambda}{2}(2m + 1)$$

and the corresponding maxima are at path differences of an integer number of wavelengths

$$a \sin \theta = \lambda m .$$

3.3 Quantum Mechanics

One of the most important findings that lead to the development of quantum mechanics as a new branch of physics was the observation that particles can



behave as waves, a phenomena that is not explainable with the laws of classical mechanics that we just revisited. Such a **particle-wave dualism** is for instance observed when a beam of electrons (i.e. particles!) travels through a small aperture or is reflected by a surface and a diffraction pattern results that is a typical characteristic of waves (Fig. 3.8). Consequently, electrons can behave at the same time as particles and waves!

Fig. 3.8 Diffraction of electrons.

3.3.1 Particle-Wave Dualism

One of the central postulates of quantum mechanics is that *every particle possesses also a wave character and vice versa*. The wave character is characterized by the **de Broglie wavelength** λ . [de Broglie](#) could demonstrate that in the nonrelativistic limit (i.e. for velocities $v \ll c$ (the velocity of light)) the relation

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

that was originally derived for electromagnetic radiation only is in fact valid for all matter. The de Broglie equation relates the linear momentum p of a particle with mass m and velocity v to its wavelength λ . $h = 6.63 \times 10^{-34} \text{ Js}$ is the **Planck constant**. The de Broglie relation tells us that the associated wavelength of a moving particle is indirectly proportional to its mass, i.e. very light masses have very long wave lengths.

Question 3.1:

What is the wavelength of an electron that moves with a velocity of 100 m/s?

Answer 3.1:

7.28 μm .

De Broglie could also demonstrate that the **energy of one quantum** of any wave (electromagnetic wave or matter wave) is given by the relation

$$E = h\nu.$$

A **quantum** is the smallest, indivisible portion of energy associated with a wave. For instance, in a particle picture one can think of light as being composed of photons. A photon is a massless particle that carries the energy of one quantum of light given in the equation above. The higher the frequency of a wave the higher its energy.

Question 3.2:

Which radiation has the higher energy: microwaves or visible light?

Answer 3.2:

Visible light.

3.3.2 Energy Quantization

The notion of quanta that we just introduced in the preceding chapter is a further important characteristic of quantum mechanics, in fact the one that gives it its name! The energy of a quantum system cannot be divided into arbitrarily small parts, instead there is a smallest undividable energy package called a quantum. We will see that in contrast to classical systems where the accessible energies are continuous, quantum systems can often only adopt specific energy values whereas others are forbidden, i.e. do not exist. This property is what is described by the term **energy quantization**.

An experimental indication for the existence of quantized systems is the **photoelectric effect**.

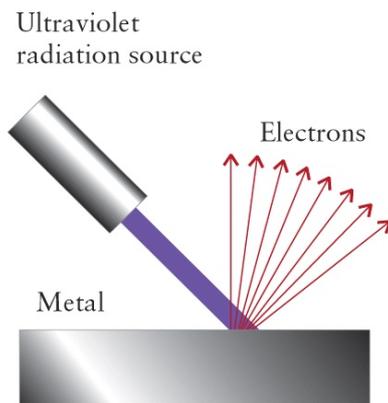
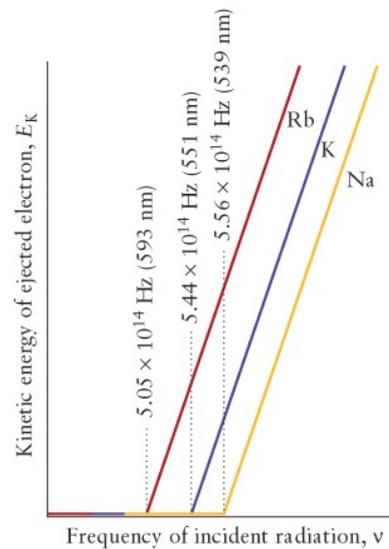


Fig. 3.9 Photoelectric effect.



Upon exposing a metallic surface to ultraviolet or x-ray radiation, electrons are emitted if the energy of the incident light is above a given threshold that is characteristic of the metallic material (Figure 3.9). If the frequency of the light is increased further the kinetic energy of the emitted electrons increases linearly. The photoelectric effect can only be explained if one assumes that the incident light has a given energy and that one needs a well defined energy to remove an electron from a metallic surface atom. The energy of the photon is absorbed by the electron and, if sufficient, the electron can escape from the material with a finite kinetic energy. A single photon can only eject a single electron, as the energy of one photon may only be absorbed by one electron. By conservation of energy, for incident light of frequency ν the relation

$$h\nu = E^I + E^{kin} = E^I + \frac{1}{2} m_e v^2$$

holds where E^I is the ionization energy⁸ needed to remove an electron from an atom.

Question 3.3:

Upon radiation an electron is emitted from a sodium surface ($E^I = 2.28$ eV) with a velocity of 100 m/s. What was the wave length of the incident light?

⁸ In the case of a solid, the minimal energy needed to remove an electron is also called the *work function*.

Answer 3.3:

544nm.

The photoelectric effect also shows that the electrons of the metal atoms with the lowest ionization energies occupy a well defined, discrete energy level $-E^I$. The discovery of the photoelectric effect contributed significantly to the formulation of quantum mechanics.

3.3.3 The Basic Axioms of Quantum Mechanics

Quantum mechanics is based on few basic axioms⁹.

The first axiom: wavefunctions and probability distributions

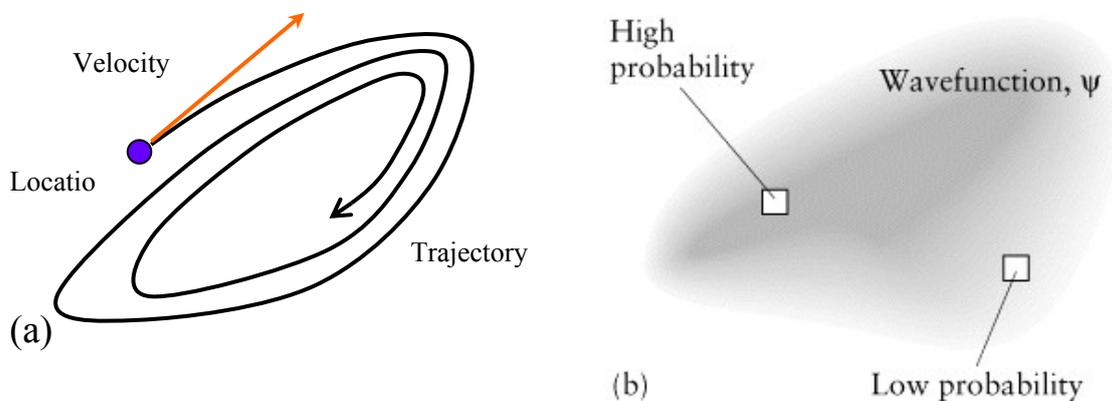


Fig. 3.10 (a) trajectory of a classical particle; (b) probability distribution of a quantum particle.

The first axiom of quantum mechanics states that every system can be described by a wavefunction $\psi(r,t)$ that is a function of all the particle coordinates and possibly the time. The square of the wavefunction gives us the probability of finding a particle at position r in space. For a time-independent stationary system containing one particle, the probability $P(r)$ to find the particle in an infinitesimal small volume element dV around r is:

$$P(\vec{r}) = \Psi^2(\vec{r})dV$$

If the particle is an electron, the square of the wavefunction is also called the **electron density** ρ (i.e. the number of electrons per volume element).

$$\rho(\vec{r}) = \frac{N^{el}(\vec{r})}{dV} = |\Psi(\vec{r})|^2$$

⁹ An axiom is a postulate that forms the basis of a theory but cannot be derived or formally proven.

The wavefunction is normalized in such a way that the total probability to find the particle anywhere in space integrates to 1:

$$\int_V \Psi^2(\vec{r}) dV = 1.$$

This tells us that a quantum system behaves fundamentally different from a classical system. For a classical particle, we can determine its position and velocity at any instant in time. In fact a classical particle follows an accurately determined trajectory such as the one shown in Fig. 3.10(a). For a quantum particle instead, we can only say that the particle is at a given position with a certain probability. We can represent the position of a quantum particle with a [probability distribution](#) which defines regions in space where we find it with high probability and others where the probability to find the particle is very low (Fig.3.10(b)).

Question 3.4:

A quantum particle is confined in a linear box of length L surrounded by infinitely high potential walls. The ground state of this system is described by the wavefunction

$$\Psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\pi \frac{x}{L}\right).$$

What is the probability to find the particle at a given position x ? At which position is the probability maximal? What is the total probability to find the particle in the box?

Answer 3.4:

[Click here to see the solution.](#)

The second axiom: observables and operators

The second axiom deals with the question of how we can calculate the properties of a quantum system. It states that every observable¹⁰ \mathcal{A} in classical mechanics can be described by a corresponding [operator](#) $\hat{O}_{\mathcal{A}}$ in quantum mechanics that acts on the wavefunction to produce the value of the observable \mathcal{A} multiplied by the wavefunction (a so called ['eigenvalue equation'](#)):

$$\hat{O}_{\mathcal{A}} \Psi = A \Psi .$$

¹⁰ An observable is any property of the system that can be measured such as e.g. the position, the velocity, the linear momentum or the energy.

Some examples:

Observable	Expression in classical mechanics	operator in quantum mechanics
Position	$\vec{r} = (x, y, z)$	$\hat{\vec{r}} = (x, y, z)$
Momentum	$\vec{p} = m\vec{v}$	$\hat{\vec{p}} = -i\hbar\vec{\nabla} = -i\hbar\left(\frac{\delta}{\delta x}, \frac{\delta}{\delta y}, \frac{\delta}{\delta z}\right)$

With these two transformations, one can construct the corresponding quantum operators of all classical quantities such as e.g. the operator for the kinetic energy $\hat{\mathcal{E}}_{kin}$

$$E_{kin} = \frac{p^2}{2m} \quad \rightarrow \quad \hat{E}_{kin} = -\frac{\hbar^2}{2m} \nabla^2 .$$

Question 3.5:

What is the linear momentum of a free particle that is described by the wavefunction

$$\Psi(x) = e^{-ikx} .$$

Answer 3.5:

$\hbar k$

The third axiom: expectation values and uncertainties

We have seen that the position of a quantum particle is not described by a single sharp value but by a probability distribution. We cannot ask where the particle is but only what is the most probable position to find it. The most probable value of a probability distribution is called the **expectation value** (or the mean value or first moment of the distribution). For instance, the expectation value of the particle position $\langle r \rangle$ is

$$\langle \vec{r} \rangle = \int_V \vec{r} \Psi^2(\vec{r}) dV \approx \sum_i \vec{r}_i P(\vec{r}_i) .$$

The second equality is obtained after a “discretization” of the space, which consists in dividing it in an infinite number of “small” cubes (labelled with the index i) of volume dV placed at position r_i .

This means that we take every possible value of r and do a weighted average over all values with the weight of each r given by its probability (i.e. the square of the wavefunction at r). In the same way as for the particle position, we have to calculate any property \mathcal{A} of the quantum system as expectation value over the probability distribution given by the square of the wavefunction:

$$\langle A \rangle = \int_V \Psi \hat{O}_A \Psi dV$$

where we can think of the operator \hat{O}_A as an operator that produces the expectation value for the property \mathcal{A} .

If we do many measurements of a property \mathcal{A} , the width of the resulting probability distribution determines how likely it is to find values that deviate from the mean value $\langle \mathcal{A} \rangle$. This uncertainty $\Delta \mathcal{A}$ is given by the standard deviation of the probability distribution.

$$\Delta A = \sqrt{\frac{\sum_{i=1}^N P_i (A_i - \langle A \rangle)^2}{\sum_{i=1}^N P_i}}$$

Question 3.6:

What is the expectation value when you throw an ideal dice?

Answer 3.6:

3.5 ([for an explicit solution click here](#)).

Question 3.7:

An electron is described by a Gaussian wavefunction of the form

$$\Psi(x) = \sigma^{-1/2} \pi^{-1/4} e^{-(x-\mu)^2/2\sigma^2}$$

What is the expectation value for its position? What is the standard deviation?

Answer 3.7:

μ, σ ([for an explicit solution click here](#)).

The fourth axiom: the Hamilton operator and the Schrödinger equation

All properties of a quantum system can be determined once its wavefunction is known. The equation that determines the wavefunction and its time evolution is the **time-dependent Schrödinger equation**

$$\hat{H} \Psi(r, t) = i\hbar \frac{\delta \Psi}{\delta t}$$

For stationary states (i.e. non-time dependent systems) one can use the ***time-independent Schrödinger equation***

$$\hat{H}\Psi(r) = E\Psi(r)$$

where \hat{H} is the ***Hamilton operator*** of the system. The Hamilton operator is the quantum operator for the total energy \mathcal{E} of the system

$$\hat{H} = \hat{E}_{kin} + \hat{V}(r) = \frac{\hbar^2}{2m} \vec{\nabla}^2 + \hat{V}(r)$$

The lowest of its eigenvalues (E_0) is the ground state energy of the system.

3.3.4 Heisenberg's Uncertainty Relation

The [Heisenberg](#) uncertainty principle states that the uncertainties of an infinitely precise measurement of the particle position x and its momentum p are correlated. If the particle state is such that the first measurement yields a standard deviation of values Δx , then the second measurement will have a distribution of values whose dispersion Δp is at least inversely proportional to Δx . The constant of proportionality is equal to [Planck's constant](#) divided by 4π .

$$\Delta x \Delta p \geq \frac{\hbar}{2\pi}$$

Question 3.8:

What is the uncertainty of the momentum of particle whose position can be measured with infinite accuracy ($\Delta x = 0$)?

Answer 3.8:

∞ .

3.3.5 Comparison between classical and quantum mechanics

Whereas classical mechanics fails to describe quantum phenomena, quantum mechanics is a general theory that reduces to the laws of classical mechanics for systems with high masses, energies, and temperatures, or formally, if the Planck constant becomes infinitely small $\hbar \rightarrow 0$. The following table

summarizes once more the principal differences between classical and quantum mechanics:

Classical Mechanics	Quantum Mechanics
position and linear momentum of a particle have sharply defined values r, p	$\Delta r \Delta p \geq \hbar/2$ $\psi(r,t); P(r,t) = \psi^*(r,t)\psi(r,t)$
Continuous energy spectra $E^{\text{kin}}(T=0) = 0$	Quantized energies $E^{\text{kin}}(T=0) > 0$ (zero point energy)
Time evolution is given by the classical equations of motion: Newton's equation $\vec{f} = m\vec{a} = m \frac{\delta^2 \vec{r}}{\delta t^2}$	Time evolution is given by the time-dependent Schrödinger equation $\hat{H}\Psi(r,t) = i\hbar \frac{\delta \Psi}{\delta t}$

3.3.6 Example of a Quantum System: Particle in a Box

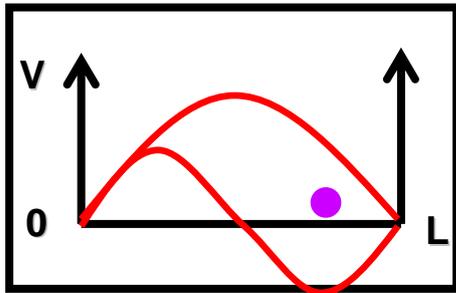


Fig. 3.11 Particle in a box.

Consider a particle with mass m in a one dimensional box of length L that is surrounded by infinitely high potential walls. The potential that the particle experiences inside the box is 0.

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < L \\ \infty & \text{for } x < 0 \text{ and } x > L \end{cases}$$

Since the potential is zero inside, the only energy that the particle has is kinetic energy E^{kin} . If we replace the momentum in the classical expression for the kinetic energy

$$E^{\text{kin}} = \frac{p^2}{2m}$$

with the de Broglie wavelength $p = \frac{h}{\lambda}$,

we get an expression for the energy of the system

$$E^{tot} = \frac{h^2}{2m} \frac{1}{\lambda^2}$$

that is inversely proportional to λ^2 . What are possible λ for a particle in a box? We know that the wavefunction has to fulfil the **boundary condition** that it is zero at the walls ($x=0$ and $x=L$). A simple trigonometric function such as the one shown in Fig. 3.11 fulfils these conditions. In fact all harmonic waves whose period is such that they become zero at the wall are acceptable wavefunctions for this system. All possible wavelengths of this system thus satisfy the condition that integer multiples of half a wavelength are equal to the box length L

$$n \frac{\lambda}{2} = L$$

where $n = 1, 2, 3, \dots$

Where n is called a **quantum number** i.e. a number that specifies each possible state of the system (in this case from $n = 1$ to infinity). If we substitute the expression for $\lambda = 2L/n$ in the expression for E^{tot} we get

$$E^{tot} = \frac{h^2}{8m} \frac{n^2}{L^2}$$

i.e. the energy of the system depends inversely on the square of the box length L and is proportional to n^2 . Figure 3.12 shows the possible energy level for each value of n with the corresponding wavefunction.

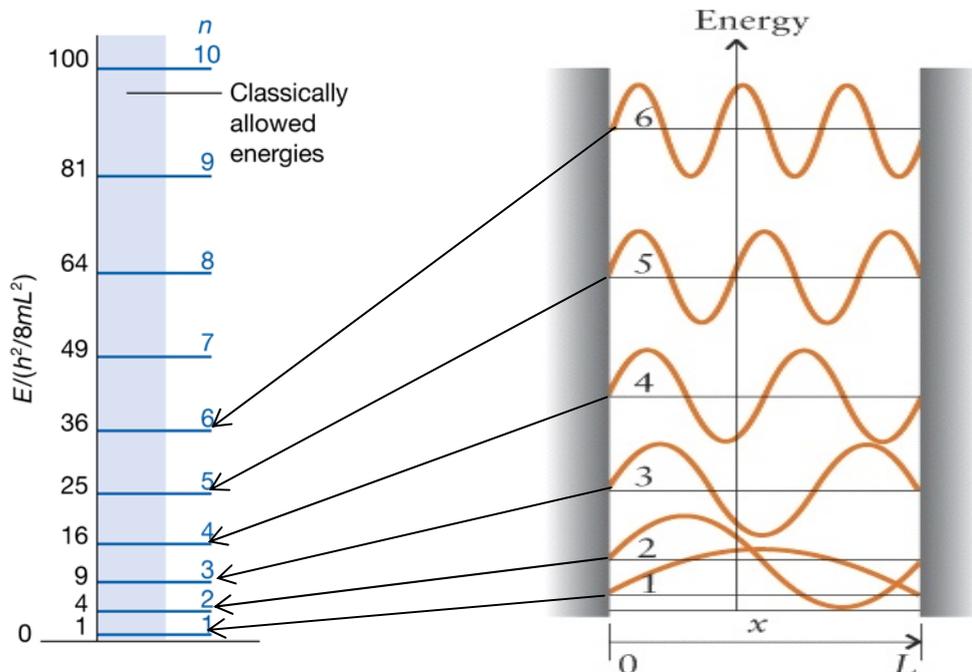


Fig. 3.12 Energy levels and wavefunctions for a particle in a box.

Note that, the system can only adopt these discrete energy values whereas for a classical system all energy values would be allowed. The state with the lowest possible energy ($n = 1$) is called the ground state. All other possible states with $n > 1$ are excited states.