Chapter 1

Light as particles

1.1 Introduction

Quantum mechanics is indispensable for the fields of modern optics and photonics. It provides an important theoretical background for engineers designing practical applications. Photonic devices are ubiquitous nowadays and quantum photonics is expected to play an important role in future quantum technologies.

For these reasons it is crucial to design an introductory course on quantum mechanics for the students of Electrooptics and Photonics at an appropriate level, building on their previous skills. Here I count on their knowledge of geometrical and wave optics, some understanding of electromagnetic waves and, particularly, on their motivation to learn more.

I will start with the historical account of the transition from the classical to the quantum world, which will lead us to the Schroedinger equation. This initial phase is rich in physics and I will try to keep mathematical details at a level which underlines the main ideas and makes it easier to follow them. Subsequent chapters will take us on a journey from simple quantum systems such as particle in a box and a quantum harmonic oscillator, to more complex systems which include hydrogen atom and multi-electron atoms. We will finish the course with an attempt to address the question 'What is a photon?' and the modern topic of entangled states and Bell's inequality.

1.2 Black body radiation

Any object emits thermal radiation which depends on the temperature T of the object. At low T, the radiation is mainly in the infrared region. As T increases, the wavelengths emitted shift to the visible region and the object starts to glow red and eventually white. Studies of very hot bodies showed that their thermal radiation spectrum covers all regions from the ulraviolet to the visible and the infrared one. The intensity $I(\lambda, T)$ of radiation is a continuous function of the wavelength λ, as shown in Fig. 1.1 for three different temperatures for a black
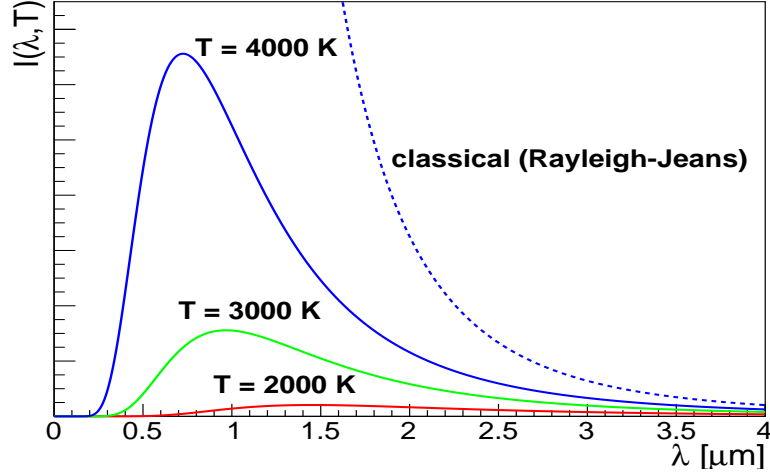
Figure 1.1: Intensity $I(\lambda, T)$ of blackbody radiation as a function of the wavelength λ, for three different temperatures. The blue dashed line shows the prediction of the classical calculation for $T = 4000$ K.

body. A black body is an ideal object that absorbs all radiation hitting its surface. Is is a convenient approximation since the blackbody radiation does not depend on the specific properties of the body, just on the temperature of its surface. Two features of the spectrum stand out. First, the total radiated energy, given by the area under the curve, significantly increases with temperature. Second, the peak position defined by the wavelength λ_{max} with maximum intensity, shifts to the left with temperature. This latter feature is described by the Wien's displacement law:

$$\lambda_{max} T = 0.2898 \cdot 10^{-2} \text{ mK} \tag{1.1}$$

Classical physics failed to explain the blackbody spectrum. The classical prediction, known as Rayleigh-Jeans law:

$$I(\lambda, T) = \frac{2\pi c k T}{\lambda^4}, \tag{1.2}$$

is plotted in Fig. 1.1 as the blue dashed line for $T = 4000$ K. The deviation from the blue solid line is obvious. They agree only for the large wavelengths. For $\lambda \to 0$ the Rayleigh-Jeans law predicts infinite radiated intensity, an obvious conflict with observation.

The correct formula for the spectrum was found by Max Planck in 1900,

$$I(\lambda, T) = \frac{2\pi h c^2}{\lambda^5 \left(e^{\frac{hc}{\lambda k T}} - 1\right)}. \tag{1.3}$$

The Planck's law, as it is known, rests on a radical assumption: oscillating molecules at the surface of the black body do not simply take on any values of energy as expected in classical physics, only discrete ones are allowed, given by

$$E_n = n\,h\,f \tag{1.4}$$

where $n = 1, 2, 3, ...$ is a quantum number, $h = 6.626 \times 10^{-34} Js$ is Planck's constant and f is the frequency of oscillations of the molecules. The states of molecules with energies E_n are called quantum states. This postulate was soon extended from the oscillating molecules to the discrete energies of the electromagnetic field, given by the same equation with f being the frequency of the electromagnetic waves.

The blackbody spectrum represents the beginning of quantum mechanics. The Planck's law described the spectrum extremely well but his assumptions about the quantized states needed further support to become generally accepted.

1.3 Photoelectric effect

The black body spectrum provides an important indirect piece of evidence for the quantization of light. The photoelectric and the Compton effects provide stronger, more direct evidence [1, 2].

The photoelectric effect was discovered by Hertz in 1887. He irradiated a metal electrode (photocathode) inside a vacuum glass tube with ultraviolet light, and, as a result, a current flowed in the tube between the cathode and the anode. Lenard proved in 1900 that the current consisted of electrons liberated from the cathode by ultraviolet (UV) light. He also measured the kinetic energy of electrons and found that while it varied, for a given frequency f of UV light it did not exceed a maximum value E_{max}. E_{max} was independent of UV light intensity, instead, it was proportional to the frequency f. If f fell below a critical frequency f_c, electrons were not emitted and the photoelectric effect disappeared. What did depend on UV light intensity, was the current (the number of liberated electrons).

These findings were difficult for classical theory to explain. In 1905 Einstein came with a profound and at the same time simple explanation. In his theory of the photoelectric effect, he extended Planck's ideas and proposed that when a molecule (or oscillating electromagnetic field) changes its state from the one with energy E_n to the one with energy E_{n-1}, it emits a quantum of electromagnetic radiation of frequency f and energy E given by

$$E = E_n - E_{n-1} = nhf - (n-1)hf = hf \tag{1.5}$$

He further assumed that the quantum is completely absorbed by the electron observed in the photoelectric effect. The quantum behaves as a localized bundle of energy E, a particle, now known as the photon. The correct equation, Einstein suggested, is the energy conservation in this process,

$$E_{max} = hf - W \tag{1.6}$$

where W is energy required for an electron to escape the surface of the metal photocathode. Thus, electron absorbs energy hf, then, overcoming the surface barrier it loses energy W and what remains is E_{max}. This is true for electrons directly from the surface, an electron from inside the surface loses some more energy so that its energy is $E < E_{max}$. Einstein's theory explains all features of the photoelectric effect discovered by Lenard.

1.4   Compton effect

To understand the photoelectric effect, we needed only the energy of the photon, not its momentum. What could the momentum p be? The total relativistic energy of a particle with mass m and speed v is

$$E = \frac{mc^2}{\sqrt{1 - \frac{v^2}{c^2}}}. \tag{1.7}$$

Photon, as the particle of light, moves with the speed od light $v = c$. This makes the denominator in the above equation equal to zero and if the photon had mass $m > 0$, its energy would be infinite. We know however, that its energy is finite, $E = hf$. The only way to keep energy in Eq. 1.7 finite, is to set $m = 0$, i.e., to assume that the photon is a massless particle. Then we get from another relativistic formula which relates the particle's energy E to its momentum p,

$$E = \sqrt{p^2c^2 + m^2c^4} = \sqrt{p^2c^2} = pc \tag{1.8}$$

From here we get for the momentum of the photon

$$p = \frac{E}{c} = \frac{hf}{c} = \frac{h}{\lambda}. \tag{1.9}$$

The Compton effect is the scattering of an X-ray beam of a wavelength λ_0 off a graphite target. The X-rays scattered by angle θ are observed to have a wavelength $\lambda_1 > \lambda_0$ given by

$$\lambda_1 - \lambda_0 = \frac{h}{mc}(1 - \cos\theta) \tag{1.10}$$

Classical physics failed to explain the effect since according to classical electromagnetic theory, the X-ray electromagnetic wave of a frequency $f_0 = c/\lambda_0$ forces the electron to oscillate with the same frequency f_0 and reradiate an X-ray wave of the yet again frequency f_0. Thus the scattered wave should have the same wavelength λ_0 as the incident wave.

Compton used the $p = h/\lambda$ prescription for the photon momentum plus momentum conservation in 1924 to explain the effect as the result of a collision of a quantum (photon) of X-ray radiation (wavelength λ_0) with a single electron of mass m (Fig. 1.2 and Problem 1.4.4).

The lesson we learned from this introduction is that the electromagnetic radiation exhibits not just wave properties (when it propagates) but also particle properties (when it interacts). The particle of light is the photon, its energy $E = hf$ and momentum $p = h/\lambda$.
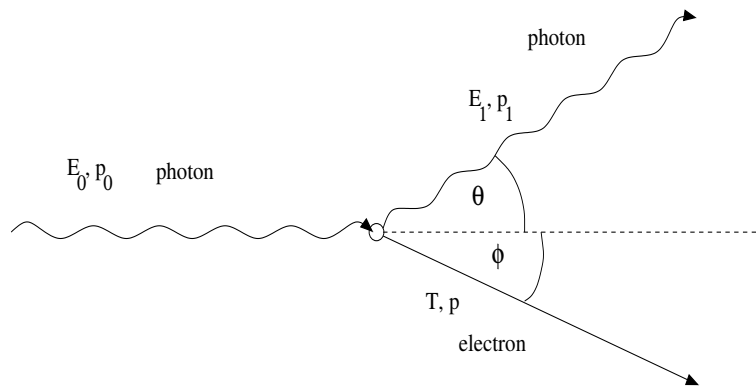
Figure 1.2: An X-ray photon with energy E_0, momentum p_0, and wavelength λ_0 scatters off an electron of mass m by angle θ. The scattered photon is described by E_1, p_1, λ_1.

1.4.1 Problem

The temperature of the surface of a human body is $t = 35°$C. What is the λ_{max} for radation from the surface if we assume that the human body is a black body?

1.4.2 Problem

What is the energy and the wavelength of a photon of light of frequency $f = 6 \times 10^{14}$ s^{-1}?

1.4.3 Problem

An object of mass $m = 2$ kg is suspended from a spring with a spring constant $k = 25$ Nm^{-1}. The object is pulled from an equilibrium position by $A = 0.4$ m and released, which leads to its oscillations about the equilibrium.
a) Find, working within the framework of classical physics, the total energy and frequency of the oscillations.
b) Assuming that the energy is quantized (quantum oscillator), find the quantum number n corresponding to the total energy of oscillations found in part a).
c) What is the energy released in the transition from E_n state to E_{n-1} state?

1.4.4 Problem

Derive the Compton shift equation, 1.10! Hint: use the energy and momentum conservation.

1.4.5   Problem

The surface of sodium is illuminated with ultraviolet light with $\lambda = 300$ nm. The energy for an electron to escape the surface is $W = 2.46$ eV.
a) Find the maximum kinetic energy of photoelectrons E_{max}.
b) Find the critical wavelength $\lambda_c = c/f_c$ of the incident light at which the photoelectric effect appears/disappears.

1.4.6   Problem

X-rays with $\lambda_0 = 0.20$ nm are scattered off the carbon surface. The scattered rays are observed at an angle of $45°$ with respect to the incident rays. Find the wavelength λ_1 of the scattered X-rays!

Chapter 2

Particles as waves

2.1 Louis de Broglie

In 1924 Louis de Broglie, who was 24 at the time, realized that asymmetry had risen between electromagnetic radiation which has both wave and particle properties, and particles with only particle properties. He explored a revolutionary possibility (no matter how natural it appears in hindsight) that particles with mass $m > 0$ could also behave as waves under some circumstances. What would the wavelength of these waves be?

De Broglie inverted Eqs. 1.5, 1.9 for the energy and momentum of the photon to postulate the frequency and wavelength of the particle waves as

$$f \;\; = \;\; \frac{E}{h} \tag{2.1}$$

$$\lambda \;\; = \;\; \frac{h}{p} \tag{2.2}$$

The (phase) velocity of propagation of these waves is

$$v_p = \lambda f = \frac{hE}{ph} = \frac{\sqrt{p^2c^2 + m^2c^4}}{p} > c, \tag{2.3}$$

that is, greater than the speed of light. This is disturbing for a wave which is supposed to represent a particle with mass m moving with velocity $v < c$. However, if we consider a group of waves, a wave packet localized in space around the particle, there are in fact, two velocities to describe the group. Besides v_f, there is also the group velocity v_g. The wave packet approach is very useful here since the mathematics is the same as for classical waves, in particular electromagnetic waves.

A simple group of waves can be constructed starting with a simple wave (we follow Ref. [3])

$$\Psi_1(x, t) = \sin{(kx - \omega t)} \tag{2.4}$$

here x is the single space coordinate, t is time, $\omega = 2\pi f$ and $k = 2\pi/\lambda$ is the wave number. This wave propagates with the phase velocity

$$v_p = \lambda f = \frac{\omega}{k} \tag{2.5}$$

We now add the second wave with a slightly different wavenumber $k + \Delta k$ and slightly different angular frequency $\omega + \Delta\omega$:

$$\Psi_2(x,t) = \sin\left[(k + \Delta k)x - (\omega + \Delta\omega)t\right] \tag{2.6}$$

The sum of the two waves is

$$\begin{aligned}
\Psi(x,t) &= \Psi_1(x,t) + \Psi_2(x,t) \\
&\doteq 2\cos\left(\frac{\Delta k\, x}{2} - \frac{\Delta\omega\, t}{2}\right)\sin\left(kx - \omega t\right)
\end{aligned} \tag{2.7}$$

where we neglected terms proportional to Δk and $\Delta\omega$ in the sine term. $\Psi(x,t)$, depicted in Fig. 2.1 as a function of x at time $t = 0$, represents an infinite train of wave packets moving along the positive x-axis. The phase velocity is controlled by the sine term and in our approximation it remains the same as for $\Psi_1(x,t)$, i.e., $v_p = \frac{\omega}{k}$. A single wave packet has a frequency f', a wavelength λ'
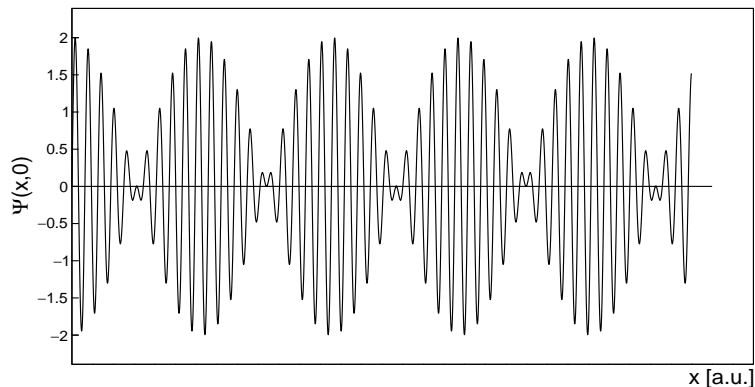

Figure 2.1: An infinite train of wave packets shown at $t = 0$ as a function of x in arbitrary units.

and a group velocity v_g, all determined by the cosine term in Eq. 2.7:

$$v_g = \lambda' f' = \frac{2\pi}{k'}\frac{\omega'}{2\pi} = \frac{2\pi}{\frac{1}{2}\Delta k}\frac{\frac{1}{2}\Delta\omega}{2\pi} = \frac{\Delta\omega}{\Delta k} \tag{2.8}$$

In the limit of $\Delta k, \Delta\omega \to 0$ we get

$$v_g = \frac{d\omega}{dk} = \frac{d}{dk}\frac{E}{\hbar} = \frac{d}{dk}\left(\frac{1}{\hbar}\sqrt{\hbar^2 c^2 k^2 + m^2 c^4}\right) = \frac{pc^2}{E} = v \tag{2.9}$$

where v is the speed of a relativistic particle with energy E and momentum p. Obviously, $v_g = v < c$. In the last step we used relativistic expressions

$$p = \frac{mv}{\sqrt{1 - \frac{v^2}{c^2}}}, \qquad (2.10)$$

$$E = \frac{mc^2}{\sqrt{1 - \frac{v^2}{c^2}}}. \qquad (2.11)$$

Interpretation of a particle as a wave packet is now on safer ground. The wave packet is localized with a dimension

$$\Delta x = \frac{\lambda'}{2} = \frac{2\pi}{\Delta k} \qquad (2.12)$$

and the velocity of the packet v_g is equal to the particle velocity v. Our classical thinking would prefer $\Delta x \to 0$ for a pointlike particle, but maybe that is a special case that we achieve if $\Delta k \to \infty$.

Note that it is possible to construct a single wave packet instead of the infinite train, however, instead of the two waves we used to construct the latter, we would have to sum infinite number of waves, each with a slightly different frequency. The result, a single packet, is nicer than an infinite train but mathematics needed is more complicated.

2.2 Davisson-Germer experiment

We have a plausible hypothesis that a particle could be represented by a single wave packet. But why didn't anyone notice the wave properties of particles until 1929?

An important clue can be obtained from a single slit diffraction experiment using light (classical electromagnetic waves), Fig. 2.2. A crucial factor which determines the outcome is the size of the wavelength of light λ relative to the size of the slit d. If $\lambda << d$ (Fig. 2.2 a), we see a sharp image of the slit on the screen consistent with geometrical optics in which a ray of light propagates along a straight line. If light consisted of particles, the result would be the same. On the other hand, if $\lambda \gtrsim d$ (Fig. 2.2 b), light seems to bend around the slit and a series of maxima appears on the screen with intensity decreasing with the distance from the central maximum. The maxima are separated by dark areas with minimum intensity. This is a diffraction phenomenon in which light manifests its wave nature.

We have come to an important point:

$$\lambda \quad << \quad d \quad \text{light hides its wave nature} \qquad (2.13)$$
$$\lambda \quad \gtrsim \quad d \quad \text{light manifests its wave nature} \qquad (2.14)$$

What is the typical value of d for a diffraction pattern to appear if $\lambda = 650$ nm (red light)? The $\lambda \gtrsim d$ condition is fulfilled for $d \lesssim 1500$ nm in this case.
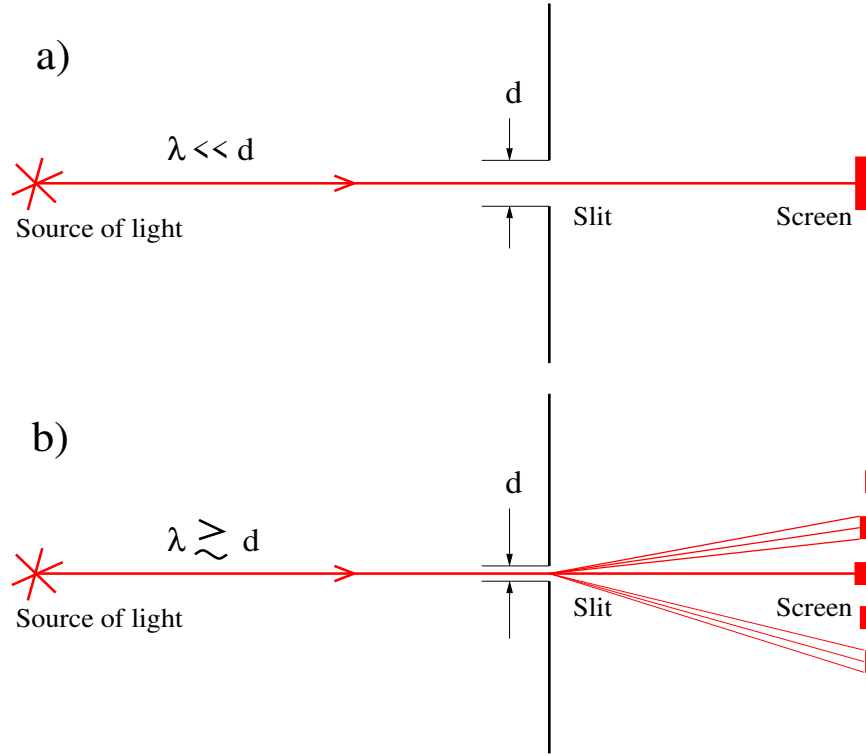
Figure 2.2: A single slit experiment. a) If $\lambda << d$, we see a sharp image of the slit on the screen with no diffraction. b) If $\lambda \gtrsim d$, a series of diffraction maxima appears with intensity decreasing with the distance from the central maximum.

Let us return to our question of why nobody noticed the wave behaviour of electrons before 1929. De Broglie thought that the wavelength of the electron could be much smaller than the typical size d of slits in the above experiment or, generally, than the size od objects that electrons used to interact with. Let us consider an electron with a rather small kinetic energy $W_k = 54$ eV (for electrons with greater energy the wavelength will be smaller) and find its wavelength. We obtain

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mW_k}} = 1.67 \times 10^{-10} \text{m}, \tag{2.15}$$

which is of the order of the distance d between atoms in a crystal. Clearly, electrons of this wavelength cannot manifest wave properties on slits and objects with $d \sim 1500$ nm $= 1.5 \times 10^{-6}$ m.

However, in 1929 Davisson and Germer used an Ni crystal as a diffraction grating with the distance between neighbouring atoms $d = 2.15 \times 10^{-10}$ m (the grating parameter) and scattered electrons of the kinetic energy $W_k = 54$ eV off

the surface of the crystal. The wavelength of electrons, Eq. 2.15, now meets the condition $\lambda \sim d$, Fig. 2.3. We know from classical electromagnetic theory that
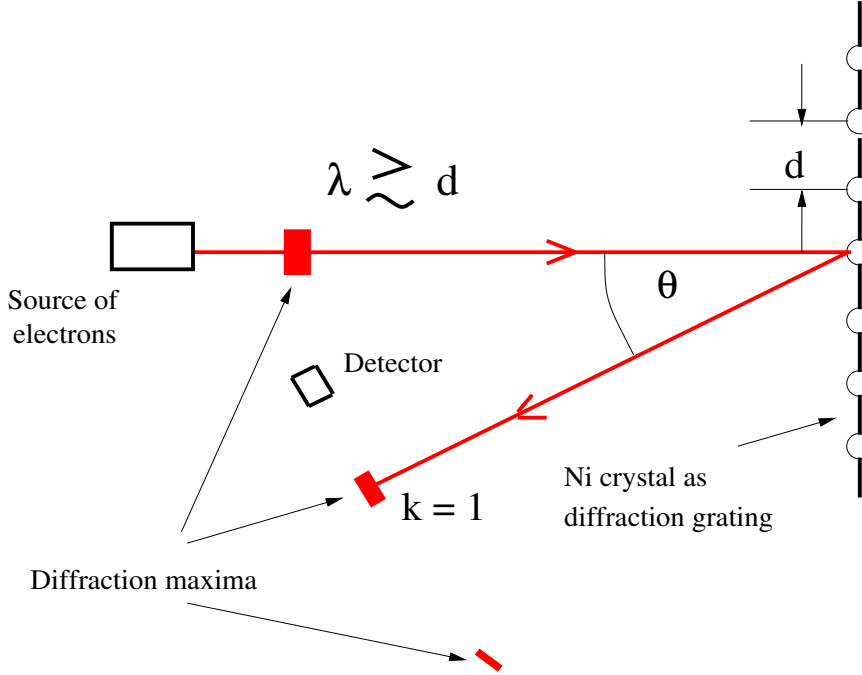

Figure 2.3: Diffraction of electrons after scattering off the Ni crystal surface.

light scattered by the diffraction grating manifests diffraction similar to a single slit experiment except that the diffraction maxima are narrower, separated by wider regions of minimum intensity. The maxima are given by

$$d \sin \theta = k\lambda, \tag{2.16}$$

where θ is the angle at which the maxima of order $k = 1, 2, 3, ...$ are observed.

Using the same equation for electrons, Davisson and Germer observed the $k = 1$ maximum at $\theta = 50°$, yielding $\lambda = d \sin 50° = 1.65 \times 10^{-10}$ m, in agreement with Eq. 2.15 within the measurement uncertainty. Further, diffraction was observed even for very low intensities of an electron beam, when just a single electron was emitted by the source and detected by the detector at a time. After a sufficient number of electrons was detected, the same diffraction pattern developed. Hence, it is a wave of a single electron that diffracts, not interference between waves of several electrons.

The typical wave phenomenon of diffraction was thus established also for particles.

2.3   Heisenberg uncertainty principle

The wave packet approach of Sec. 2.1 turns out to be very useful also for the uncertainty principle. If a single wave packet is to represent a free particle, it seems plausible that the position of the particle must be within the interval Δx given by the size of the packet (see Eq. 2.7 and Fig. 2.1)

$$\Delta x = \frac{\lambda'}{2} = \frac{2\pi}{2k'} = \frac{4\pi}{2\Delta k} = \frac{2\pi}{\Delta k} \tag{2.17}$$

Here $\lambda' = 2\pi/k' = 4\pi/\Delta k$ is the wavelength associated with the cosine term of Eq. 2.7. We get from Eq. 2.17

$$\Delta x \, \Delta k = 2\pi \tag{2.18}$$

To get a similar relation for time t and angular frequency ω, we could plot $\Psi(x,t)$ of Eq. 2.7 as a function of t at $x = 0$ and get a similar infinite train of packets along the time axis. The length of the packet would represent the time of passage of the packet through a point x, that is, the duration of the pulse Δt. Following the procedure shown in Eq. 2.17, we would get

$$\Delta t \, \Delta \omega = 2\pi \tag{2.19}$$

Our previous treatment could be technically improved: it is possible to construct a single packet which is not part of the train in a way which reduces the factor of 2π on the righthand side of Eqs. 2.18, 2.19 to 1 (Ref. [3]):

$$\Delta x \, \Delta k = 1 \tag{2.20}$$
$$\Delta t \, \Delta \omega = 1 \tag{2.21}$$

Equations 2.20, 2.21 hold for any waves including the classical waves [3]. They might be viewed as uncertainty relations in classical physics. For example, it follows from Eq. 2.21 that if we transmit radio or TV signals in pulses of duration $\Delta t \sim 10^{-6}$ s, then the pulses have the range of frequencies

$$\Delta f = \frac{\Delta \omega}{2\pi} = \frac{1}{\Delta t}\frac{1}{2\pi} \sim 10^6 \, \text{s}^{-1} \tag{2.22}$$

This range defines the broadcast band. If we used frequency $f = 1$ MHz for a broadcast, the whole band could fit just one channel since $\Delta f = 1$ MHz as well. To accommodate more channels we are forced to broadcast at frequencies much higher than 1 MHz.

To move from classical waves to particles, i.e. to quantum mechanics, we use de Broglie relations, Eqs. 2.1, 2.2, to convert Δk to Δp and $\Delta \omega$ to ΔE:

$$\Delta k = \frac{2\pi}{\Delta \lambda} = \frac{2\pi}{h}\Delta p = \frac{\Delta p}{\hbar} \tag{2.23}$$

$$\Delta \omega = 2\pi\Delta f = 2\pi\frac{\Delta E}{h} = \frac{\Delta E}{\hbar} \tag{2.24}$$

Plugging this into Eqs 2.20, 2.21, we obtain Heisenberg uncertainty relations

$$\Delta x \ \Delta p \ \geq \ \hbar \tag{2.25}$$
$$\Delta t \ \Delta E \ \geq \ \hbar. \tag{2.26}$$

The equality sign applies to the wave packet constructed in an optimal way, for the packets of other shapes the greater-than sign applies.

The Heisenberg uncertainty relation for the position and momentum, Eq. 2.25, tells us that if we want to localize particle by measuring its position x with unlimited precision, making the uncertainty $\Delta x \to 0$, the uncertainty in our knowledge of its momentum will grow as a result of the measurement, $\Delta p \to \infty$. It is impossible to know both the position and momentum of a particle with arbitrary high precision. In other words, a very precise measurement of x squeezes the packet and this requires larger Δk (Eq. 2.17).

We do not typically observe the uncertainty principle in the macroscopic world because the Planck constant has a very small value. If, e.g., we measure the position of an object with 1 kg mass with a precision $\Delta x = 10^{-4}$ m, then $\Delta p = \hbar/10^{-4}$m and hence $\Delta v = \Delta p/m = \hbar/10^{-4}$m/kg $= 6.626 \times 10^{-30}$m/s. The uncertainty in velocity is too small to observe.

Note, however, that infrared light can be used to determine the position of a visible-to-the-naked-eye membrane so precisely that the membrane recoils when the infrared pulse reflects from it, leading to a measurable uncertainty in its momentum [4].

2.4 The Bohr model of hydrogen

In a familiar school lab exercise, one uses a discharge lamp filled with a gas such as helium or neon. The gas is heated by an electric current and the lamp emits light characteristic of the gas. If the light is passed through a diffration grating, a series of lines (diffraction maxima) appears on the screen - a line spectrum of helium or neon. Each element has its own spectrum which can be used to identify the element. As a matter of fact, helium was first seen in the solar spectrum in 1868 in the form of unknown spectral lines before it was discovered directly on Earth in 1895.

The spectrum of hydrogen is the simplest one of all elements. In the visible region it is dominated by four spectral lines at the wavelengths 656.3 nm, 486.1 nm, 434.1 nm, and 410.2 nm, see Fig. 2.4. Johann Balmer found a simple empirical formula which gives the wavelengths of these lines:

$$\lambda \ = \ \frac{2^2}{R}\Big(\frac{n^2}{n^2 - 2^2}\Big) \tag{2.27}$$

where $n = 3, 4, 5, 6...$ and $R = 1.09737 \times 10^7$ m^{-1} is the Rydberg constant.

Again, classical physics failed to explain atomic spectra, not even the Balmer formula. In 1913 Niels Bohr provided an explanation known as the Bohr model of hydrogen. The Bohr model stands as a fascinating testimony of the transition
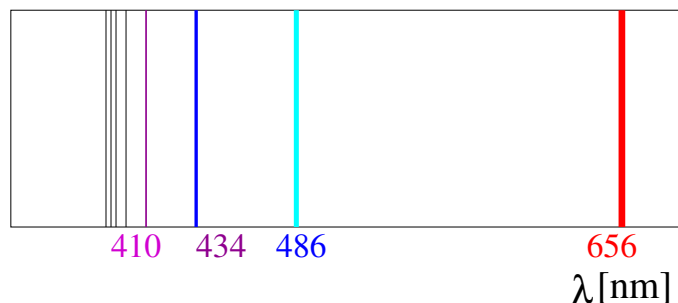
Figure 2.4: The line spectrum of atomic hydrogen - the Balmer series.

from classical physics to radically new quantum mechanics. It is a strange mixture of both theories, mathematically simple enough to be introduced even at the high school level. The lesson we learn from it is that new theories are typically formulated step by step over many years aided by experimental discoveries and ideas contributed by many people.

The Bohr model is defined by the following assumptions (postulates):

1. The negatively charged electron moves about the positively charged nucleus in a circular orbit under the action of the centripetal Coulomb force

$$F = \frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \tag{2.28}$$

where m, e, v is the mass, the size of the charge, and the speed of the electron, respectively, r the radius of the orbit, ϵ_0 the vacuum electric permitivity. The charge of the nucleus is also e.

2. The electron is allowed to move only in those orbits which obey the following equation for the angular momentum $L = mvr$,

$$mvr = n\hbar, \quad n = 1, 2, 3, 4, ... \tag{2.29}$$

3. The electron does not radiate energy when moving in orbits allowed by Eq. 2.29.

4. The atom radiates energy hf when the electron jumps from a higher allowed orbit (larger r) to a lower one (smaller r),

$$hf = E_i - E_f \tag{2.30}$$

where E_i, E_f are the energies corresponding to the higher and the lower orbits, respectively.

The strangest postulate is the second one which introduces the so-called quantization of the angular momentum L: only discrete values, $L = n\hbar$, are allowed. It was not clear why this should be true even though this quantization did lead to the correct prediction of the Balmer formula, Eq. 2.27 (Problem 2.4.3).

In 1924 Louis de Broglie interpreted the second postulate as a natural conse-
quence of the wave properties of the electron. It is crucial for this interpretation
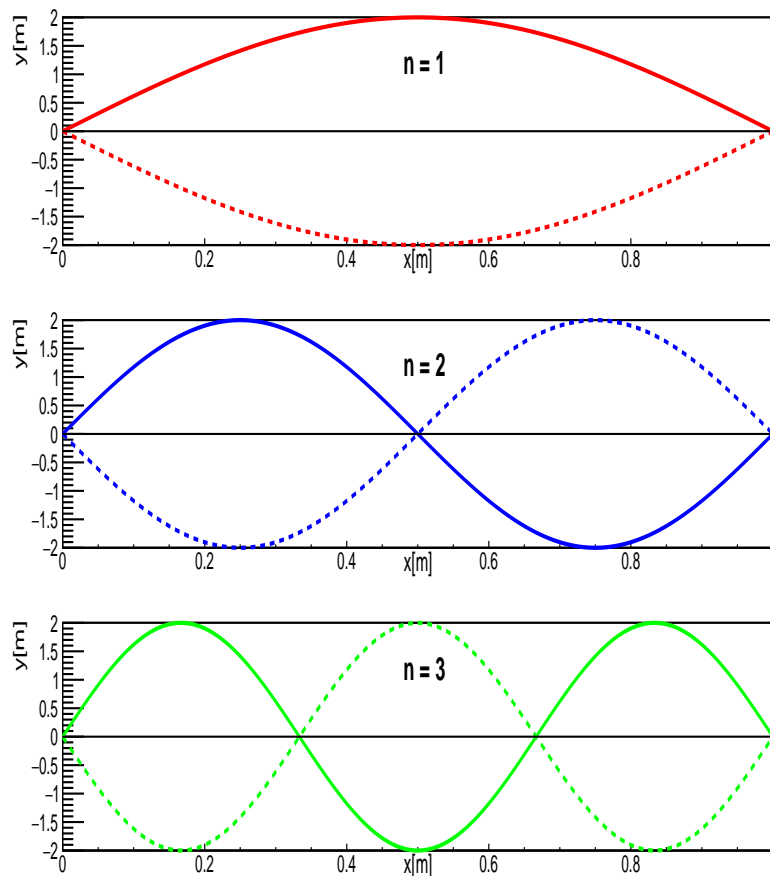to understand classical standing waves, e.g., on a guitar string, Fig. 2.5. So

Figure 2.5: Standing waves on a guitar string. The first three harmonics (n =
1, 2, 3).

far we have considered only the travelling waves in the form of freely moving
wave packets. The electron in the atom is, however, not free but rather bound.
Thus, the wave associated with the electron is forced to travel along the same
trajectory again and again, possibly creating standing waves in analogy with the
standing waves on a string. These waves can have only certain discrete values
of the wavelength given by

$$\lambda \quad = \quad \frac{2L}{n}, \quad n = 1, 2, 3, 4, ... \tag{2.31}$$

The $n = 1$ wave is called the first harmonic, $n = 2$ the second harmonic etc.[1] If we now rewrite the second postulate in terms of momentum $p = mv$,

$$p\,r \quad = \quad n\hbar, \tag{2.32}$$

and make a substitution $p = h/\lambda$, we obtain

$$\lambda \quad = \quad \frac{2\pi r}{n}. \tag{2.33}$$

Comparing this with Eq. 2.31, we can see that the circumference of the electron's orbit, $2\pi r$, plays the role of $2L$, twice the length of the string. On the string, the travelling wave returns to the beginning after it covers the distance of $2L$ (and creates the standing wave via interference), in the atom the same happens after the wave covers the distance of $2\pi r$. Indeed, it seems plausible that the second postulate stems from our representation of the electron as the standing wave inside the atom.

The image of the electron standing wave goes against the naive picture of a pointlike particle moving about the nucleus along the circular orbit. As we have seen with the wave packets, the position of a particle is uncertain at the level of the width of the packet. Here, the uncertainty is of the order of the atom's size since the standing wave fills the volume of the atom. We have made some progress but the overall picture of the hydrogen atom is still covered in a haze. To learn more, we need to move on to the Schrödinger equation.

2.4.1   Problem

Use Eqs. 2.28, 2.29 to derive the radii r of the allowed orbits of the hydrogen atom. The correct answer is

$$r \quad = \quad r_n = \frac{4\pi\epsilon_0\hbar^2}{me^2}n^2, \quad n = 1, 2, 3, 4, ... \tag{2.34}$$

2.4.2   Problem

Use Eqs. 2.28, 2.29 to derive the energies E of the allowed orbits of the hydrogen atom. The classical formula for the total energy (the sum of kinetic and potential energies, $W_k + U$) is

$$E \quad = \quad W_k + U = \frac{1}{2}mv^2 - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}. \tag{2.35}$$

The correct answer is

$$E \quad = \quad E_n = -\frac{1}{2}\frac{me^4}{(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n^2} = -\frac{13.6}{n^2} \text{ eV}, \quad n = 1, 2, 3, 4, ... \tag{2.36}$$

---

[1]We might call this phenomenon *classical quantization* although it could be misleading since it is just the classical analogy with the quantization in quantum mechanics.

2.4.3 Problem

Use Eqs. 2.30 and 2.36 to derive the Balmer formula, Eq. 2.27!

2.4.4 Problem

a) Find the photon with the largest wavelength in the Balmer series and its energy.
b) Find the photon with the smallest wavelength in the Balmer series and its energy.

Chapter 3

The Schrödinger equation

3.1   A path to the Schrödinger equation

In preparation for the Schrödinger equation, we will show how one might guess the well-known wave equation for the electromagnetic field, i.e., for the photon. The photon travels in the vacuum with the speed of light $c = \lambda f = \omega/k$ so that

$$\omega = kc. \tag{3.1}$$

Hence, the correct differential equation should be consistent with Eq. 3.1 and give simple solutions of the type $\Psi(x,t) = \sin{(kx - \omega t)}$, from which we already know how to construct the wave packets. We will now speculate about the proper form of the equation. One can exclude terms such as $\Psi(x,t)^2$, $\Psi(x,t)^3$, ... since they do not allow the superposition of waves required by various interference and diffraction phenomena (and the wave packets). On the other hand, linear terms with partial derivatives with respect to x and t are allowed,

$$\frac{\partial}{\partial t}\Psi(x,t) = -\omega \cos{(kx - \omega t)} \tag{3.2}$$

$$\frac{\partial^2}{\partial t^2}\Psi(x,t) = -\omega^2 \sin{(kx - \omega t)} \tag{3.3}$$

$$\frac{\partial}{\partial x}\Psi(x,t) = k \cos{(kx - \omega t)} \tag{3.4}$$

$$\frac{\partial^2}{\partial x^2}\Psi(x,t) = -k^2 \sin{(kx - \omega t)} \tag{3.5}$$

One can easily see that Eq. 3.1 is consistent with

$$\frac{\partial^2}{\partial t^2}\Psi(x,t) = c^2 \frac{\partial^2}{\partial x^2}\Psi(x,t). \tag{3.6}$$

We can recognize this as the wave equation for the electromagnetic field where $\Psi(x,t)$ represents one of the components of the electric (or magnetic) field $\vec{E}$.

This is not a rigorous derivation, just a plausible guess, one which paves the way for the Schrödinger equation.

Let us now consider a particle with mass $m > 0$. Instead of $E = pc$, we have

$$E = \sqrt{p^2 c^2 + m^2 c^4}. \tag{3.7}$$

After running into difficulties with Eq. 3.7, Schrödinger decided to simplify the task and instead of a relativistic quantum equation sought a nonrelativistic one, based on the total mechanical energy

$$E = \frac{p^2}{2m} + U(x, t) \tag{3.8}$$

where $U(x, t)$ is the potential energy.

As a first step, he assumed that the particle is non-interacting, described by the wave $\Psi(x, t) = \sin(kx - \omega t)$ and $U(x, t) = \text{const}$. We will now repeat the procedure we have used to find the wave equation for the electromagnetic field. Substituting $E = hf$ and $p = h/\lambda$ into Eq. 3.8 and using $\omega = 2\pi f$, $\lambda = 2\pi/k$, we get

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} + U(x, t) \tag{3.9}$$

It turns out that it is not possible to find the right combination of partial derivatives of Eqs. 3.2 - 3.5 with $\Psi(x, t) = \sin(kx - \omega t)$, which would be consistent with Eq. 3.9. Schrödinger was forced to try instead

$$\Psi(x, t) = a\cos(kx - \omega t) + b\sin(kx - \omega t) \tag{3.10}$$

and finally succeeded with $a = 1$ and $b = i$ so that the quantum wave for a free particle, known as the *wave function*, became a complex function

$$\Psi(x, t) = \cos(kx - \omega t) + i\sin(kx - \omega t) = e^{i(kx - \omega t)}, \tag{3.11}$$

the solution of the famous Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\Psi(x, t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x, t) + U(x, t)\Psi(x, t) \tag{3.12}$$

As a final and very nontrivial point, Schrödinger generalized his treatment postulating that the same equation holds also for the general case of $U(x, t) \neq \text{const}$, i.e., for a particle that is not free.

3.2 Interpretation of the wave function

The Schrödinger equation describes the time development and the distribution in space of the wave function $\Psi(x, t)$. But what is the meaning of the wave function? We described a free particle as a wave packet with a group velocity equal to the velocity of the particle. It seems natural to assume that the particle

is somewhere inside the packet where $\Psi(x,t) > 0$. We will now give a more precise meaning to this vague idea.

In Sec. 2.2 we have seen that the diffraction pattern in the Davisson-Germer experiment developed even at very low intensities of an electron beam, when just a single electron was emitted by the source. We concluded that it is a wave of a single electron that diffracts, not interference between waves of several electrons. But does this wave have a physical existence similar to water waves? We could arrange a large number of electron detectors in a half-circle to cover all angles θ in the experiment simultaneously to see what happens. If the electron's wave function behaved as a water wave, it would reach all detectors and presumably leave a signal in each of them in proportion to its amplitude at a given θ. The single electron would be present in all detectors: more present in the detectors at $\theta = 0°$ and $\theta = 50°$ and less present at other angles. That was how Schrödinger originally interpreted the wave function. In reality, only one of the detectors detects the whole of a single electron at a time. It is impossible to predict which detector it will be, we can only assign the probability of detection to each detector based on the diffraction pattern of the Davisson-Germer experiment, with the highest probabilities at $\theta = 0°$ and $\theta = 50°$.

This brings us to the probability interpretation due to Max Born, published in 1926 before the Davisson-Germer experiment (1929). The wave function does not have a physical existence in the sense that water waves do. It is a probability wave related to the probability with which we can detect a particle at a point in space and time. In particular, Born suggested and supported with arguments that the probability[1] dP for a particle to be found within the interval $(x, x+dx)$ at time t, is given by

$$dP = \rho(x,t)\,dx = \Psi^*(x,t)\Psi(x,t)\,dx, \qquad (3.13)$$

where $\rho(x,t) = \Psi^*(x,t)\Psi(x,t)$ is the probability per unit length (the probability density) and $\Psi^*(x,t)$ is the complex conjugate of $\Psi(x,t)$. It is easy to show that $\rho(x,t)$ is real, as it should be. If $\Psi(x,t) = R(x,t) + i\,Im(x,t) = R + i\,I$, then

$$\rho(x,t) = \Psi^*(x,t)\Psi(x,t) = (R - i\,I).(R + i\,I) = R^2 + I^2. \qquad (3.14)$$

The total probability to find a particle anywhere along the x-axis is

$$P = \int_{-\infty}^{\infty} \rho(x,t)\,dx = 1. \qquad (3.15)$$

3.3 Expectation values and operators

It is a postulate of quantum mechanics that the wave function contains all information about a particle or a quantum system such as, e.g., a hydrogen atom. All means all: not just information about (the probability of) its position but also about its energy, momentum and other quantities. Here we will show how this vital knowledge can be extracted from the wave function.

---

[1]We show this for a particle moving in one direction.

The expectation value of x is postulated as

$$\bar{x} = \int_{-\infty}^{\infty} x \, \rho(x,t) \, dx = \int_{-\infty}^{\infty} \Psi^*(x,t) \, x \, \Psi(x,t) \, dx. \tag{3.16}$$

The value of x in the integrand is weighted by the probability of observing that value. After we integrate, we obtain the average of all possible values of x. Likewise, for the expectation value of x^2 we get

$$\overline{x^2} = \int_{-\infty}^{\infty} \Psi^*(x,t) \, x^2 \, \Psi(x,t) \, dx. \tag{3.17}$$

The expectation value of the potential energy is

$$\overline{U(x,t)} = \int_{-\infty}^{\infty} \Psi^*(x,t) \, U(x,t) \, \Psi(x,t) \, dx. \tag{3.18}$$

The expectation value of momentum is a bit different. The expression is still as expected,

$$\bar{p} = \int_{-\infty}^{\infty} \Psi^*(x,t) \, p \, \Psi(x,t) \, dx, \tag{3.19}$$

however, the integrand must be expressed as a function of x and t and it is not obvious how one can do that with p since once we know x, p cannot be known due to the uncertainty principle. We can find a way around if we consider a free particle with $\Psi(x,t) = e^{i(kx - \omega t)}$. For a partial derivative with respect to x we have

$$\frac{\partial \Psi}{\partial x} = ike^{i(kx-\omega t)} = i\frac{p}{\hbar}e^{i(kx-\omega t)} = i\frac{p}{\hbar}\Psi. \tag{3.20}$$

From here we get multiplying both sides by $-i\hbar$

$$p\Psi = -i\hbar\frac{\partial}{\partial x}\Psi. \tag{3.21}$$

This suggests an association between p and the operator $\hat{p} = -i\hbar\frac{\partial}{\partial x}$. We are led to postulate

$$\bar{p} = \int_{-\infty}^{\infty} \Psi^*(x,t) \, \hat{p} \, \Psi(x,t) \, dx = \int_{-\infty}^{\infty} \Psi^*(x,t) \, (-i\hbar)\frac{\partial}{\partial x}\Psi(x,t). \tag{3.22}$$

The operator of kinetic energy is

$$\hat{W}_k = \frac{1}{2m}\hat{p^2} = \frac{1}{2m}\hat{p}\hat{p} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{3.23}$$

and the operator of the total energy E, the so-called Hamiltonian, is

$$\hat{H} = \hat{W}_k + \hat{U}(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x,t). \tag{3.24}$$

In general, the expectation value of quantity A is

$$\bar{A} = \int_{-\infty}^{\infty} \Psi^*(x,t) \, \hat{A} \, \Psi(x,t) \, dx. \tag{3.25}$$

A quantum operator[2] $\hat{A}$ corresponds to each classical quantity A. As we have seen, the operators for quantities $x, f(x), U(x,t)$ are equal to these quantities, $\hat{x} = x, \hat{f}(x) = f(x), \hat{U}(x,t) = U(x,t)$. For quantities which depend on p, we replace p with $\hat{p} = -i\hbar\frac{\partial}{\partial x}$.

Finally, let us consider an operator $\hat{A}$. If a function f exists for which

$$\hat{A}f = af \tag{3.26}$$

where a is a constant, then f is an eigenfunction of $\hat{A}$ and a is the corresponding eigenvalue. It is a postulate of quantum mechanics that a physical quantity A can take on only those values which are the eigenvalues of the operator $\hat{A}$.

3.4 The time-independent Schrödinger equation

The Schrödinger equation is time dependent as manifested by the presence of time t,

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) \;\; = \;\; -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + U(x,t)\Psi(x,t). \tag{3.27}$$

If the potential energy does not depend on time, $U(x,t) = U(x)$, we can look for solutions of the time-dependent Schrödinger equation, the so-called stationary states, in the form

$$\Psi(x,t) \;\; = \;\; \psi(x) \, \Phi(t). \tag{3.28}$$

Stationary states are states for which $\Phi(t) = e^{-i\omega t}$ and hence the probability density is independent of time:

$$\rho \;\; = \;\; \Psi^*(x,t)\Psi(x,t) \;\; = \;\; \psi^*(x)\psi(x)e^{+i\omega t}e^{-i\omega t} \;\; = \;\; \psi^*(x)\psi(x). \tag{3.29}$$

We will now show that $\Phi(t) = e^{-i\omega t}$ for $U(x,t) = U(x)$. Substituting Eq. 3.28 into Eq. 3.27, we obtain

$$-\frac{\hbar^2}{2m}\Phi(t)\,\frac{\partial^2}{\partial x^2}\psi(x) + U(x)\,\psi(x)\,\Phi(t) \;\; = \;\; i\hbar\,\psi(x)\frac{\partial}{\partial t}\Phi(t). \tag{3.30}$$

Dividing both sides by $\psi(x)\Phi(t)$ we obtain

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + U(x)\psi(x)\right] \;\; = \;\; i\hbar\,\frac{1}{\Phi(t)}\frac{\partial}{\partial t}\Phi(t). \tag{3.31}$$

---

[2]A technical note: in quantum mechanics these operators are hermitian, $\hat{A}^\dagger = \hat{A}$.

The left-hand side is a function of x and the right-hand side is a function of t with the consequence that both sides must be equal to the same constant C,

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + U(x)\psi(x) \;=\; C\psi(x), \tag{3.32}$$

$$i\hbar\frac{\partial}{\partial t}\Phi(t) \;=\; C\Phi(t). \tag{3.33}$$

The solution of Eq. 3.33 is

$$\Phi(t) \;=\; e^{-i\frac{C}{\hbar}t}. \tag{3.34}$$

The constant $C/\hbar$ is the angular frequency of oscillations, ω. From de Broglie relations we know that $\omega = E/\hbar$, hence C is energy, $C = E$. Eq. 3.32 now becomes the time-independent Schrödinger equation

$$\hat{H}\,\psi(x) \;=\; E\,\psi(x), \tag{3.35}$$

where

$$\hat{H} = \hat{W}_k + \hat{U} \;=\; -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x) \tag{3.36}$$

is the energy operator, the Hamiltonian, the sum of kinetic energy operator $\hat{W}_k$ and potential energy operator $\hat{U} = U(x)$. The time-independent Schrödinger equation is the equation for the eigenvalues E and eigenfunctions $\psi(x)$ of the Hamiltonian $\hat{H}$ (compare with Eq. 3.26).

To conclude, stationary states have the form

$$\psi(x,t) \;=\; \psi(x)e^{-i\frac{E}{\hbar}t} \tag{3.37}$$

where $\psi(x)$ is the solution of the time-independent Schrödinger equation, the eigenfunction of the Hamiltonian. In the following chapters we will seek this solution for different systems of increasing complexity, starting with particle in a box and continuing with harmonic oscillator and hydrogen atom.

Chapter 4

Two simple quantum systems

4.1 Particle in a box

The simplest quantum system is particle in an infinite square well (a box), see Fig. 4.1. The potential energy $U(x) = 0$ for $0 < x < L$ and $U(x) = \infty$ for $x = 0$ and $x = L$. Once the particle is in the well, it is trapped inside since when it approaches the walls it is reflected back by the infinite energy barrier. Our motivation to study this system is primarily due to its mathematical simplicity, however, from a practical point of view, certain organic molecules form linear strings of length L and the motion of an electron along the string can be approximately described as that of the particle in a box. We will show now that unlike a classical particle, the particle in the well can occupy only certain discrete energy levels, the lowest ones indicated in Fig. 4.1 as E_1, E_2 and E_3.

The potential energy $U(x)$ is independent of time, hence the wavefunction has the form

$$\psi(x,t) \quad = \quad \psi(x)e^{-i\frac{E}{\hbar}t} \tag{4.1}$$

with $\psi(x)$ being the solution of the time-independent Schroedinger equation

$$\hat{H}\psi(x) \quad = \quad E\psi(x). \tag{4.2}$$

Recalling that

$$\hat{H} \quad = \quad \hat{W}_k + \hat{U}(x), \tag{4.3}$$

we obtain for $0 < x < L$ (where $U(x) = 0$)

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) \quad = \quad E\ \psi(x). \tag{4.4}$$
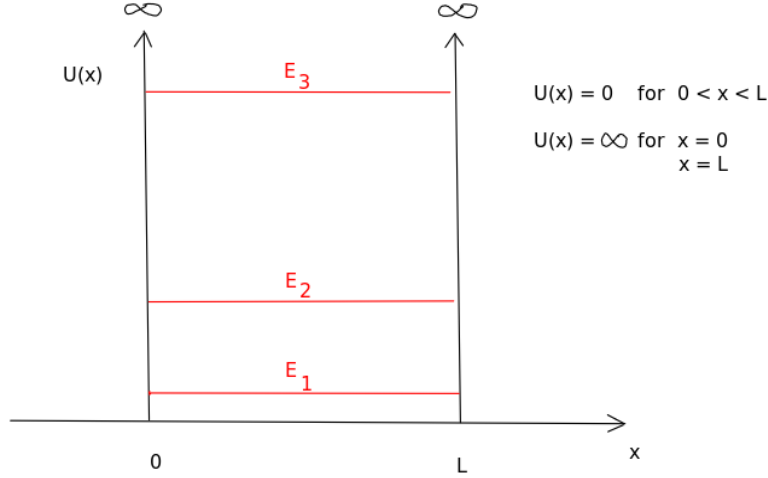
Figure 4.1: Infinite square well with the lowest three quantum levels (energies E_1, E_2, E_3) that a particle can occupy indicated in red.

After rearrangement our equation takes the form

$$\frac{d^2}{dx^2}\psi(x) + \frac{2mE}{\hbar^2}\psi(x) \quad = \quad 0. \tag{4.5}$$

Outside $0 < x < L$, $\psi(x)$ has to vanish since the particle cannot penetrate through the infinite barriers. Thus, our boundary condition will be

$$\psi(0) \quad = \quad \psi(L) \quad = \quad 0. \tag{4.6}$$

The solution of Eq. 4.5 has the form (as can be easily verified)

$$\psi(x) \quad = \quad A\sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) + B\cos\left(\sqrt{\frac{2mE}{\hbar^2}}x\right). \tag{4.7}$$

The boundary condition $\psi(0) = 0$, which the solution has to respect, requires that $B = 0$ and only the first part with constant A survives. The second boundary condition, $\psi(L) = 0$, forces us either to $A = 0$ with trivial solution $\psi(x) = 0$ (particle is not in the well), or to a nontrivial solution with a special condition for energy E,

$$\sqrt{\frac{2mE}{\hbar^2}}L \quad = \quad n\,\pi, \quad n = 1, 2, 3, 4, ..., \tag{4.8}$$

or,

$$E_n \quad = \quad \frac{\pi^2\hbar^2}{2mL^2}n^2 \quad n = 1, 2, 3, 4, ... \tag{4.9}$$

We interpret this result as quantization of energy inside the infinite square well. Only positive integer values of n are allowed, implying that energy can take only discrete values. The minimum energy,

$$E_1 \;=\; \frac{\pi^2\hbar^2}{2mL^2} \;>\; 0, \tag{4.10}$$

so one cannot have quantum particle in a box with $E = 0$. This conclusion is also supported by Heisenberg uncertainty relation,

$$\Delta x\,\Delta p \;\geq\; \hbar. \tag{4.11}$$

Uncertainty in position is in our case

$$\Delta x = L. \tag{4.12}$$

Uncertainty Δp in the minimum energy state follows from

$$p_1^2 \;=\; 2mE_1 \;=\; \frac{\pi^2\hbar^2}{L^2} \tag{4.13}$$

which suggests that $p_1 = \pm\pi\hbar/L$, leading to uncertainty

$$\Delta p \;=\; 2|p_1| \;=\; \frac{2\pi\hbar}{L}. \tag{4.14}$$

Plugging both uncertainties (Eqs. 4.12, 4.14) into Eq. 4.11,

$$L\frac{2\pi\hbar}{L} \;=\; 2\pi\hbar \geq \hbar. \tag{4.15}$$

The minimum energy state (as all higher quantum states) thus obeys the uncertainty relation. However, a hypothetical state with $E = 0$ has $p_1^2 = 0$ and $\Delta p = 0$, violating Eq. 4.11. The uncertainty relation does not allow $E = 0$ state. This is strikingly different from a classical particle in a box. A marble ball inside an empty glass can, of course, sit still $(E = 0)$ at the bottom. The quantum particle is always in motion.

Let us return now to our solution in Eq. 4.7. Using Eq. 4.9 and $B = 0$, we get for the eigenfunctions

$$\psi_n(x) \;=\; A\sin\left(\frac{n\pi}{L}x\right), \quad n = 1, 2, 3, 4, ... \tag{4.16}$$

According to the probability interpretation of the wavefunction, the probability density integrated over all x has to be equal to one,

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 dx \;=\; \int_{-\infty}^{\infty} \psi_n(x)^*\psi_n(x)e^{+i\frac{E}{\hbar}t}e^{-i\frac{E}{\hbar}t}dx \tag{4.17}$$

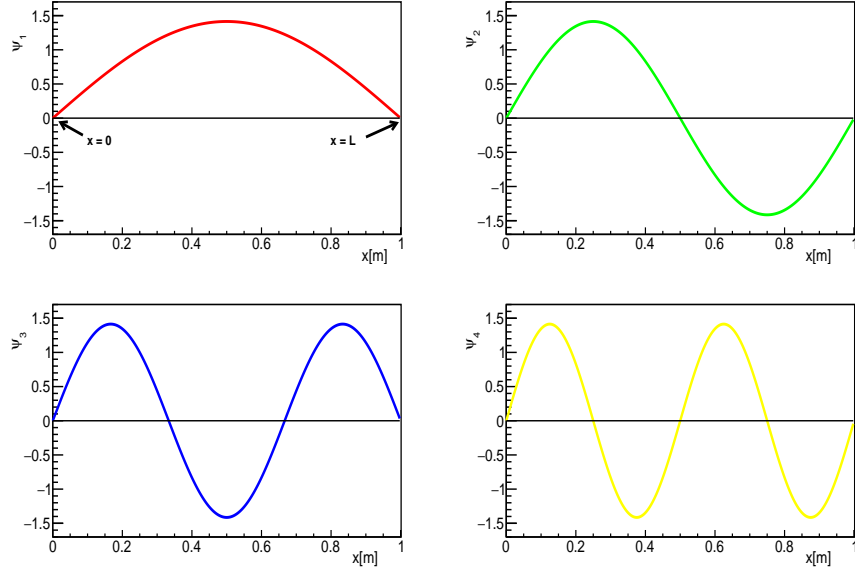$$=\; \int_{-\infty}^{\infty} \psi_n(x)^*\psi_n(x)\,dx \;=\; 1.$$

Figure 4.2: Eigenfunctions for the four lowest energy states of the infinite square well.

Substituting from Eq. 4.16,

$$\int_{-\infty}^{\infty} \psi_n(x)^* \psi_n(x) dx \;\; = \;\; A^2 \int_0^L \sin^2 \left(\frac{n\pi}{L}x\right) dx \;\; = \;\; A^2 \frac{L}{2} \;\; = \;\; 1, \quad (4.18)$$

which is true only if $A = \sqrt{2/L}$. The final form of eigenfunctions is

$$\psi_n(x) \;\; = \;\; \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right). \tag{4.19}$$

We plot $\psi_n(x)$ for $n = 1, 2, 3, 4$ in Fig. 4.2. The eigenfunctions $\psi_n(x)$ have the same mathematical form with respect to position x as the classical vibrations of the guitar string attached at $x = 0$ and $x = L$, i.e., standing waves,

$$
\begin{aligned}
y_n(x,t) \;\; &= \;\; A' \sin(kx - \omega t) + A' \sin(kx + \omega t) \\
&= \;\; 2A' \sin\left(\frac{n\pi}{L}x\right) \cos(\omega t)
\end{aligned}
\tag{4.20}
$$

where $y_n(x,t)$ is the displacement of the string from equilibrium, $k = 2\pi/\lambda_n$, $\omega = vk = 2\pi/T$ is angular frequency of vibrations, and

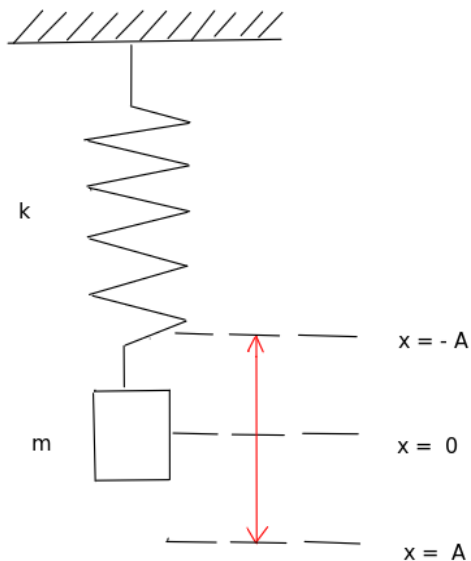$$\lambda_n \;\; = \;\; \frac{2L}{n}, \quad n = 1, 2, 3, 4, ... \tag{4.21}$$

Figure 4.3: Vibrating mass m on a spring with constant k representing classical harmonic oscillator.

In particular, ψ_1 (y_1) represents fundamental vibration of the string with fundamental frequency $f_1 = v/\lambda_1$, or the first harmonic, ψ_2 represents vibration of the second harmonic etc. The physics of particle in a infinite quantum square well is mathematically equivalent to the physics of classical musical instruments.

4.2 Classical harmonic oscillator

If a mass m, attached to a spring with a spring constant k, is pulled from its equilibrium position at $x = 0$ down to $x = -A$ and released, it will be driven back and exercise oscillations about the equilibrium (Fig. 4.3).

The force is given by the Hooke's law as $F_x = -kx$, leading to the differential equation

$$m\frac{d^2x(t)}{dt^2} = -kx(t) \tag{4.22}$$

with the solution

$$x(t) = A\cos(\omega t + \phi), \quad \text{where } \omega = \sqrt{\frac{k}{m}} \tag{4.23}$$

and ϕ is a phase constant. Typically, it is sufficient to show $x(t)$ to understand the classical harmonic oscillations, however, we would like to determine some-
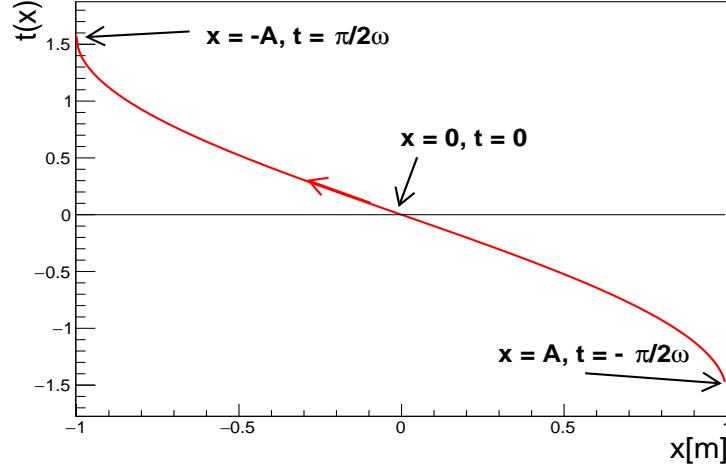
Figure 4.4: This graph shows the time $t(x)$ corresponding to the position x of the classical harmonic oscillator during half a period. The vibration starts at $x = A$ and proceeds through the equilibrium at $x = 0$ to $x = -A$. $A = 1$m and $\omega = 1$s^{-1}.

thing else, the probability that we find the oscillator at $(x, x+dx)$ when we look at it at random time. For that purpose we invert Eq. 4.23 to get the time t at which the oscillator was at the position x,

$$t(x) \quad = \quad \frac{1}{\omega} \arccos(\frac{x}{A}) - \frac{\phi}{\omega}. \tag{4.24}$$

Function $t(x)$ is plotted in Fig. 4.4 for $A = 1$m, $\omega = 1$s^{-1}, and $\phi = \frac{\pi}{2}$. The oscillator starts its vibration at $t = -\frac{\pi}{2\omega}$ when it is at $x = A$, later, for $t = 0$, it is at $x = 0$ and, finally, for $t = \frac{\pi}{2\omega}$ it arrives at $x = -A$. It spends most of the time near the two boundaries $x = \pm A$ when its velocity is approaching zero.

Probability dP to find the oscillator at $(x, x+dx)$, which we derive here for a later comparison with the corresponding probability for the quantum oscillator, is given by the time dt it spends there divided by the total time $T/2$ it takes to oscillate from $x = A$ to $x = -A$,

$$dP \quad = \quad \frac{dt}{T/2} = \frac{|\frac{dt}{dx}|dx}{T/2} = \frac{|\frac{dt}{dx}|dx}{\frac{\pi}{\omega}} = \frac{\omega}{\pi}|\frac{dt}{dx}|dx = \rho_c \, dx, \tag{4.25}$$

with classical probability density ρ_c given by

$$\rho_c \quad = \quad \frac{\omega}{\pi}|\frac{dt}{dx}| = \frac{\omega}{\pi}|\frac{d}{dx}t(x)|. \tag{4.26}$$

The absolute value of $\frac{d}{dx}t(x)$ is needed since the derivative is negative (with increasing x we go back in time towards $x = A$ where the oscillations began). Taking the derivative of Eq. 4.24 we get

$$\rho_c = \frac{1}{\pi A \sqrt{1 - \frac{x^2}{A^2}}}. \tag{4.27}$$

We can easily check that the total probability P to find the oscillator anywhere between $x = -A$ and $x = A$ is

$$P = \int_{-A}^{A} \frac{dx}{\pi A \sqrt{1 - \frac{x^2}{A^2}}} = 1, \tag{4.28}$$

as expected.

Finally, the potential energy of the oscillator is given by

$$U(x) = \frac{1}{2}kx^2. \tag{4.29}$$

4.3 Quantum oscillator

The quadratic dependence of the potential energy on x, found for the mass on a spring represents a wider class of physical systems. Atoms in the crystal lattice can vibrate about their equilibrium positions and so can atoms in molecules. In both cases, the potential energy is approximated for small vibrations by Eq. 4.29. However, instead of the classical solution (Eqs. 4.22, 4.23), for atoms and molecules we have to solve Schroedinger equation with the potential energy operator $\hat{U}(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2$. Since $\hat{U}(x)$ is independent of time, the wavefunction has the form

$$\psi(x,t) = \psi(x)e^{-i\frac{E}{\hbar}t} \tag{4.30}$$

with $\psi(x)$ being the solution of the time-independent Schroedinger equation

$$\hat{H}\psi(x) = E\psi(x). \tag{4.31}$$

The Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2, \tag{4.32}$$

so that Eq. 4.31 takes the form

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + \frac{1}{2}m\omega^2 x^2\psi(x) = E\psi(x) \tag{4.33}$$

We now multiply both sides by $-\frac{2m}{\hbar^2}$,

$$\frac{\partial^2}{\partial x^2}\psi(x) - \frac{m^2\omega^2}{\hbar^2}x^2\psi(x) + \frac{2m}{\hbar^2}E\psi(x) = 0. \tag{4.34}$$

With two more substitutions,

$$y = a^{\frac{1}{4}}x = \left(\frac{m^2\omega^2}{\hbar^2}\right)^{\frac{1}{4}}x,$$

$$\alpha = \frac{2E}{\hbar\omega}, \tag{4.35}$$

we obtain

$$\frac{\partial^2}{\partial y^2}\psi(y) + \left(\alpha - y^2\right)\psi(y) = 0. \tag{4.36}$$

We first find the asymptotic form that $\psi(y)$ takes for $y \to \pm\infty$. In this limit $\alpha \ll y^2$ and Eq. 4.34 simplifies to

$$\frac{\partial^2}{\partial y^2}\psi_\infty(y) - y^2\psi_\infty(y) = 0 \tag{4.37}$$

where $\psi_\infty(y)$ is the asymptotic form of $\psi(y)$. The mathematical solution for $y \to \infty$ is

$$\psi_\infty(y) = C_1 e^{\frac{y^2}{2}} + C_2 e^{-\frac{y^2}{2}}. \tag{4.38}$$

The probabilistic interpretation of the wavefunction, $\int_{-\infty}^{\infty} \psi^*(y)\psi(y)dy = 1$, requires that $\psi_\infty(y)$ must vanish for $y \to \infty$, implying $C_1 = 0$ and

$$\psi_\infty(y) = C_2 e^{-\frac{y^2}{2}}. \tag{4.39}$$

Knowing the asymptotic behavior, we look for the solution of Eq. 4.36 in the form

$$\psi(y) = g(y)e^{-\frac{y^2}{2}}, \tag{4.40}$$

which, upon inserting in Eq. 4.36, yields

$$\frac{d^2}{dy^2}g(y) - 2y\frac{d}{dy}g(y) + (\alpha - 1)g(y) = 0, \tag{4.41}$$

known as the *Hermite* differential equation whose solution is sought as an infinite power series

$$g(y) = A_0 + A_1 y + A_2 y^2 + A_3 y^3 + ... = \sum_{n=0}^{+\infty} A_n y^n \tag{4.42}$$

with unknown coefficients A_n. Substituting the power series into Eq. 4.41, we obtain after some rearrangements

$$\sum_{n=0}^{+\infty}\left[(n+2)(n+1)A_{n+2} - (2n+1-\alpha)A_n\right]y^n = 0. \tag{4.43}$$

If this equation is to hold for any y, we have to demand that the term in the square brackets is zero for all n, yielding the recursion relation

$$A_{n+2} = \frac{2n+1-\alpha}{(n+2)(n+1)} A_n, \tag{4.44}$$

which can be used to calculate coefficients $A_2, A_3, A_4, ...A_n$ if we know A_0, A_1.

An arbitrary value of α leads to a truly infinite series of Eq. 4.42 with all coefficients A_n nonzero. As shown in, e.g., [3, 5], the consequence is that $\psi(y)$ diverges,

$$\lim_{y\to\infty} \psi(y) = g(y)e^{-\frac{y^2}{2}} = \infty. \tag{4.45}$$

Once again, the proper probabilistic normalization, $\int_{-\infty}^{\infty} \psi^*(y)\psi(y)dy = 1$, forces us to choose the finite series from the most general mathematical solution of Eq. 4.42. This is achieved by demanding

$$\alpha = 2n+1. \tag{4.46}$$

If, e.g., $n = 2$ ($\alpha = 5$), the only nonzero even coefficients are A_0 and A_2 since for $n = 2$ we get from Eq.4.44 $A_4 = 0$. At the same time the odd coefficients are eliminated by the choice $A_1 = 0$. Likewise, if n is odd, only the finite number of odd A_n coefficients survive and the even coefficients are eliminated by the choice $A_0 = 0$.

Equation 4.46 has nontrivial consequences. Since $\alpha = \frac{2E}{\hbar\omega}$, we get the quantization of the energy of the harmonic oscillator,

$$E = E_n = \hbar\omega(n + \frac{1}{2}), \quad n = 0, 1, 2, 3, ... \tag{4.47}$$

For each E_n we have a different solution of Eq. 4.36,

$$\psi_n = g(y)e^{-\frac{y^2}{2}} = N_n H_n(y)e^{-\frac{y^2}{2}}, \tag{4.48}$$

where $H_n(y)$ are Hermite polynomials and N_n are normalization constants,

$$N_n = (\frac{m\omega}{\hbar\pi})^{\frac{1}{4}} (2^n n!)^{-\frac{1}{2}}. \tag{4.49}$$

The Hermite polynomials for $n = 0, 1, 2, 3$ and 10 are shown explicitly in Tab. 4.3.

In Fig. 4.5 we plot eigenfunctions of the quantum harmonic oscillator for $n = 0, 1, 2, 3$ and 10 as functions of position x. To be specific, we chose a vibrating CO molecule with $k = 187$ Nm^{-1} and reduced mass $m = 1.14 \times 10^{-26}$ kg. We also plot (see bottom right) the probability density $|\psi_{10}|^2$ for a quantum harmonic oscillator at $n = 10$ and the corresponding probability density for a classical oscillator of the same energy.

n	$H_n(y)$	E_n
0	1	$\frac{1}{2}\hbar\omega$
1	$2y$	$\frac{3}{2}\hbar\omega$
2	$4y^2 - 2$	$\frac{5}{2}\hbar\omega$
3	$8y^3 - 12y$	$\frac{7}{2}\hbar\omega$
...	...	...
10	$1024\,y^{10} - 23040\,y^8 + 161280\,y^6 - 403200\,y^4$ $+302400\,y^2 - 30240$	$\frac{21}{2}\hbar\omega$

Table 4.1: Hermite polynomials

4.4   Classical versus quantum oscillators

There are important differences between the classical and the quantum oscillator.

1. The classical oscillator can take on any value of energy E, the quantum one just discrete ones $E_n = (n+\frac{1}{2})\hbar\omega$. A direct proof of the latter are vibrational spectra of molecules and of atoms in the crystal lattices. An indirect proof is offered by the specific heat capacities which grow abruptly with temperature as vibrational degrees of freedom are excited.

2. The quantum oscillator, unlike the classical one, cannot be stopped - it has a nonzero energy in the lowest energy state,

$$E_0 \;\; = \;\; \frac{1}{2}\hbar\omega, \tag{4.50}$$

responsible for vibrations even at zero temperature $(T = 0)$.

The zero-point vibrations were proven by R. W. James in 1929 during his studies of the light diffusion on inhomogeneities in the crystals. The diffusion in an ideal monocrystal is due to the vibrations of atoms in the crystal lattice and for a classical oscillator it should vanish in the limit $T \to 0$. James has shown that diffusion persisted in this limit, the behaviour consistent with the existence of the zero-point vibrations.

The zero-point energy is also responsible for the fluidity of ^{3}He and ^{4}He at $T \to 0$. The small mass m of the helium atom leads to a large value of $E_0 = \frac{1}{2}\hbar\sqrt{\frac{k}{m}}$ which overwhelms weak attractive forces between helium atoms and melts any lattice.

3. The quantum oscillator can be found beyond the limit set by the amplitude A of the classical oscillations, since eigenstates ψ_n are nonzero for $|x| > A$, see Fig. 4.5.

4. The probability density, shown explicitly in Fig. 4.5 bottom right for $n = 10$ state, highlights another difference between classical and quantum vibrations. For $n = 0$, the highest probability to find the quantum oscillator is at $x = 0$ while for its classical counterpart it is at $x = \pm A$. At $n = 10$, the difference between the two gets smaller. Indeed, when the quantum oscillations are effectively
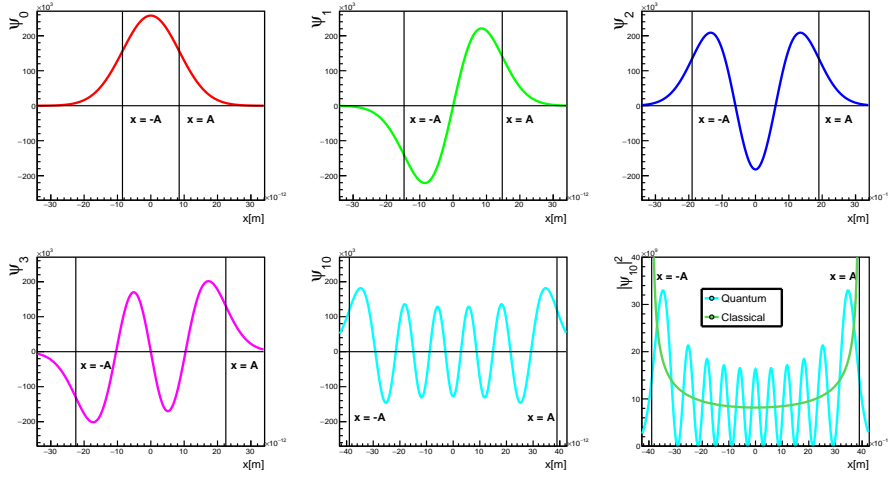
Figure 4.5: Harmonic oscillator eigenfunctions ψ_n for $n = 0, 1, 2, 3$ and 10. Vertical lines at $x = \pm A$ show boundaries between which a classical oscillator with the same energy would oscillate. Also shown are probability densities for a quantum harmonic oscillator $|\psi_{10}|^2$ and the corresponding probability density for a classical oscillator of the same energy.

averaged out, we get close to the classical probability density with the minimum at $x = 0$ and maxima at $x = \pm A$. Thus in the limit of large quantum numbers, $n \to \infty$, we retrieve classical mechanics - behaviour known as correspondence principle, formulated by Bohr in 1920.

4.4.1 Problem

Find the lowest energy E_1 for a neutron in an infinite square well with the width of the well $L = 10^{-14}$ m (about the size of a nucleus)!

4.4.2 Problem

Show that eigenfunctions ψ_n of the harmonic oscillator given by Eq. 4.48 form an orthonormal set, i.e.,

$$\int_{-\infty}^{\infty} \psi_n^* \psi_m dx = \delta_{nm} \tag{4.51}$$

where

$$\delta_{nm} = 0 \quad \text{for} \quad n \neq m \tag{4.52}$$
$$\delta_{nm} = 1 \quad \text{for} \quad n = m \tag{4.53}$$

Do this for all combinations of $n, m = 0, 1, 2, 3$ using an appropriate software tool for integration (for example using Wolfram Alpha, www.wolframalpha.com)!

4.4.3   Problem

Prepare the mixed state out of the eigenfunctions ψ_2 and ψ_3 of the harmonic oscillator

$$\psi \quad = \quad c_2\psi_2 + c_3\psi_3 \tag{4.54}$$

so that (performing measurement on this mixed state) we can measure the energy $E_2 = \hbar\omega(2 + \frac{1}{2})$ of the oscillations with the probability 30 %. In effect, you have to find the coefficients c_1 and c_2. Remember and check that the mixed wavefunction ψ is properly normalized: $\int_{-\infty}^{\infty} \psi^*\psi dx = 1$.

4.4.4   Problem

Let us assume that the harmonic oscillator is in the state ψ_m (the eigenstate with energy $E_m = \hbar\omega(m + \frac{1}{2})$). The probability of transition from ψ_m to the state ψ_n (the eigenstate with energy E_n) is proportional to the integral

$$I \quad = \quad \int_{-\infty}^{\infty} x\, \psi_m^*\psi_n dx \tag{4.55}$$

If $I > 0$, the transition is allowed and will proceed via the photon emission (for $m > n$) or absorbtion (for $m < n$). The photon energy has to be $E = |E_m - E_n|$. If $I = 0$, the transition is forbidden.

Check for all combinations of $n, m = 0, 1, 2, 3, 4$ which transitions are allowed and on the basis of your results try to guess the *selection rules* for harmonic oscillator for arbitrary n, m (selection rules tell us for which combinations of m, n the transitions are allowed).

4.4.5   Problem

A natural frequency of vibrations for a hydrogen molecule is $f = 1.26 \times 10^{14}$ s^{-1}. Find the energy of the zero-point vibrations E_0! Can the vibrational degrees of freedom with energy $E_1 = E_0 + hf$ be excited at the temperature $T = 600$ K? Hint: the states with energy E_1 are excited at the temperature T_e for which the thermal energy $3\, kT_e/2 = E_1 - E_0$.

Chapter 5

Hydrogen atom

5.1 Angular momentum

Angular momentum plays an important role in the hydrogen atom, in particular it is linked to quantum numbers l and m_l. In view of this we will derive the angular momentum operator starting from the definition of the angular momentum in classical mechanics,

$$\vec{L} \;=\; \vec{r} \times \vec{p} \;=\; m\,\vec{r} \times \vec{v} \tag{5.1}$$

where $\vec{r} = (x, y, z)$ is the vector pointing from the origin to the position of the particle with mass m, $\vec{p} = (p_x, p_z, p_z)$ is the momentum of the particle and $\vec{v}$ its velocity, see Fig. 5.1.

The components of the angular momentum are then given by

$$L_x \;=\; yp_z - zp_y \tag{5.2}$$
$$L_y \;=\; zp_x - zp_z \tag{5.3}$$
$$L_z \;=\; xp_y - yp_x \tag{5.4}$$

It turns out that it is the square of the magnitude of the angular momentum that appears in the equations describing the hydrogen atom,

$$L^2 \;=\; L_x^2 + L_y^2 + L_z^2. \tag{5.5}$$

In quantum mechanics, to get the angular momentum operator $\hat{\vec{L}}$, we replace $\vec{r}$ and $\vec{p}$ with corresponding operators $\hat{\vec{r}} = \vec{r}$ and $\hat{\vec{p}} = -i\hbar\nabla$,

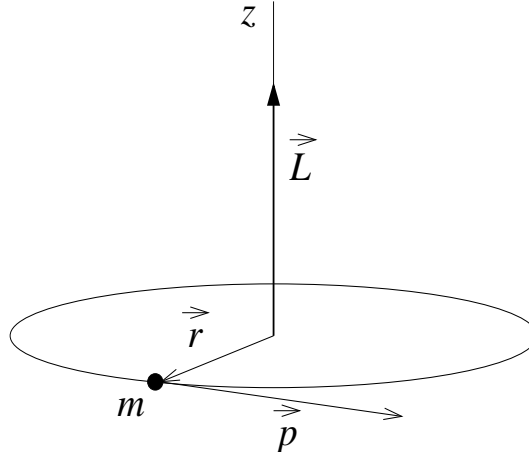$$\hat{\vec{L}} \;=\; \vec{r} \times \hat{\vec{p}} \;=\; -i\hbar\,\vec{r} \times \nabla, \tag{5.6}$$

Figure 5.1: Definition of angular momentum. If the particle moves in the xy plane about the z-axis, the angular momentum $\vec{L}$ has a fixed direction along the z-axis.

which gives us for the operators of the components

$$\hat{L}_x = -i\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}) \tag{5.7}$$

$$\hat{L}_y = -i\hbar(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}) \tag{5.8}$$

$$\hat{L}_z = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}). \tag{5.9}$$

In the spherical coordinate system, Fig. 5.2, these operators are given by

$$\hat{L}_x = i\hbar(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}) \tag{5.10}$$

$$\hat{L}_y = i\hbar(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}) \tag{5.11}$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi} \tag{5.12}$$

and the operator of the square of the magnitude of the angular momentum by

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \tag{5.13}$$
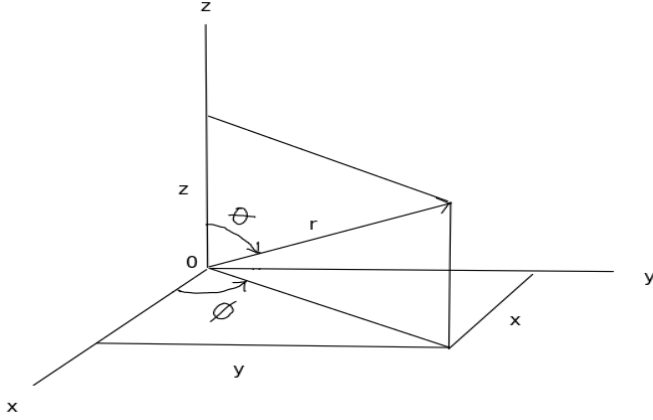
Figure 5.2: Spherical coordinate system. $x = r\sin\theta\cos\phi, y = r\sin\theta\sin\phi, z = r\cos\theta$.

It can be shown (Problem) that the commutators of operators $\hat{L}_x, \hat{L}_y, \hat{L}_z$, are

$$\left[\hat{L}_x, \hat{L}_y\right] = +i\hbar\hat{L}_z \tag{5.14}$$

$$\left[\hat{L}_y, \hat{L}_z\right] = +i\hbar\hat{L}_x \tag{5.15}$$

$$\left[\hat{L}_z, \hat{L}_x\right] = +i\hbar\hat{L}_y \tag{5.16}$$

and

$$\left[\hat{L}_x, \hat{L}^2\right] = \left[\hat{L}_y, \hat{L}^2\right] = \left[\hat{L}_z, \hat{L}^2\right] = 0, \tag{5.17}$$

i.e., the component operators do not commute with each other, however, the $\hat{L}^2$ operator does commute with the component operators. The commuting operators can share the same eigenfunctions, i.e., their eigenvalues can label the same quantum state (e.g., the state of hydrogen atom can be described by the eigenvalues of both $\hat{L}^2$ and $\hat{L}_z$ at the same time), which is not possible for the noncommuting operators for which Heisenberg uncertainty relation applies.

Next, we are interested in the possible values of the size of the quantum angular momentum, given by

$$\hat{L}^2 Y = L^2 Y. \tag{5.18}$$

where L^2 (the size of the angular momentum squared) are the eigenvalues and $Y = Y(\theta, \phi)$ the eigenfunctions of the operator $\hat{L}^2$. Substituting for the operator from Eq. 5.13, we obtain

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} + \frac{L^2}{\hbar^2}Y = 0. \tag{5.19}$$

This partial differential equation in variables θ, ϕ is a well-known equation for the spherical functions $Y(\theta, \phi)$. The first steps of its solution are addressed in Problem 3.4, the full details can be found in the textbooks on quantum mechanics, e.g. [5]. Here we simply summarize the main results. The finite and continuous solution exists only for discrete values of L^2, given by

$$L^2 = \hbar^2 l(l+1), \quad l = 0, 1, 2, 3, \ldots \tag{5.20}$$

where l, in the context of hydrogen atom, is known as the *orbital* quantum number. For the size of the angular momentum this implies

$$L = \hbar\sqrt{l(l+1)}, \quad l = 0, 1, 2, 3, \ldots \tag{5.21}$$

with the lowest possible values $L = 0, \sqrt{2}\hbar, \sqrt{6}\hbar, \ldots$ for $l = 0, 1, 2, \ldots$. For each l there are $2l+1$ corresponding solutions, spherical functions $Y(\theta, \phi) \equiv Y_{lm_l}(\theta, \phi)$, given by

$$Y_{lm_l}(\theta, \phi) = \sqrt{\frac{(l - |m_l|)!(2l+1)}{(l + |m_l|)!4\pi}} P_l^{|m_l|}(\cos\theta)e^{im_l\phi} \tag{5.22}$$

where m_l, in the context of hydrogen atom known as *magnetic* quantum number, is an integer number limited by the orbital number l to

$$m_l = 0, \pm 1, \pm 2, \ldots, \pm l; \quad l = 0, 1, 2, 3, \ldots \tag{5.23}$$

i.e., $(2l + 1)$ values. For completeness, $P_l^{|m_l|}(\cos\theta)$ is defined by

$$P_l^{|m_l|}(x) = (1 - x^2)^{\frac{|m_l|}{2}}\frac{d^{|m_l|}}{dx^{|m_l|}}P_l(x), \quad x = \cos\theta, \tag{5.24}$$

and $P_l(x)$ are Legendre polynomials,

$$P_l(x) = \frac{1}{2^l\, l!}\frac{d^l}{dx^l}[(x^2 - 1)^l]. \tag{5.25}$$

The spherical functions are also eigenfunctions of the operator $\hat{L}_z$, with eigenvalues L_z,

$$\hat{L}_z Y_{lm_l}(\theta, \phi) = L_z Y_{lm_l}(\theta, \phi). \tag{5.26}$$

We prove this by substituting for $\hat{L}_z$ from Eq. 5.10 and for $Y_{lm_l}(\theta, \phi)$ from Eq. 5.22,

$$\hat{L}_z Y_{lm_l}(\theta, \phi) = -i\hbar\frac{\partial}{\partial\phi}Y_{lm_l}(\theta, \phi) = -i\hbar\, im_l\, Y_{lm_l}(\theta, \phi). \tag{5.27}$$

Comparing the right-hand sides of the last two equations, we conclude that indeed the spherical functions are the eigenfunctions of both $\hat{L}^2$ and $\hat{L}_z$ operators and the eigenvalues L_z are

$$L_z = m_l\hbar, \quad m_l = 0, \pm 1, \pm 2, \ldots, \pm l. \tag{5.28}$$

To summarize, both the size of the angular momentum (L) and the projection of the angular momentum to the z-axis (L_z) are quantized as given by equations Eqs. 5.21 and 5.28 (the z-axis can point in any direction since nothing in our considerations forced us to fix it in any particular way). Any other values are not allowed in nature. We can know precise values of L and L_z at the same time but once they are known, the Heisenberg uncertainty relations prevent us to determine precisely the values of L_x and L_y, which is the consequence of Eqs. 5.14 - 5.16.

We illustrate the quantization of the angular momentum in Fig. 5.3. For $l = 2$, the size of the angular momentum $L = \hbar\sqrt{l(l+1)} = \hbar\sqrt{6}$ defines the radius of the sphere and hence the angular momentum vector $\vec{L} = (L_x, L_y, L_z)$ is represented by the points lying on the surface of the sphere. The projection of the angular momentum to the z-axis, L_z, is restricted to $L_z = 0, \pm\hbar, \pm 2\hbar$ for $m_l = 0, \pm 1, \pm 2$, which further limits $\vec{L}$ to the points lying on the five parallels shown in the figure. As argued above, L_x and L_y remain uncertain with the uncertainty given by the diameters of the five (parallel) circles. The angular momentum vector is thus not fixed in space - it keeps changing its direction precessing about the z-axis.

5.2 Schrödinger equation for hydrogen atom

To solve hydrogen atom we have to consider the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t}\psi(r,t) \quad = \quad \hat{H}\psi(r,t) \tag{5.29}$$

with the Hamiltonian

$$\begin{aligned}
\hat{H} &= \hat{W}_k + \hat{U}(r) = -\frac{\hbar^2}{2m}\nabla^2 + U(r) \\
&= -\frac{\hbar^2}{2m}\Big(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\Big) - \frac{e^2}{4\pi\epsilon_0 r}
\end{aligned} \tag{5.30}$$

and $U(r) = -\frac{e^2}{4\pi\epsilon_0 r}$ the potential energy between two electric charges ($-e$ electron, e proton) separated by the distance r.

We seek the stationary solutions in the form

$$\psi(r,t) \quad = \quad \psi(r)\, e^{-i\frac{E}{\hbar}t} \tag{5.31}$$

where $\psi(r)$ is the solution of the time-independent Schrödinger equation 3.35,

$$\hat{H}\,\psi(r) \quad = \quad E\,\psi(r). \tag{5.32}$$

This equation is easier to solve in the spherical coordinate system, Fig. 5.2. In the spherical coordinates,

$$\begin{aligned}
\nabla^2 &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \\
&= \frac{1}{r^2}\frac{\partial}{\partial r}\Big(r^2\frac{\partial}{\partial r}\Big) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}.
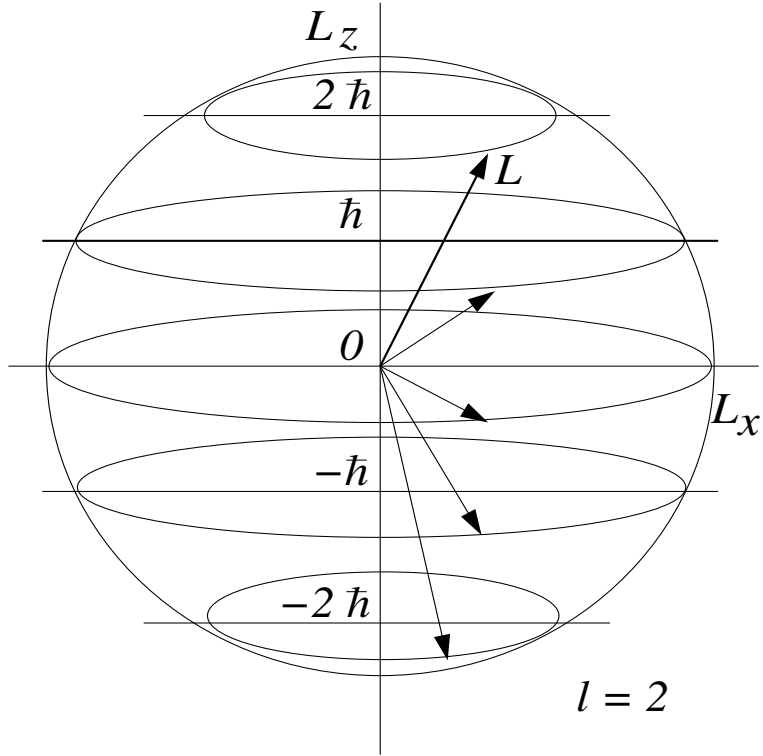\end{aligned} \tag{5.33}$$

Figure 5.3: Angular momentum quantization. The case of $l = 2, L = \sqrt{l(l+1)} = \sqrt{6}\hbar, L_z = 0, \pm\hbar, \pm 2\hbar$.

Recalling Eq. 5.13, we get for the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(r) = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2mr^2} + U(r). \quad (5.34)$$

The first (r-dependent) term on the right-hand side represents radial kinetic energy; the second one, $\frac{\hat{L}^2}{2mr^2}$, which is θ and ϕ dependent, represents orbital kinetic energy. The operator of the square of the magnitude of the angular momentum is thus part of the hydrogen hamiltonian.

Substituting Eq. 5.34 into Eq. 5.32,

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi(r)\right) + \frac{\hat{L}^2}{2mr^2}\psi(r) + U(r)\psi(r) = E\psi(r). \quad (5.35)$$

This partial differential equation of three variables is solved by the separation of variables, putting

$$\psi(r) = R(r)\,F(\theta,\phi). \quad (5.36)$$

Substituting Eq. 5.36 into Eq. 5.35 we obtain after some manipulation

$$-\hbar^2 \frac{\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} R(r)\right)}{R(r)} + 2mr^2\left(U(r) - E\right) = -\frac{\hat{L}^2 F(\theta,\phi)}{F(\theta,\phi)} \qquad (5.37)$$

Since the left-hand side depends on r and the right-hand side on θ and ϕ, both sides can be equal for all values of r, θ, ϕ only if they are both equal to the same constant k so that

$$-\hbar^2 \frac{\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} R(r)\right)}{R(r)} + 2mr^2\left(U(r) - E\right) = k \qquad (5.38)$$

$$\hat{L}^2 F(\theta,\phi) = -kF(\theta,\phi) \qquad (5.39)$$

We see that the function $F(\theta,\phi) \equiv Y_{lm_l}(\theta,\phi)$ is the eigenfunction of the $\hat{L}^2$ operator with the eigenvalue $-k \equiv L^2 = \hbar^2 l(l+1)$. Eq. 5.38 can be rewritten as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} R(r)\right) + \frac{2m}{\hbar^2}\left(E - U\right)R(r) + \frac{kR(r)}{\hbar^2 r^2} = 0. \qquad (5.40)$$

For the solution of Eq. 5.40, we refer the reader to the existing literature [3, 5]. The result, shown explicitly in Tab. 5.2 as $R(r) \equiv R_{nl}$ for the lowest quantum states, can be expressed in terms of *associated Laguerre functions*. For $E < 0$ (electron bound in the hydrogen atom), the energy is quantized as

$$E_n = -\frac{me^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} \quad \text{where } n = 1, 2, 3, ..., \qquad (5.41)$$

in agreement with the Bohr's model. The positive integer n is the principal quantum number for which the following inequality holds

$$n \geq l + 1. \qquad (5.42)$$

This restricts the orbital quantum number to values

$$l = 0, 1, 2, ..., n-1. \qquad (5.43)$$

The eigenfunctions of the Hamiltonian for the hydrogen atom are thus labelled by the three quantum numbers,

$$\psi \equiv \psi_{nlm_l} = R_{nl} Y_{lm_l}(\theta,\phi) = R_{nl} \Theta_{lm_l} \Phi_{m_l}. \qquad (5.44)$$

We show the eigenfunctions in Tab. 5.2 for $n = 1, 2$ and 3.

Although the energy quantization is the same as in the much simpler Bohr's model, the quantum mechanical treatment yielded nontrivial results in the form of existence of several states which all belong to the same energy level E_n. These, so-called degenerate states, are described by eigenfunctions ψ_{nlm_l} which differ in quantum numbers l and m_l but share the same n. As seen in the table, $n = 1$

n	l	m_l	$\Phi_{m_l}(\phi)$	$\Theta_{lm_l}(\theta)$	$R_{nl}(r)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}}e^{-\frac{r}{a_0}}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}a_0^{3/2}}(2-\frac{r}{a_0})e^{-\frac{r}{2a_0}}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{1}{2\sqrt{6}a_0^{3/2}}\frac{r}{a_0}e^{-\frac{r}{2a_0}}$
2	1	± 1	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{2\sqrt{6}a_0^{3/2}}\frac{r}{a_0}e^{-\frac{r}{2a_0}}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3}a_0^{3/2}}(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2})e^{-\frac{r}{3a_0}}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{4}{81\sqrt{6}a_0^{3/2}}(6-\frac{r}{a_0})\frac{r}{a_0}e^{-\frac{r}{3a_0}}$
3	1	± 1	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{4}{81\sqrt{6}a_0^{3/2}}(6-\frac{r}{a_0})\frac{r}{a_0}e^{-\frac{r}{3a_0}}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4}(3\cos^2\theta-1)$	$\frac{4}{81\sqrt{30}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-\frac{r}{3a_0}}$
3	2	± 1	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	$\frac{\sqrt{15}}{2}\sin\theta\cos\theta$	$\frac{4}{81\sqrt{30}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-\frac{r}{3a_0}}$
3	2	± 2	$\frac{1}{\sqrt{2\pi}}e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$	$\frac{4}{81\sqrt{30}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-\frac{r}{3a_0}}$

Table 5.1: Eigenfunctions $\psi = R_{nl}\,\Theta_{lm_l}\,\Phi_{m_l}$ for the hydrogen atom for $n = 1, 2$ and 3.

state is nondegenerate, $n = 2$ has four degenerate states and $n = 3$ nine. We know degenerate states exist since in certain cases, e.g. if hydrogen is in the external magnetic field, the degeneracy is lifted and the originally degenerate states have different energies.

Probability density is given by

$$\rho \;=\; \psi^*\psi \;=\; R_{nl}^* \, R_{nl} \, \Theta_{lm_l}^* \, \Theta_{lm_l} \, \Phi_{m_l}^* \, \Phi_{m_l}. \tag{5.45}$$

The probability densities for $n = 2, 3, 4$ states are plotted in Fig. 5.4.
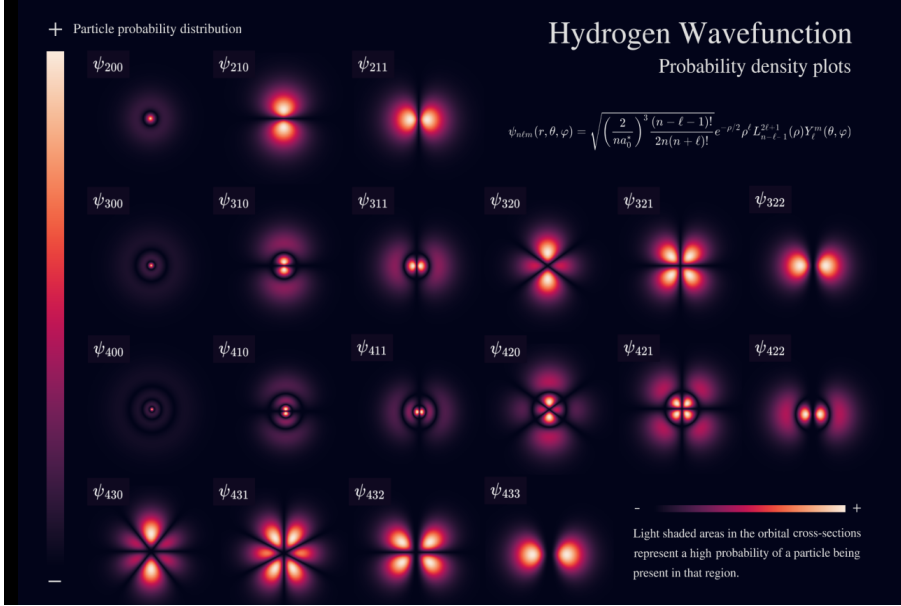
Probability for an electron in the eigenstate ψ to be found in the volume dV is given by

$$dP \;=\; \psi^*\psi \, dV. \tag{5.46}$$

The volume element in the sperical coordinate system is given by

$$dV \;=\; r^2 \sin\theta \, dr \, d\theta \, d\phi. \tag{5.47}$$

If we integrate Eq. 5.46 over angles θ and ϕ, we get the probability dP_r to find

Figure 5.4: Hydrogen probability densities for $n = 2, 3, 4$ states. Source: [6].

the electron within the spherical shell given by radii r and $r + dr$,

$$
\begin{aligned}
dP_r &= \int_0^\pi \int_0^{2\pi} \psi^* \psi \, r^2 \sin\theta \, dr \, d\theta \, d\phi & (5.48) \\
&= \int_0^\pi \int_0^{2\pi} R_{nl}^* \Theta_{lm_l}^* \Phi_{m_l}^* R_{nl} \Theta_{lm_l} \Phi_{m_l} r^2 \sin\theta dr d\theta d\phi \\
&= r^2 R_{nl}^* R_{nl} dr \int_0^\pi \Theta_{lm_l}^* \Theta_{lm_l} \sin\theta d\theta \int_0^{2\pi} \Phi_{m_l}^* \Phi_{m_l} d\phi \\
&= r^2 R_{nl}^* R_{nl} dr,
\end{aligned}
$$

since (see Problem 3.5)

$$
\int_0^\pi \Theta_{lm_l}^* \Theta_{lm_l} \sin\theta d\theta = 1, \qquad (5.49)
$$

$$
\int_0^{2\pi} \Phi_{m_l}^* \Phi_{m_l} d\phi = 1. \qquad (5.50)
$$

The corresponding radial probability density is

$$
\rho_{nl}(r) = \frac{dP_r}{dr} = r^2 R_{nl}^* R_{nl}. \qquad (5.51)
$$

5.3   Problems

Problem 3.1
   Prove that $[\hat{L}_x, \hat{L}_y] = +i\hbar\hat{L}_z$!

Problem 3.2
   Prove that $[\hat{L}_x, \hat{L}^2] = 0$!

Problem 3.3
   From Eqs. 5.22, 5.24 and 5.25 find the explicit form of the spherical functions $Y_{lm_l}(\theta, \phi)$ for $l = 0, 1, 2$ and corresponding allowed values of m_l ! Check your result comparing it with $Y_{lm_l}(\theta, \phi) = \Theta_{lm_l} \Phi_{m_l}$ where Θ_{lm_l} and Φ_{m_l} are given in Tab. 5.2.

Problem 3.4 Try to solve Eq. 5.19 by the method of the separation of variables. Assuming

$$Y(\theta, \phi) \quad = \quad \Theta(\theta)\Phi(\phi), \tag{5.52}$$

show that we obtain two separated equations

$$\frac{d^2\Phi}{d\phi^2} \quad = \quad -k'\Phi, \tag{5.53}$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\Big(\sin\theta\frac{d\Theta}{d\theta}\Big) + \Big[\frac{L^2}{\hbar^2} - \frac{k'}{\sin^2\theta}\Big]\Theta \quad = \quad 0. \tag{5.54}$$

where k' is a constant. Now prove that the solution of Eq. 5.53 is

$$\Phi(\phi) \quad = \quad Ne^{i\sqrt{k'}\phi} \tag{5.55}$$

where N is normalization constant. Finally, show that the condition $\Phi(\phi) = \Phi(\phi + 2\pi)$ requires that

$$\sqrt{k'} \quad = \quad m_l, \tag{5.56}$$

where $m_l = 0, \pm 1, \pm 2, \ldots$ is the magnetic quantum number. Note: we will not attempt to solve Eq. 5.54, the reader is referred to the quantum mechanics textbooks, e.g. Ref. [5].

Problem 3.5
   Show that Eqs. 5.49, 5.50 hold for $l = 0, 1, 2$ and corresponding allowed values of m_l!

Problem 3.6
   Plot radial probability density $\rho_{nl}(r) = r^2 R_{nl}^* R_{nl}$ for $n = 1, 2, 3$ and corresponding allowed values of the orbital quantum number l!

Problem 3.7

In Problem 3.6 you have plotted the radial probability density $\rho_{nl}(r)$. This gives us the probable distance of the electron from the proton, however, since we had integrated over θ and ϕ, we lost information about the probability to find electron in different directions, given by $\Theta^*_{lm_l}\Theta_{lm_l}\Phi^*_{m_l}\Phi_{m_l}$. Your task is to fix this by showing that $\Phi^*_{m_l}\Phi_{m_l} = constant$, and then plotting polar diagrams of $\Theta^*_{lm_l}\Theta_{lm_l}$ for all combinations of l and m_l for $l = 0, 1, 2, 3$ and $l = 4$. To plot polar diagrams, choose the $z - y$ plane ($x = 0$, y - the horizontal axis, z - the vertical one). Plot a line with the length of $\Theta^*_{lm_l}\Theta_{lm_l}$ for a single chosen value of θ; the line starts at the origin and its end point has coordinates

$$z = \Theta^*_{lm_l}\Theta_{lm_l}\cos(\theta), \tag{5.57}$$
$$y = \Theta^*_{lm_l}\Theta_{lm_l}\sin(\theta) \tag{5.58}$$

Plot now just the end points for many values of θ from $-\frac{\pi}{2}$ to $\frac{\pi}{2}$ to get a full polar graph.

Chapter 6

Spin

6.1 Magnetic dipole moment

Let us assume that the classical particle we used to define the angular momentum $\vec{L}$ in Fig. 5.1 is charged with negative charge of $-e$ (the electron) and it is moving along a circle with radius r in the xy plane, see Fig. 6.1. Then $\vec{L}$ is pointing along the positive z-axis as before and the current I in the loop, defined by the flow of the positive charge, is flowing in the opposite direction to the electron. The magnetic dipole moment is defined by

$$\vec{\mu} = I\,\vec{S}, \tag{6.1}$$

where $\vec{S}$ is the vector of the area inside the loop, $\vec{S} = \pi\,r^2\vec{n}$. Its direction is given by the unit vector $\vec{n}$, perpendicular to the area and pointing up or down according to the right hand rule: four fingers wrapped around the thumb indicate the flow of the current and the thumb in this case points down along the negative z-axis. The period of rotation is given by $T = 2\pi r/v$, implying the size of the current

$$I = \frac{|Q|}{T} = \frac{ev}{2\pi r}. \tag{6.2}$$

For the magnetic dipole moment we thus get

$$\begin{aligned}
\vec{\mu} &= \frac{ev}{2\pi r}\,\pi r^2\,\vec{n} = \frac{e\,m\,r\,v}{2m}\,\vec{n} = \frac{eL}{2m}\,\vec{n} \\
&= -\frac{e}{2m}\vec{L}.
\end{aligned} \tag{6.3}$$

This is the magnetic dipole moment of electron associated with its motion around the center (= proton in the case of hydrogen atom). Eq. 6.3 is responsible for gyromagnetic phenomena (such as Einstein-de Haas experiment) which connect magnetic properties of objects to their mechanical rotation. The multiplicative factor $-\frac{e}{2m}$ is the so-called gyromagnetic ratio.
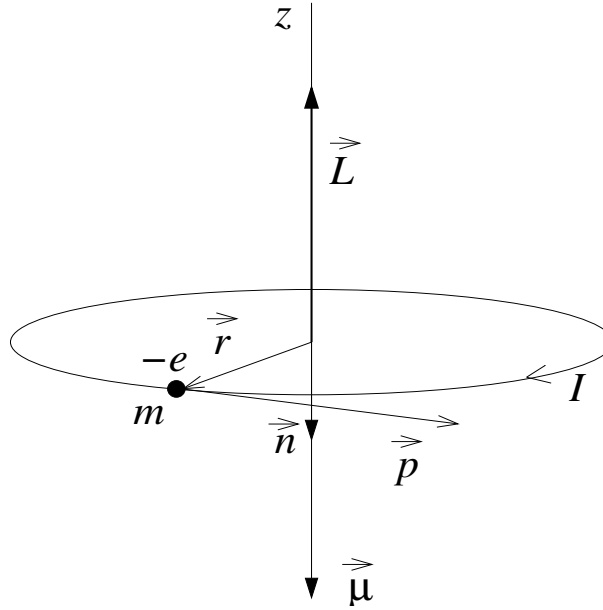
Figure 6.1: The magnetic dipole moment $\vec{\mu}$ of a current loop.

If we insert a magnet with a dipole moment $\vec{\mu}$ in a magnetic field $\vec{B}$, the magnetic energy of the dipole is

$$W_m \quad = \quad -\vec{\mu} \cdot \vec{B}. \tag{6.4}$$

The size of magnetic energy depends on the angle between $\vec{\mu}$ and $\vec{B}$. Substituting for $\vec{\mu}$ from Eq. 6.3, we get

$$W_m \quad = \quad \frac{e}{2m}\vec{L} \cdot \vec{B}. \tag{6.5}$$

Choosing the z axis parallel to $\vec{B}$, this becomes

$$W_m \quad = \quad \frac{e}{2m}L_z \, B. \tag{6.6}$$

So far our treatment has been entirely classical. Switching to quantum mechanics, the eigenvalues of the magnetic energy operator obey the same formula, however, the z component of the angular momentum is quantized, see Eq. 5.28 and Fig. 5.3:

$$L_z \quad = \quad m_l\,\hbar, \quad m_l = 0, \pm 1, \pm 2, \pm 3, ..., \pm l, \tag{6.7}$$

yielding

$$W_m \quad = \quad \frac{e\hbar}{2m}m_l\,B \quad m_l = 0, \pm 1, \pm 2, \pm 3, ..., \pm l. \tag{6.8}$$
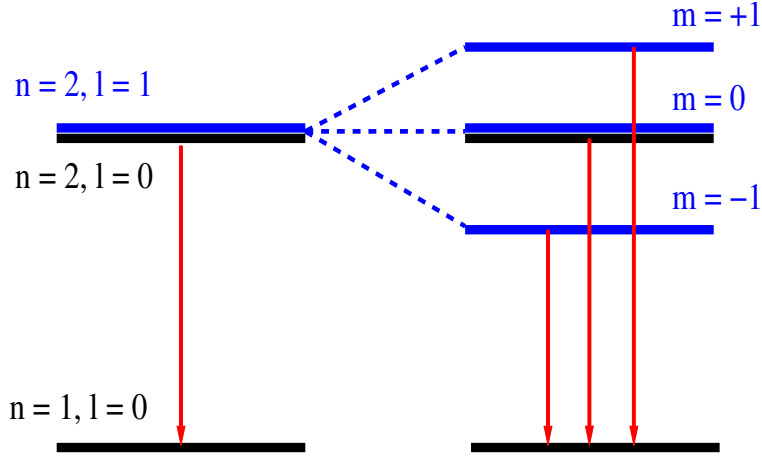
Figure 6.2: Left: the Lyman alpha line for $\vec{B} = 0$. Right: In the presence of nonzero magnetic field the Lyman alpha line splits into three lines as a consequence of the splitting of the $n = 2, l = 1$ state into three energy levels as given by Eq. 6.9

The factor $e\hbar/2m = 9.27 \times 10^{-24}$ JT is the unit of $\vec{\mu}$ in atomic physics.

Let us now consider a hydrogen atom in a magnetic field. The interaction of the electron magnetic moment with the field leads to the modification of the energy of the state with quantum numbers n and m_l from $E_n = E_1/n^2$ to

$$E_n = \frac{E_1}{n^2} + W_m = \frac{E_1}{n^2} + \frac{e\hbar}{2m} m_l \, B. \qquad (6.9)$$

The result is that the energy levels with $l > 0$ will split into $2l + 1$ levels and the original single line splits into a triplet[1], see Fig. 6.2 for the case of a Lyman alpha line. The size of the splitting is controlled by the magnetic field B and m_l, which explains why m_l is called the *magnetic* quantum number. The observation of hydrogen lines in external magnetic fields confirmed the splitting of the original lines into triplets, the effect which became known as the normal Zeeman effect.

6.2 The spin hypothesis

There are two subtle difficulties which complicate the agreement of experimental results with our prediction for the Zeeman effect in the previous section. First, it turned out that the Lyman alpha line in a zero external field ($\vec{B} = 0$) is actually a doublet as depicted in Fig. 6.3, not a singlet shown in Fig. 6.2 left.

---

[1]For $l > 1$ one might expect the splitting into more lines than three, however, it turns out that the selection rules limit the number of lines to three for any l.
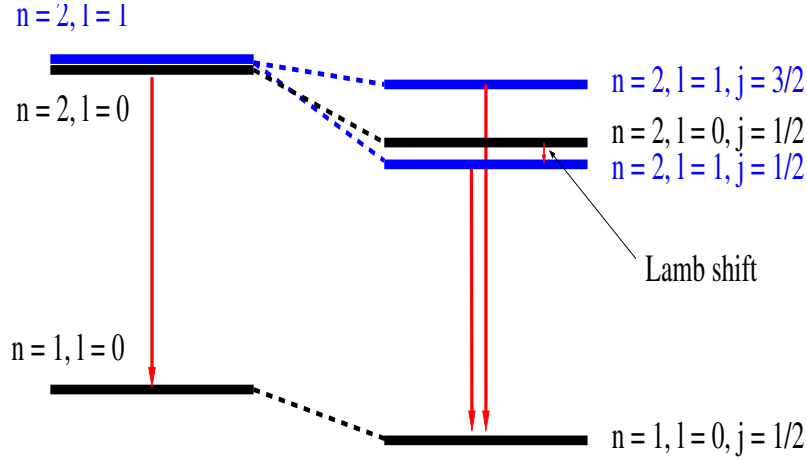
Figure 6.3: Left: The Lyman alpha line without an electron spin correction, no relativistic correction, external field $\vec{B} = 0$. Right: The Lyman alpha line with the electron spin correction and the relativistic correction, external field $\vec{B} = 0$. The state $n = 2, l = 1$ splits into two levels, $n = 2, l = 1, j = 3/2$ and $n = 2, l = 1, j = 1/2$. The Lyman alpha line splits into a doublet (two lines) as a result. The splittings are much smaller than shown.

This effect is known as the fine structure of the hydrogen spectrum. Second, in many atoms other than hydrogen the external magnetic field $\vec{B} > 0$ splits the original lines not into three but into four, six, or even more lines - the so-called "anomalous Zeeman effect". Both difficulties are a manifestation of an intrinsic angular momentum of electron - the spin. Spin was introduced in 1925 by Uhlenbeck and Goudsmit. Their idea was that an electron is a small rotating sphere with a spin angular momentum $S = L = I\omega = \frac{2}{5}mr^2\omega$ where I is the moment of inertia, ω the angular velocity, m the mass of electron, and r its radius. They fixed the value of the electron spin at $S = 1/2$ in order to explain both the fine structure and the anomalous Zeeman effect. The total angular momentum $\vec{J}$ is the sum of the orbital angular momentum $\vec{L}$ and the spin angular momentum $\vec{S}$. The magnitude of the total angular momentum is (compare with Eq. 5.21)

$$J = \hbar\sqrt{j(j+1)} \tag{6.10}$$

where for $l > 0$ we have two possible values

$$j = l + \frac{1}{2}, l - \frac{1}{2} \tag{6.11}$$

and for $l = 0$ a single value

$$j = \frac{1}{2}, \tag{6.12}$$

which explains the labelling of states in Fig. 6.3 (right). The split between the states $l = 1, j = 3/2$ and $l = 1, j = 1/2$ is due to the so-called spin-orbit interaction with energy

$$W_{so} = -\vec{\mu}_s \cdot \vec{B}, \tag{6.13}$$

where $\vec{\mu}_s$ is the electron's spin magnetic moment and $\vec{B}$ is not the external field but a magnetic field generated by the proton which orbits the electron in the electron's rest frame. The energy W_{so} is very small, leading to the split of 4.5×10^{-5} eV between the two $l = 1$ states. Compare this to the energy of 10.2 eV separating these two states from the $n = 1, l = 0$ ground state. Finally, there is a minute split between the $n = 2, l = 0, j = 1/2$ state and the $n = 2, l = 1, j = 1/2$ state, known as the Lamb shift. The Lamb shift is a correction due to the quantum field theory.

The original picture of an electron as a small rotating sphere is not valid. For $S = 1/2$ ($S_z = \hbar/2$) and the radius of electron $r < 10^{-19}$m, we get an impossible value for the velocity of the surface rotation $v = \omega r > c$! However, the electron's spin value of $1/2$ stands, confirmed by both observations and a theoretical prediction by Dirac.

6.3 Stern-Gerlach experiment

6.4 Multi-electron atoms

6.4.1 Problem

If atoms could contain electrons with pricipal quantum numbers up to and including $n = 6$, how many elements would there be?

6.4.2 Bonus problem

The ionization energies of the elements of atomic numbers 20 through 29 are very nearly equal. Why should this be so when considerable variations exist in the ionization energies of other consecutive sequences of elements?

6.4.3 Problem 3.1

The subshell is defined by a fixed quantum number l. If all states from $m_l = -l$ to $m_l = +l$ are occupied by electrons, the subshell is closed. *Unsöld's* theorem states that the sum of probability densities over all these states is a constant independent of angles θ and ϕ, so that

$$\sum_{m_l=-l}^{+l} |\Theta|^2 |\Phi|^2 = constant, \tag{6.14}$$

which implies that the effective distribution of electric charge in a closed sub-shell is spherically symmetric and the atoms with all subshells closed have no electric dipole moments (on top of being electrically neutral). As a consequence, they do not attract other electrons, nor it is easy to detach their own electrons. Such atoms are chemically passive and this is the case of the inert gasses.

Verify *Unsöld's* theorem for $l = 0, 1$ and 2.

Chapter 7

Mixture of eigenstates

Let ψ_n be a set of eigenfunctions of the Hamiltonian operator $\hat{H}$ with eigenvalues E_n,

$$\hat{H}\psi_n = E_n\psi_n. \tag{7.1}$$

It can be shown that this set of eigenfunctions is complete, which means that we can expand arbitrary wavefunction in terms of it,

$$\psi(\overrightarrow{r}) = \sum_{n=0}^{\infty} c_n\psi_n(\overrightarrow{r}). \tag{7.2}$$

It is important to note that the wavefunction $\psi(\overrightarrow{r})$, a linear combination of eigenstates, represents a possible state of the system. Being a mixture of energy eigenstates, one may wonder what the energy corresponding to this state is. It turns out that, unlike eigenstates, $\psi(\overrightarrow{r})$ in general has no sharp value of energy and the measurement on this state would yield different values E_n with probabilities that we will now determine.

The wavefuncion should be normalized to one,

$$\int \psi^*(\overrightarrow{r})\psi(\overrightarrow{r})d^3\overrightarrow{r} = 1, \tag{7.3}$$

and the complex conjugate function is

$$\psi^*(\overrightarrow{r}) = \sum_{m=0}^{\infty} c_m^*\psi_m^*(\overrightarrow{r}). \tag{7.4}$$

Plugging the expansions of Eqs. 7.2, 7.4 into Eq. 7.3 and using the fact that the eigenfunctions form an orthonormal set,

$$\int \psi_m^*\psi_n d^3\overrightarrow{r} = \delta_{mn}, \tag{7.5}$$

we get the first property of c_n,

$$
\begin{aligned}
\int \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} c_m^* c_n \psi_m^* \psi_n d^3 \overrightarrow{r} &= \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} c_m^* c_n \int \psi_m^* \psi_n d^3 \overrightarrow{r} \\
&= \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} c_m^* c_n \delta_{mn} \\
&= \sum_{n=0}^{\infty} c_n^* c_n = 1.
\end{aligned} \tag{7.6}
$$

Before we discuss this result, we express the mean value of energy in the state $\psi(\overrightarrow{r}) \equiv \psi$,

$$
\begin{aligned}
\bar{E} &= \int \psi^* \hat{H} \psi d^3 \overrightarrow{r} = \int \sum_{m=0}^{\infty} c_m^* \psi_m^* \hat{H} \sum_{n=0}^{\infty} c_n \psi_n d^3 \overrightarrow{r} \\
&= \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} c_m^* c_n E_n \int \psi_m^* \psi_n d^3 \overrightarrow{r} \\
&= \sum_{n=0}^{\infty} c_n^* c_n E_n.
\end{aligned} \tag{7.7}
$$

Upon inspection of Eqs. 7.6, 7.7, we conclude that $c_n^* c_n$ can be interpreted as the probability P_n that the measurement on the state $\psi(\overrightarrow{r})$ yields the energy E_n,

$$
P_n = c_n^* c_n. \tag{7.8}
$$

7.1   Entangles states and Bell's inequality

Mixed states and their interpretation bring us to the heart of quantum mechanics which deals with the role of measurement/observer and reality of the Universe. According to the standard Copenhagen interpretation of quantum mechanics due to Niels Bohr, quantum systems in general exist as superpositions of eigenstates (see Eq. 7.2) and it is the measurement process which causes the collapse of the wavefunction to a particular eigenstate with a sharp eigenvalue measured by the observer with the probability P_n. In this sense, the Universe is not real - the quantities describing quantum systems take on definite, "real" values only during the measurement.

This view was opposed by Einstein who argued for the real Universe in which the system was in the measured eigenstate already before the measurement due to the presence of hidden variables. These variables simply instruct the observed quantities about the value they should turn in. System is thus the same before and after the observation, *i.e.*, independent of the measurement.

Let us take a closer look at the essence of the argument between the two physicists. We will consider a very simple quantum system, a single electron

with spin $1/2$, which can be in just two eigenstates, spin up ($\psi_1 = |\uparrow\rangle$) or spin down ($\psi_2 = |\downarrow\rangle$). A general mixed state, according to the Copenhagen interpretation, would then be given by

$$\psi = c_1\psi_1 + c_2\psi_2 = c_1 \uparrow\rangle + c_2|\downarrow\rangle. \tag{7.9}$$

This is the state before the measurement of the spin. The measurement will yield spin up with the probability $P_1 = c_1^* c_1$ and spin down with the probability $P_2 = c_2^* c_2$. During this experiment the wavefunction ψ collapses to either ψ_1 or ψ_2.

According to Einstein, the electron was in $\psi_1 = |\uparrow\rangle$ (or ψ_2) state all the time, before and after the experiment.

Now, both Einstein and Bohr agree about *the results of the measurement* so the debate about what form the wavefunction had before the experiment may seem interesting but irrelevant for physics. Indeed, for about 30 years the reality debate was perceived as pure philosophy with no physical consequences. In the meantime, Schroedinger sided with Einstein saying "I don't like quantum mechanics, and I'm sorry I ever had anything to do with it" and offering a thought experiment involving unfortunate cat in a mixed state of both alive and dead eigenstates to illustrate absurdities of the Copenhagen interpretation applied to macroscopic objects. Einstein also made a succinct point asking Abraham Pais "Do you really believe that the Moon exists only when you look at it? [7].

Bohr and Einstein had many intense discussions of the subject over the years during which Bohr refuted many objections of his opponent. Finally, in 1935, Einstein wrote a paper with Podolsky and Rosen, known as EPR, in which they formulated the most clever objection thus far. The crucial idea was to consider the mixture of spin eigenstates of two electrons rather than one,

$$\psi = c_1|\uparrow\rangle|\uparrow\rangle + c_2|\downarrow\rangle|\downarrow\rangle + c_3|\uparrow\rangle|\downarrow\rangle + c_4|\downarrow\rangle|\uparrow\rangle. \tag{7.10}$$

In a special state, the so-called Bell state, $c_3 = c_4 = 0, c_1 = c_2 = 1/\sqrt{2}$ and

$$\psi = \frac{1}{\sqrt{2}}|\uparrow\rangle|\uparrow\rangle + \frac{1}{\sqrt{2}}|\downarrow\rangle|\downarrow\rangle. \tag{7.11}$$

Although nowadays the Bell state can be prepared experimentally, for the EPR trio it was a pure thought experiment: the two electrons are emitted from the source in the Bell state in opposite directions, Fig. 7.1.

Electron e_A flies to the left where Alice measures its spin with her detector, electron e_B flies to the right to the Bob's detector. If Alice measures first, she will find the electron in the spin up state with the probability $P_1 = c_1^* c_1 = 0.5$ and the spin down state with the probability $P_2 = c_2^* c_2 = 0.5$. As a result of her measurement, the Bell state collapses either to (if Alice measured spin up)

$$\psi = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\uparrow\rangle + |\downarrow\rangle|\downarrow\rangle) \rightarrow |\uparrow\rangle|\uparrow\rangle. \tag{7.12}$$
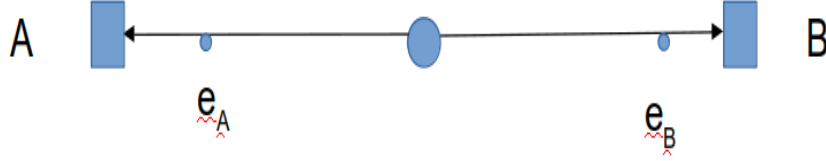
Figure 7.1: EPR thought experiment.

or (if Alice measured spin down)

$$\psi = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\uparrow\rangle + |\downarrow\rangle|\downarrow\rangle) \quad \rightarrow \quad |\downarrow\rangle|\downarrow\rangle. \tag{7.13}$$

As a consequence, if Alice measured spin up, Bob, performing measurement after Alice on the collapsed state, will find spin up with probability 1 and spin down with probability 0. If Alice measured spin down, Bob will measure spin down with probability 1 and spin up with probability 0.

Now, if Bob measured first, he would find spin up with probability $P_1 = c_1^* c_1 = 0.5$ and spin down with probability $P_2 = c_2^* c_2 = 0.5$. Clearly, Bob's results (the same holds for Alice) depend on who measures first. The Alice's measurement changes the probabilities of the Bob's measurement from 0.5 to 1 or 0. If such a change occurs, we say that the original state is *entangled*. If there is no change in the probabilities, the state is not entangled (not every mixed state is entangled). The Bell state was chosen to be maximally entangled.

EPR continued their argument assuming that Alice and Bob are far away from each other and Alice measures first with the result of spin up. If Bob performs his experiment shortly after Alice but before any signal from Alice could arrive, he will find spin up with probability 1. The question is, how the Bob's electron knew that it should turn its spin up before the signal from Alice arrived? EPR concluded that either the universe is not local (the signal in this case travels faster than light) or the two electrons are indeed in the Bell state before Alice performs her measurement and the Bell state collapses immediately during her observation. The universe is then not real in the sense that there is no definite value for the spin of the electron before Alice's observation. For Einstein, the non-local and/or unreal universe were equally bad options. As a way out of the dilemma, he proposed his hidden variables theory mentioned before: if Alice measures spin up, all it means is that the electron, instructed by the hidden variable, was emitted with the spin up right from the source and was in the same state before, during and after the Alice's observation.

The EPR objection seemed solid and the debate ended with a draw. In 1964 John Bell wrote a seminal paper in which he showed that the subject does belong to physics. He derived Bell's inequality which describes the results of an experiment which could, at least theoretically, differentiate between quantum
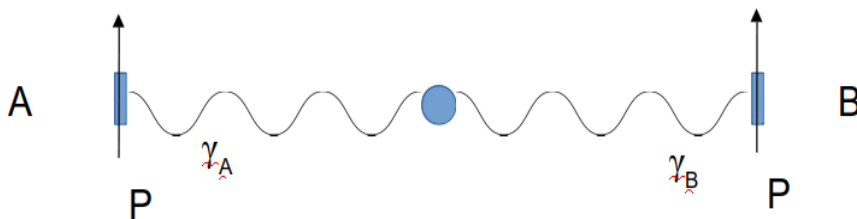
Figure 7.2: Two photons emitted in the Bell state.

mechanics and hidden variable theory. The experiment, based on the Bell state of two electrons described above, seemed impossible to perform at the time.

In 1972 John Clauser modified the Bell's proposal, suggesting the use of two photons instead of electrons which proved to be a game changer. The two photons are emitted from the source in the Bell state in opposite directions, Fig. 7.2. The role of spin is played by the photon's polarization. The photon with vertical polarization, denoted as $|+\rangle$, will pass the linear polarizer oriented vertically (and not pass the linear polarizer oriented horizontally). On the other hand, the photon with horizontal polarization, denoted as $|-\rangle$, will not pass the linear polarizer oriented vertically (and pass the linear polarizer oriented horizontally). The Bell state of the two pohotons is given by

$$\psi \;\; = \;\; \frac{1}{\sqrt{2}}(|+\rangle|+\rangle + |-\rangle|-\rangle) \tag{7.14}$$

As before with electrons, if Alice measures first, she will find her photon in the $|+\rangle$ state with the probability $P_1 = 0.5$ and in the $|-\rangle$ state with the probability $P_2 = 0.5$. As a result of her measurement, the Bell state collapses either to $|+\rangle$ (if Alice measured vertical polarization) or to $|-\rangle$ (if Alice measured horizontal polarization). As a consequence, if Alice measured vertical (horizontal) polarization, Bob, performing measurement after Alice on the collapsed state, will find vertical (horizontal) polarization with probability 1 and horizontal (vertical) polarization with probability 0.

The crucial point of the experiment is the rotation of the linear polarizers. So far both linear polarizers were oriented vertically. Let us rotate the Bob's polarizer by angle α, see Fig. 7.3. If Alice measures first and finds her photon in the vertical polarization state, the collapse of the Bell state sends the Bob's photon to the vertical polarization state as well. The Bob's photon is now approaching the polarizer rotated by α. The probability that it passes (not passes) the polarizer is given by $P = \cos^2\alpha$ ($\sin^2\alpha$), the dependence we know from optics for the decrease in intensity of the light after it passes the linear polarizer. Table 7.1 summarizes probabilities for photons to pass (P^+) or not to pass (P^-) the Alice's (P_A) and Bob's (P_B) polarizers, and the combined probabilities $P^{++}, P^{--}, P^{+-}, P^{-+}$ where the first sign corresponds to the Alice's polarizer and the second one to the Bob's polarizer so that, e.g., P^{+-} is
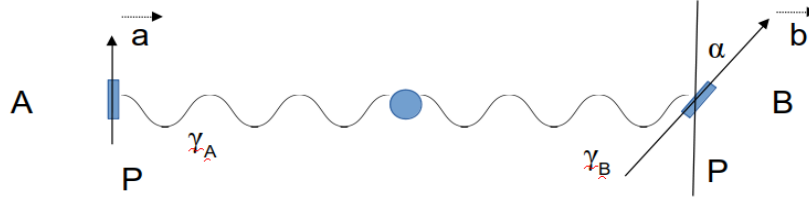
Figure 7.3: Bob's polarizer is rotated by angle α from vertical direction.

the probability that Alice's photon will pass her polarizer and the Bob's photon will not pass his polarizer. We define the following important combination

P_A	P_B^+	P_B^-	P^{++}, P^{--}	P^{+-}, P^{-+}
$P_A^+ = \frac{1}{2}$	$\cos^2 \alpha$	$\sin^2 \alpha$	$P^{++} = \frac{1}{2}\cos^2 \alpha$	$P^{+-} = \frac{1}{2}\sin^2 \alpha$
$P_A^- = \frac{1}{2}$	$\sin^2 \alpha$	$\cos^2 \alpha$	$P^{--} = \frac{1}{2}\cos^2 \alpha$	$P^{-+} = \frac{1}{2}\sin^2 \alpha$

Table 7.1: Probabilities for photons to pass (+) or not (-) polarizers shown in Fig. 7.3. Alice measures first.

of probabilities, the so-called correlation, for the directions $\vec{a}$ and $\vec{b}$ of the polarizers,

$$E(a, b) \quad = \quad P^{++} + P^{--} - P^{+-} - P^{-+} \quad = \quad \cos 2\alpha. \tag{7.15}$$

The final step is to rotate both polarizers and perform measurements at two directions of each polarizer (Fig. 7.4), which effectively leads to four correlations, $E(a_1, b_1)$, $E(a_1, b_2)$, $E(a_2, b_1)$ and $E(a_2, b_2)$. John Bell showed that the quantum
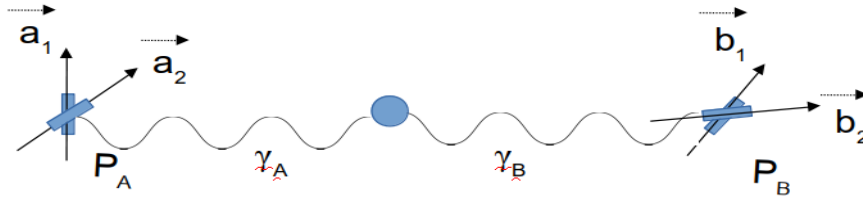
Figure 7.4: Each polarizer has two orientations: a_1, a_2 for Alice, b_1, b_2 for Bob.

mechanical prediction of the quantity

$$S \quad = \quad E(a_1, b_1) - E(a_1, b_2) + E(a_2, b_1) + E(a_2, b_2) \tag{7.16}$$

is (for $a_1 = 0°, a_2 = 45°, b_1 = 22, 5°, b_2 = 67, 5°$)

$$S \quad = \quad 2\sqrt{2}, \tag{7.17}$$

which is different from the prediction of the hidden variable theories given by the Bell's inequality

$$|S| \quad \leq \quad 2. \tag{7.18}$$

John Clauser was the first one to perform the experiment with entangled photons and show that quantum mechanics was correct. His results, however, were not conclusive since important loopholes remained. In 1982-83 Alain Aspect improved the experiment in several steps which included the photon source upgrade (calcium atoms were excited by crypton laser to ramp up statistics), the replacement of single-channel polarizers with two-channel ones (this made the direct detection of both polarization states possible), and the use of polarizers with variable orientation which was determined after the photons were emitted but before they reached the polarizers. The setup of the Aspect's two-channel experiment is shown in Fig. 7.5. The orientation of polarizers is denoted with
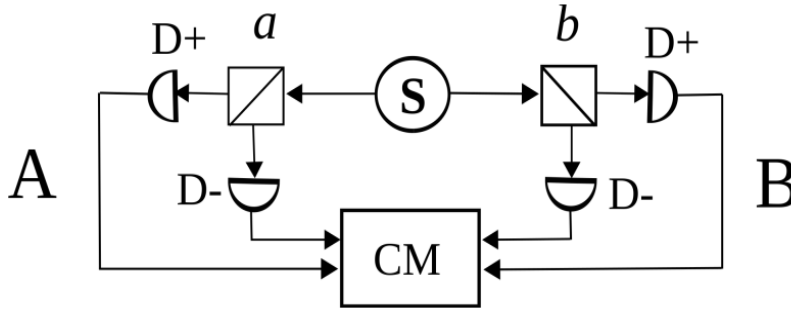

Figure 7.5: Aspect's two-channel experiment. Source: Wikipedia, 2023.

letters a, b, detectors $D+$ and $D-$ detect vertical (+) and horizontal (-) polarization, and coincidence monitor CM counts coincidences of the four types (++, --, +-, -+). The coincidences are used to determine the correlation $E(a, b)$ experimentally as

$$E(a, b) \quad = \quad \frac{N^{++} + N^{--} - N^{+-} - N^{-+}}{N^{++} + N^{--} + N^{+-} + N^{-+}}. \tag{7.19}$$

Aspect's experiments confirmed beyond reasonable doubt the quantum mechanical prediction and excluded hidden variable theory. Clauser, Aspect and Anton Zeilinger (who, using entangled photons, demonstrated the phenomenon of quantum teleportation) were awarded the Nobel Prize in Physics in 2022. Their research with entangled photons pioneered quantum information science. It is fascinating to see how the fundamental physics subject first received the label of pure philosophy, then found its way back to physics and finally became the basis of new quantum technologies such as quantum communication, quantum sensors and quantum computing.

Chapter 8

What is a particle?

8.1 Spin of the photon

We would like to show that a circularly polarized electromagnetic wave can represent a photon. We will start with a simple form of electromagnetic field, a linearly polarized (LP) plane wave

$$\vec{A}(x,y,z,t) \quad = \quad \frac{E_0}{\omega}e^{i\omega t - i\omega z/c}\,\vec{i}, \tag{8.1}$$

where $\vec{A}(x,y,z,t)$ is the complex vector potential, E_0 is the amplitude of the electric field, ω the angular frequency, t time, c the speed of light in the vacuum. The wave propagates in free space along the z axis and the tip of the vector $\vec{A}$ moves over the line parallel to the x axis defined by the unit vector $\vec{i}$.

We can form a circularly polarized wave from the superposition of the two orthogonal LP plane waves,

$$\vec{A}(x,y,z,t) \quad = \quad i\,\frac{E_0}{\omega}e^{i\omega t - i\omega z/c}\,(\vec{i}\pm i\,\vec{j}), \tag{8.2}$$

where $\vec{j}$ is the unit vector along the y axis and the $\pm$ sign indicates the right and left circular wave, respectively. The factors $i = \sqrt{-1}$ ensure the phase difference of $\pi/2$ between the two LP waves needed for the formation of the circularly polarized waves. We will see that this is indeed a circular wave in a moment.

The complex electric field $\vec{E}(x,y,z,t)$ is given by

$$\vec{E}(x,y,z,t) \quad = \quad -\frac{\partial \vec{A}(x,y,z,t)}{\partial t} \quad = \quad E_0 e^{i\omega t - i\omega z/c}\,(\vec{i}\pm i\,\vec{j}), \tag{8.3}$$

and the physical electric field $\vec{E}(x,y,z,t)$ by the real part of the complex field

$$\vec{E}(x,y,z,t) \quad = \quad Re\Big(E_0 e^{i\omega t - i\omega z/c}\,(\vec{i}\pm i\,\vec{j})\Big) \tag{8.4}$$

$$= \quad E_0\cos(\omega t - \omega z/c)\vec{i} \mp E_0\sin(\omega t - \omega z/c)\vec{j}. \tag{8.5}$$

The tip of the electric field vector moves on a circle clockwise (right circular wave) for the minus sign in Eq. 8.5, see Fig. 8.1. Note that this minus sign corresponds to the plus sign in Eqs. 8.3 and 8.4. Likewise, the tip of $\vec{E}(x, y, z, t)$ moves on a circle counterclockwise (left circular wave) for the plus sign in Eq. 8.5.
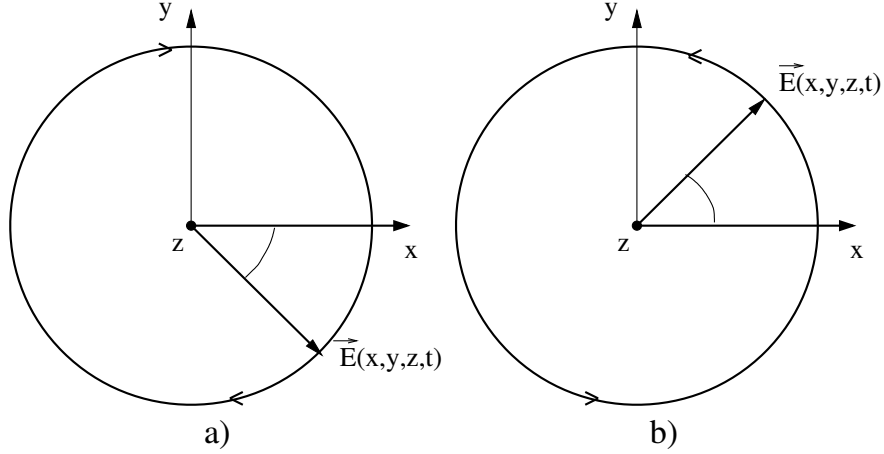

Figure 8.1: Schematic of a) right circularly polarized wave and b) left circular wave. The z axis points out of the screen towards the viewer.

The complex magnetic field is given by

$$\vec{B}(x, y, z, t) \;=\; \vec{\nabla} \times \vec{A}(x, y, z, t) \;=\; \frac{E_0}{c} e^{i\omega t - i\omega z/c} \left(\mp i\, \vec{i} + \vec{j} \right). \qquad (8.6)$$

According to the classical theory of electromagnetism, the energy flow in the electromagnetic field in vacuum is given by the Poynting vector

$$\vec{S} \;=\; \frac{1}{\mu_0} \vec{E} \times \vec{B} \qquad (8.7)$$

and the momentum density by

$$\vec{P} \;=\; \frac{1}{\mu_0 c^2} \vec{E} \times \vec{B}. \qquad (8.8)$$

The circularly polarized wave of Eq. 8.2 is infinite in extent: its amplitude $E_0 = E_0(x, y, z) = const$ for any point including $x, y, z \to \pm\infty$. The corresponding electric field $\vec{E}(x, y, z, t)$ of Eq. 8.3 and the magnetic field $\vec{B}(x, y, z, t)$ of Eq. 8.6, having only x and y components, are everywhere perpendicular to the z axis (to the wavevector). This is a well known feature of infinite waves of our type. As a consequence, the energy flow and the momentum density are everywhere parallel to the z axis, see Fig. 8.2.
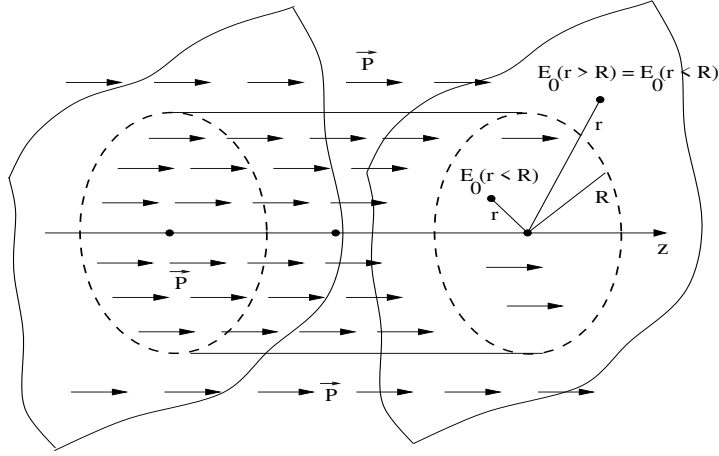
Figure 8.2: The flow of momentum density $\vec{P}$ for the circularly polarized infinite wave. It points along the z axis as indicated by arrows and is of a constant size at any point in space. The wave extends to infinity both in the transverse plane (amplitude $E_0(r < R) = E_0(r > R)$ for any r) and along the z axis. The cylinder is illustrated for a later purpose when we will bound the wave to its volume ($r < R$).

Indeed, using Eqs. 8.3 and 8.6, we get for the time-average momentum density (Problem 1)

$$\vec{P} \;=\; \frac{1}{2}Re\left\{\frac{\vec{E}\times\vec{B}^*}{\mu_0 c^2}\right\} \;=\; \frac{E_0^2}{\mu_0 c^3}\vec{k}, \tag{8.9}$$

where $\vec{k}$ is the unit vector along the z axis. With energy and momentum flowing only along the z axis, the net angular momentum $\vec{J}$, to be defined below, must be zero. The nonzero $\vec{J}$ requires that at least a small part of energy and momentum circulates in the transverse xy plane about the z axis .

This circulation can be achieved if we limit the wave to a finite transverse extent. The vector potential will still be given by Eq. 8.2, but only inside the cylinder of radius R, Fig. 8.3. Outside the cylinder the potential drops to zero, as its amplitude $E_0 = E_0(x,y) = E_0(r)$, constant for $r < R$, quickly falls to zero in the vicinity of $r = R$, as indicated by the red line in the figure. The wave has cylindrical symmetry about the z axis. The magnetic field of this finite cylindrical wave, unlike that of the original infinite wave, picks a nonzero z component,

$$
\begin{aligned}
\vec{B}(x,y,z,t) \;&=\; \vec{\nabla}\times\vec{A}(x,y,z,t) \\
&=\; \left\{\frac{E_0}{c}(\mp i\,\vec{i}+\vec{j}) + [\mp\partial_x E_0(x,y) - i\partial_y E_0(x,y)]\frac{1}{\omega}\vec{k}\right\} \\
&\quad \times e^{i\omega t - i\omega z/c}.
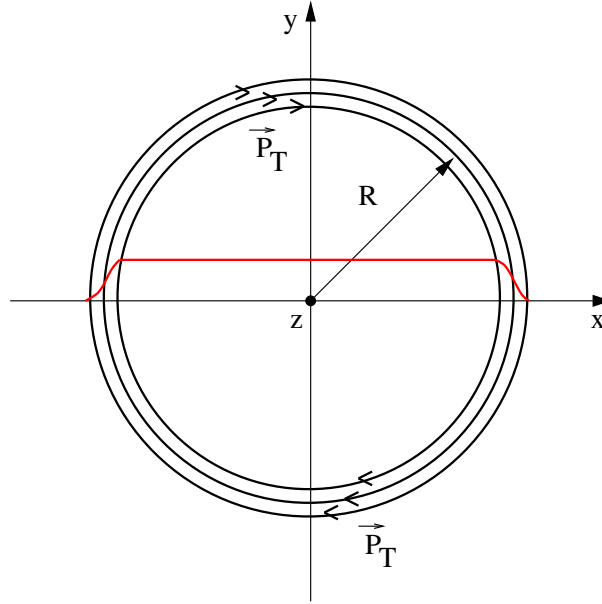\end{aligned}
\tag{8.10}
$$

Figure 8.3: Right circularly polarized wave of a finite transverse extent propagating along the z axis. The red curve shows the amplitude $E_0 = E_0(x, y)$ as a function of distance $r = \sqrt{x^2 + y^2}$ from the z axis. The three circles indicate the region where the energy flow (the momentum density) has the circular component $\vec{P_T}$. The dominant component of the flow, along the z axis, is not shown.

The presence of the nonzero B_z is crucial for the generation of the circulating component of the energy and momentum flow. If we calculate the time-average momentum density for the finite cylindrical wave (Problem 2), we get

$$
\begin{aligned}
\vec{P} &= \frac{1}{2} Re\left\{ \frac{\vec{E} \times \vec{B^*}}{\mu_0 c^2} \right\} \\
&= \frac{1}{2\mu_0 c^2}\left\{ \mp \frac{E_0}{\omega} \partial_y E_0(x, y)\vec{i} \pm \frac{E_0}{\omega} \partial_x E_0(x, y)\vec{j} + \frac{2E_0^2}{c}\vec{k} \right\}. \quad (8.11)
\end{aligned}
$$

The transverse part of $\vec{P}$,

$$
\vec{P_T} = \frac{1}{2\mu_0 c^2}\left\{ \mp \frac{E_0}{\omega} \partial_y E_0(x, y)\vec{i} \pm \frac{E_0}{\omega} \partial_x E_0(x, y)\vec{j} \right\}, \quad (8.12)
$$

is responsible for the small circulating component of the flow. It is shown as the three oriented circles in Fig. 8.3 for a right circular wave and as arrows circulating in the transverse plane on the surface of the cylinder for a left circular wave in Fig. 8.4. Note that the region of the circulating flow is limited to the

the vicinity of $r = R$ where the derivatives $\partial_{x,y} E_0(x,y) \neq 0$. This circular flow is the source of the nonzero net angular momentum of the finite circularly polarized cylindrical electromagnetic wave, which we will show now.
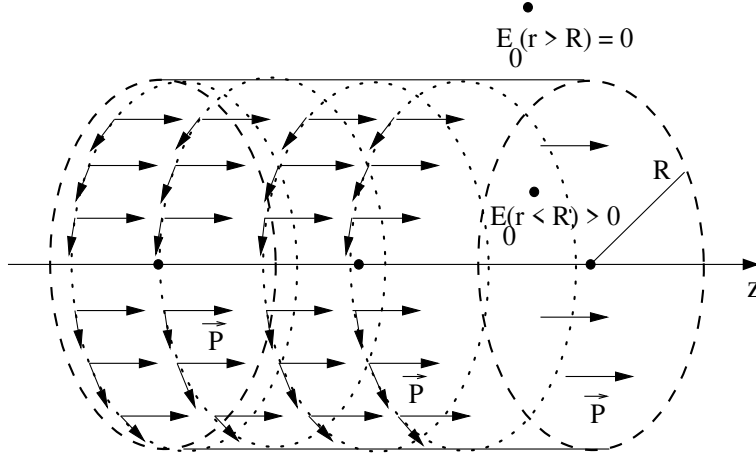

Figure 8.4: The flow of momentum density $\vec{P}$ in the circularly polarized finite wave bounded to the inside of the cylinder. The vector $\vec{P}$ has now the transverse component $\vec{P}_T$ circulating about the z axis.

The complex angular momentum density is defined by

$$\vec{j} \;=\; \vec{r} \times \vec{P}, \tag{8.13}$$

where $\vec{r} = (x, y, z)$ is the vector pointing from the origin to a point (x, y, z) in space. Compare this last equation with the definition of the angular momentum $\vec{L}$ of a particle with momentum $\vec{p}$ in Eq. 5.1. To find the net complex angular momentum, we integrate Eq. 8.13 over the volume occupied by the wave

$$\vec{J} \;=\; \int \vec{r} \times \vec{P} \, d^3r \;=\; \frac{1}{\mu_0 c^2} \int \vec{r} \times (\vec{E} \times \vec{B}) \, d^3r. \tag{8.14}$$

Using identity (to be derived as Problem 3) $\vec{E} \times \vec{B} = \vec{E} \times (\vec{\nabla} \times \vec{A}) = [E^n \vec{\nabla} A^n - (\vec{E} \cdot \vec{\nabla})\vec{A}]$, we get

$$\vec{J} \;=\; \frac{1}{\mu_0 c^2} \int \vec{r} \times (E^n \vec{\nabla} A^n) \, d^3r \;-\; \frac{1}{\mu_0 c^2} \int \vec{r} \times [(\vec{E} \cdot \vec{\nabla})\vec{A}] \, d^3r. \tag{8.15}$$

The second term in Eq. 8.15 can be transformed by integration by parts (Problem 4) into a more convenient form

$$\vec{J} \;=\; \frac{1}{\mu_0 c^2} \int \vec{r} \times (E^n \vec{\nabla} A^n) \, d^3r \;+\; \frac{1}{\mu_0 c^2} \int \vec{E} \times \vec{A} \, d^3r. \tag{8.16}$$

According to Ref. [8], the first term corresponds to the orbital angular momentum $\vec{L}$ because it is independent of the polarization of the wave (left or right). The orbital momentum $\vec{L}$ is zero for the cylindrically symmetric wave that we consider. An asymmetric wave or a wave not centered on the origin would give rise to a nonzero $\vec{L}$ [8].

The second term, as we will see, depends on the polarization of the wave and therefore corresponds to the spin angular momentum $\vec{S}$. The time average value of the spin term is

$$\vec{S} \;=\; \frac{1}{2\mu_0 c^2} \int Re(\vec{E} \times \vec{A}^*) \, d^3r. \tag{8.17}$$

The integral is performed over the volume inside the cylinder for $r < R$ and also in the thin region around $r = R$ where $E_0(r)$ suddenly drops to zero. Since the volume of the thin region is small compared to the volume inside, the spin can be calculated with reasonable accuracy considering only the constant fields of Eqs. 8.2, 8.3 in the inner region $0 < r < R$. The result is (Problem 5)

$$\vec{S} \;=\; \mp \frac{\vec{k}}{\mu_0 c^2 \omega} \int E_0^2 \, d^3r. \tag{8.18}$$

The minus (plus) sign corresponds to the right (left) circular wave, respectively.

The energy in the electromagnetic wave is according to the classical theory given by

$$E \;=\; \int \epsilon_0 \vec{E}^2 \, d^3r \;=\; \frac{\epsilon_0}{2} \int Re(\vec{E} \cdot \vec{E}^*) \, d^3r$$

$$\;=\; \frac{1}{2\mu_0 c^2} \int Re(\vec{E} \cdot \vec{E}^*) \, d^3r. \tag{8.19}$$

After substituting for $\vec{E}$ from Eq. 8.3, we arrive at (Problem 6)

$$E \;=\; \frac{1}{\mu_0 c^2} \int E_0^2 \, d^3r. \tag{8.20}$$

The integral is bounded by $r < R$ but not along the z axis (the height/length H of the cylinder is so far infinite) which would lead to an infinite energy in the wave. Since we would like the wave to represent a single photon, we have to make both R and H finite so that the energy inside the cylinder is equal to the energy of the single photon,

$$\frac{1}{\mu_0 c^2} \int E_0^2 \, d^3r \;=\; \hbar\omega. \tag{8.21}$$

This fixes the integral to

$$\int E_0^2 \, d^3r \;=\; \mu_0 c^2 \hbar\omega. \tag{8.22}$$

Plugging this expression into Eq. 8.18, we get for the spin

$$\vec{S} \;=\; \mp \hbar \vec{k}. \tag{8.23}$$

We conclude that the right circularly polarized wave bounded by the cylinder of radius R and height H with the total energy $E = \hbar \omega$, carries the spin $S_z = -\hbar$ and the left circularly polarized wave the spin $S_z = +\hbar$. These are the two of the three projections of the spin 1 particle. The third projection, $S_z = 0$, is allowed for massive particles only, not for massless photons.

Using only classical theory plus the Einstein's equation for the energy of the electromagnetic quantum, $E = \hbar \omega$, we obtained a picture of a single photon as a circularly polarized wave of Eq. 8.2, bounded by a cylinder. The energy and momentum flow mostly along the z axis but there is a small component of momentum circulating on the surface of the cylinder about the z axis which generates the spin of the photon.

8.2 Quantization of a standing electromagnetic wave

In this section we will show the formal equivalence between a free electromagnetic field and the classical harmonic oscillator. For simplicity we will consider a one dimensional problem of the electromagnetic field trapped in a box. The main conclusions are the same as for the three dimensions and for electromagnetic waves travelling freely without any boundaries. It will turn out that we can hugely benefit from our analysis of the quantum harmonic oscillator and simply take over our results for the energy spectrum and the eigenfunctions from Sec. 4.3.

Let us then consider an optical cavity with two perfectly conducting mirrors at the opposite ends (Fig. ...). Light inside the cavity forms a standing electromagnetic wave when the wave travelling to the right, $E_0 \cos(kz + \omega t) \vec{i}$, interferes with the wave reflected from the mirror, travelling to the left, $-E_0 \cos(kz - \omega t) \vec{i}$,

$$
\begin{aligned}
\vec{E} \;&=\; E_0 \cos(kz + \omega t)\, \vec{i} - E_0 \cos(kz - \omega t)\, \vec{i} \\
&=\; -2 E_0 \sin \omega t \sin kz\, \vec{i}.
\end{aligned} \tag{8.24}
$$

Boundary conditions, $\vec{E}(0, t) = \vec{E}(L, t) = 0$, impose restrictions on the wavenumber k,

$$k \;=\; \frac{n\pi}{L} \quad n = 1, 2, 3, ... \tag{8.25}$$

The positive integer n labels individual modes of the standing wave. The corresponding wavelengths and frequencies of the modes are given by

$$\lambda_n \;=\; \frac{2L}{n} \tag{8.26}$$

$$f_n \;=\; \frac{c}{\lambda_n} \;=\; n\frac{c}{2L}, \tag{8.27}$$

with $n = 1$ being the fundamental mode

We will now show how an electromagnetic field consisting of a single mode, the fundamental one, can be quantized. The electric field is given by Eq. 8.24 with $k = \pi/L$,

$$
\begin{aligned}
\vec{E} &= -2E_0 \sin \omega t \, \sin kz \, \vec{i} \\
&= -2E_0 \, q(t) \, \sin kz \, \vec{i}.
\end{aligned} \tag{8.28}
$$

The time derivative of the magnetic field follows from

$$
\frac{\partial \vec{B}}{\partial t} = -\vec{\nabla} \times \vec{E} = 2E_0 k \, q(t) \cos kz \, \vec{j} \tag{8.29}
$$

and the magnetic field itself is

$$
\vec{B} = 2E_0 k \, s(t) \cos kz \, \vec{j} \tag{8.30}
$$

where

$$
\frac{ds(t)}{dt} \equiv \dot{s}(t) = q(t). \tag{8.31}
$$

If we plug Eqs. 8.28 and 8.30 into another Maxwell equation,

$$
\frac{\partial \vec{E}}{\partial t} = c^2 \, \vec{\nabla} \times \vec{B}, \tag{8.32}
$$

we find that

$$
\frac{dq(t)}{dt} \equiv \dot{q}(t) = -\omega^2 \, s(t) \tag{8.33}
$$

where $\omega = kc$. From here we obtain $\dot{q}^2(t) = \omega^4 \, s^2(t)$ and

$$
s^2(t) = \frac{\dot{q}^2(t)}{\omega^4}. \tag{8.34}
$$

Further, if we take time derivative of Eq. 8.33, we obtain

$$
\ddot{q}(t) = -\omega^2 \, q(t). \tag{8.35}
$$

This equation has the same form as the classical harmonic oscillator, see Eq. 4.22, for which $\omega^2 = k/m$. The generalized coordinate $q(t)$ thus plays the role of the displacement $x(t)$ of the classical mechanical oscillator from the equilibrium.

We now evaluate energy E (not to be confused with the intensity of the electric field $\vec{E}$) in the electromagnetic field in the cavity,

$$
\begin{aligned}
E &= \int \left(\frac{1}{2} \epsilon_0 \vec{E}^2 + \frac{1}{2\mu_0} \vec{B}^2 \right) d^3r \\
&= S \int_0^L \left(\frac{1}{2} \epsilon_0 \vec{E}^2 + \frac{1}{2\mu_0} \vec{B}^2 \right) dz
\end{aligned} \tag{8.36}
$$

where S is the area of the mirrors. We now substitute for $\vec{E}$ from Eq. 8.28 and for $\vec{B}$ from Eq. 8.30 and after integrating over z (Problem 7) we have

$$E \quad = \quad VE_0^2 \Big(\epsilon_0 q^2(t) + \frac{1}{\mu_0} k^2 s^2(t) \Big) \tag{8.37}$$

with $V = SL$ the volume of the cavity. Next we substitute from Eq. 8.34, put $\mu_0 = 1/(\epsilon_0 c^2)$ and $\omega = kc$,

$$E \quad = \quad \epsilon_0 VE_0^2 \Big(q^2(t) + \frac{\dot{q}^2(t)}{\omega^2} \Big). \tag{8.38}$$

Finally, we introduce constant M,

$$M \quad = \quad 2\frac{\epsilon_0 VE_0^2}{\omega^2} \tag{8.39}$$

and the energy can be written as

$$\begin{aligned} E \quad &= \quad \frac{1}{2}M\omega^2 q^2(t) + \frac{1}{2}M\dot{q}^2(t) \\ &= \quad \frac{1}{2}M\omega^2 q^2(t) + \frac{1}{2M}p^2(t) \end{aligned} \tag{8.40}$$

The first (second) term is formally identical with the potential (kinetic) energy of the classical harmonic oscillator and the generalized momentum $p(t) = M\dot{q}(t)$, corresponding to the generalized coordinate $q(t)$, plays the role of momentum in the classical harmonic oscillator.

Having established that the electromagnetic field is formally equivalent to the harmonic oscillator, we can quantize it in exactly the same way as we did the oscillator. We replace the energy E with the Hamiltonian operator $\hat{H} = \hat{W}_k + \hat{W}_p$ and the generalized coordinate q and momentum p with operators $\hat{q} = q$ and $\hat{p} = -i\hbar\, \partial_q$, respectively,

$$\hat{H} \quad = \quad \hat{W}_k + \hat{W}_p \quad = \quad -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial q^2} + \frac{1}{2}M\omega^2 q^2. \tag{8.41}$$

This is the Hamiltonian operator of the harmonic oscillator of Eq. 4.32 except that x is replaced with q. Thus, the results we found for the quantum harmonic oscillator apply here with the mere replacement $x \rightarrow q$. In particular, the eigenvalues of the Hamiltonian are

$$E_n \quad = \quad \hbar\omega(n + \frac{1}{2}), \quad n = 0, 1, 2, 3, ... \tag{8.42}$$

The state of $n = 0$ is the vacuum state and the $n = 1$ state represents a single photon state. In order to visualize this state, we define the operator of the electric field, based on Eq. 8.28,

$$\hat{\vec{E}} \quad = \quad -2E_0\, \hat{q}\, \sin kz\, \vec{i} \quad = \quad -2E_0\, q\, \sin kz\, \vec{i}. \tag{8.43}$$

The wavefunction $\psi_n(E) \equiv \psi_n(q)$ is given by Eq. 4.48 and the probability to measure the electric field E by the square of the wavefunction $|\psi_n(E)|^2$. Here,

$$E = 2E_{00}\sin(kz)\, q \quad \text{for } n = 0 \tag{8.44}$$

$$E = 2E_{01}\sin(kz)\, q \quad \text{for } n = 1 \tag{8.45}$$

For the first two states, $n = 0$ and $n = 1$, we show the corresponding wavefunctions and probabilities in Fig. 8.5. For the electric field intensity we chose the length of the cavity $L = 1$ cm, the volume of the cavity $V = 1$ cm^3 and the wavelength of the fundamental mode $\lambda = 2$ cm.
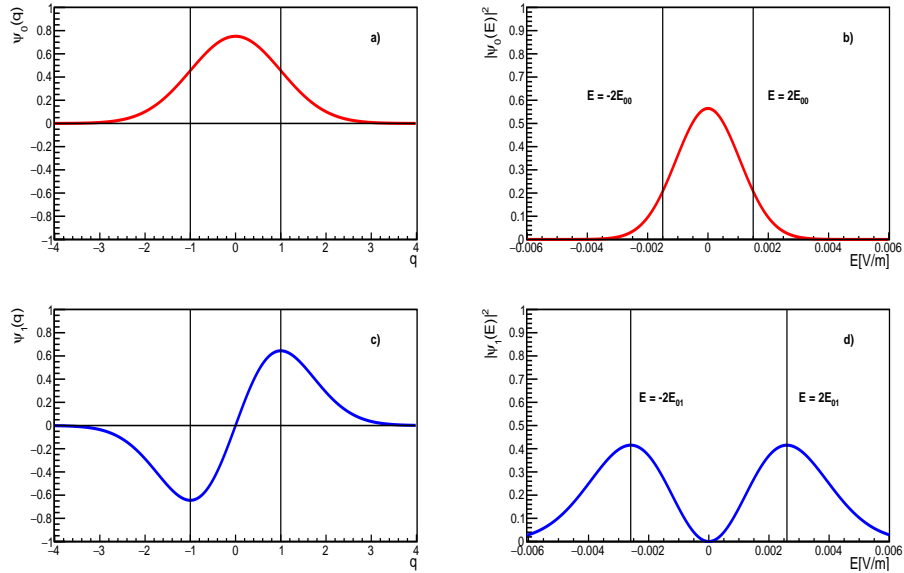

Figure 8.5: a) The wavefunction and b) the probability to measure the electric intensity E in the $n = 0$ state; c) The wavefunction and d) the probability to measure the electric intensity E in the $n = 1$ state.

Bibliography

[1] R. A. Serway, Physics for Scientists and Engineers, 2nd ed., CBS College Publishing, 1986.
pp. 924–927.

[2] A. Messiah, Quantum Mechanics, Vol. I, New York: John Wiley & Sons, 1958, pp. 11–18.

[3] Eisberg, R.M., Fundamentals of Modern Physics, New York, London, John Wiley & Sons, Inc.

[4] T. P. Purdy , R. W. Peterson, and C. A. Regal, Science 15, Feb 2013, Vol 339, Issue 6121, pp. 801-804; https://www.science.org/doi/10.1126/science.1231282

[5] Beiser, A., Concepts of Modern Physics, New York, McGraw-Hill.

[6] https://github.com/sebastian-mag/hydrogen-wavefunctions/blob/main/img/Hydrogen%20Wavefunction%20Probability%20density%20plots.png

[7] Rev. Mod. Phys. 51, 863914 (1979), p. 907.

[8] Ohanian, H.C., Am. J. Phys., Vol. **54**, No. 6, June 1986.