Lecture notes on Quantum Mechanics

for the Course *Modern Physics for Engineers*

M.S. in Energy Engineering, Nuclear Curriculum

M.S. in Energy Engineering, English language Curriculum

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Preface

Physics courses for students in Nuclear Engineering at Università di Roma "La Sapienza" were restructured following the reform of Italian University Curricula, as well as the transformation of the previous Nuclear Engineering M. S. in one of the Curricula of the Energy Engineering M.S. As a result, two previous one-semester courses on Quantum Mechanics (actually named "Atomic Physics") and Nuclear Physics were merged into a single one-semester course on *Principles of Atomic and Nuclear Physics*, now renamed *Modern Physics for Engineers*. Students attending this course have previously attended General Physics and Calculus courses, but were not thought any Modern Physics. Also, their Math courses do not include such topics as Fourier transforms, vector spaces and complex analysis.

Modern Physics for Engineers should provide the students an (at least) qualitative understanding of the main nuclear physics relevant to fission (and fusion) reactors, as well to applications of nuclear radiations in medicine and non-destructive analysis. The first part of the course introduces modern physics concepts (in particular elementary quantum mechanics), the second part concerns nuclear physics. This manuscript collects my edited lecture notes on the first part of the course.

Note:
This is just a draft. Parts of the text are still in Italian. Parts are just scans of handwritten notes. I hope to improve these Lecture Notes, in particular adding the examples and exercises discussed in the classroom (and possibly many others). I also plan to add a few additional sections and appendices. Some of these will deal with topics, such as Fermi golden rule and the proof of the Lorentian shape of a decay line, which may help the students to read introductory nuclear physics textbooks. Other planned sections, on the laser and on applications of quantum statistics, may be useful to engineering students interested in non-nuclear applications of Modern Physics.

Contents

Chapter 1

Classical physics: success and crisis

By classical physics we refer to Newton's mechanics, Maxwell's electromagnetisms, thermodynamics and the kinetic theory of ideal gases. Classical physics is neither applicable to the atomic and subatomic word, nor to bodies in motion at velocity close to the speed of light.

We should not be too much surprised. Classical physics was developed to explain (or to account for) phenomena observed by our senses, that do not allow us to see the atomic world, and are only accustomed to velocities much smaller than the speed of light.

We very briefly summarise successes and elements of crisis of classical physics.

- Netwon's mechanics

    - relativity principle
    - the three principles of mechanics
    - the law of gravitation
    - the laws of some non-fundamental forces (e.g. the elastic force)

    explains fall of bodies, Kepler's laws, etc;
    predicted, e. g. the existence of the planet Neptune (later found by astronomers).

- Maxwell's electromagnetism

    - the four Maxwell's equations
    - Coulomb-Lorentz force

    explains electrical, magnetic, optical phenomena;
    predicted the existence of electromagnetic waves (later discovered by Hertz).

- thermodynamics

    - the three laws

  sets equivalence between heat and work **explains** limitation of heat engines

- kinetic theory of gases[1], a bridge between mechanics and thermodynamics

    - Maxwell's velocity distribution function
    - Boltzmann's factor
    - Principle of equipartition of energy

  explains laws of gases, specific heats of gases, chemical kinetics, Brownian motion

Element of crisis at the end of the XIX century

- Maxwell's equations are not covariant under Galilean transformations, but are covariant under Lorentz transformations. Galileo's law of velocity addition does not apply.

- Classical physics cannot explain

    - black-body spectrum;
    - atomic spectra;
    - atom stability;
    - photoelectric effect;
    - specific heats at low temperature;
    - Compton effect (discovered in the 1920's).

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[1]See Appendix H

Chapter 2

Special relativity

Einstein developed special relativity in order to make the electrodynamics of moving bodies consistent with Maxwell's theory applying to bodies at rest.[1] Indeed, as briefly mentioned in the preceding Chapter, it was known that Maxwell's equations are not covariant for Galilean transformations. In other words, Galileo's law of addition of velocity is not consistent with Maxwell's equations. Einstein showed that the inconsistency is due to the equations of kinematics, not to electrodynamics. Indeed, when the concept of time is revised and the new postulate of constancy of the speed of light c is introduced (see below), the inconsistency is removed. Galileans transformations are replaced by a new set of transformations (Lorentz transformations), which in the limit of velocities $v \ll c$ reduce to Galilean transformations. Here we only discuss kinematics and dynamics aspects of relativity. In this chapter, we follow closely the presentation in the textbook C. Mencuccini and V. Silvestrini, *Fisica I*, Liguori, Napoli (1986, 1996), Chapter XI. I urge the students to refer to this book for enlightening discussions of the postulates of special relativity, critiques of simultaneity, and description of a few experiments confirming the accuracy of special relativity.

2.1   The postulates

Special relativity is based on the following three postulates [2]

1. The special principle of relativity
   Physical laws should be the same in every inertial frame of reference.

2. Constancy of the speed of light
   Light is always propagated in empty space with a definite velocity [speed]

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[1]See the introduction to the original Einstein's paper, *Annalen der Physik*, **17**, 891 (1905); English tr.: in A. Sommerfeld (Ed.) *The Principle of Relativity*, Dover, New York (1952)

[2]In fact, one also postulates that space is homogeneous and isotropic.

c which is independent of the state of motion of the emitting body.[3]

3. Momentum and angular momentum conservation
   In an inertial reference frame, momentum and angular momentum of an isolated system are conserved.

Notice that:

- postulate 1 just extends the relativity principle, stated by Galileo for mechanical phenomena, to any physical process;

- postulate 2 is new (and, in a sense, replaces the assumption of absolute time implicit in classical physics);

- postulate 3 is just the same as in classical mechanics.

2.2   Time and simultaneity

In classical mechanics we implicitly assume that time is universal. Clocks run at the same speed in any reference system.

However, things are not so trivial. Events judged as simultaneous by an observer are not simultaneous for another observer moving with respect to the first one.

Let us consider a source S of light pulses placed at the middle of a ruler, at distance $\Delta x/2$ by both ruler ends, a and b. For an observer at rest with respect to the ruler, the light signal emitted by S reaches a and b simultaneously. Let us assume that the ruler moves with respect to another observer (see Fig. 2.1). Also for this observer, at the time of signal emission points a and b are equidistant from S. However, as light propagates, the ruler moves, and light reaches the left hand side of the ruler (now in a') before than the right hand side.

In the special theory of relativity, the idea of absolute time is abandoned. Instead, **it is postulated that the speed of light (in vacuum) is a universal constant. It is independent of the motion of the light source**.

2.3   Consequences of the constancy of the speed of light

In this section we show two simple, unexpected consequences of the constancy of the speed of light. They concern particular cases of measurements of the same quantity performed by observers sitting in different reference systems (in relative motion). In the following Sec. 2.4 we shall deal with the general transformations relating measurements in inertial systems in relative motion.
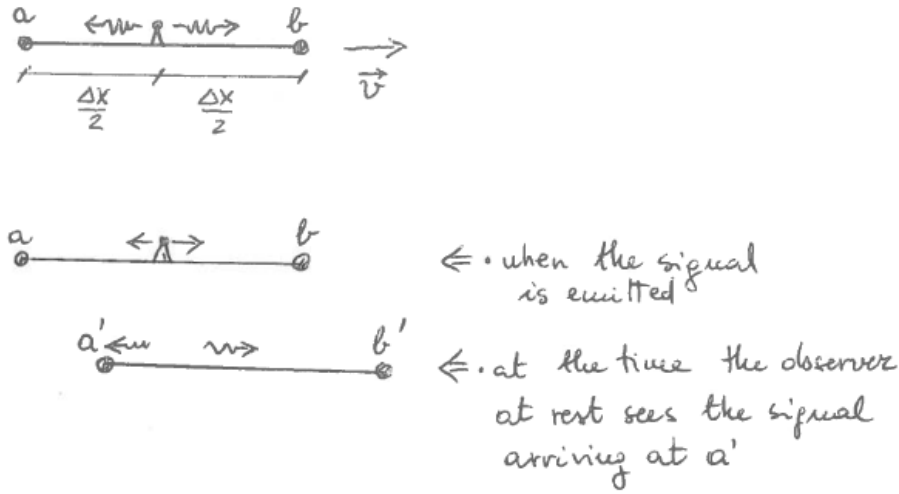
Figure 2.1: Events which are simultaneous for an observer are not simultaneous for another observer in motion relative to the first observer.

2.3.1 Time dilatation

We refer to Fig. 2.2, showing a device consisting of a pulsed light source, a detector (just in the same position as the source) and a mirror, placed at distance l from the source. We are interested in measuring the time a signal emitted by the source takes to reach the detector. An observer sitting in the device's frame measures a *proper time* interval

$$\Delta t_0 = \frac{2l}{c}. \tag{2.1}$$

Let us assume that the device moves with velocity $\vec{V} = (V, 0)$, with respect to a frame $S = (XOY)$ (see Fig. 2.3). For an observer sitting in S light has to cover a longer path,

$$2\sqrt{l^2 + (V\Delta t/2)^2}$$

to reach the detector, because the detector moves as light propagates .

He therefore measures a time interval (see Fig. 2.3)

$$\Delta t = \frac{2\sqrt{l^2 + \left(V\frac{\Delta t}{2}\right)^2}}{c} = \frac{2\sqrt{\left(c\frac{\Delta t_0}{2}\right)^2 + \left(V\frac{\Delta t}{2}\right)^2}}{c}, \tag{2.2}$$

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[3]English translation of the original statement in A. Einstein, *Annalen der Physik* **17**, 891 (1905).
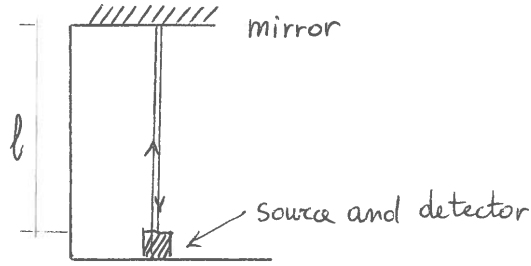
Figure 2.2: Our measuring device: source, mirror, detector.

from which we obtain

$$\Delta t = \frac{\Delta t_0}{\sqrt{1 - \dfrac{V^2}{c^2}}} : \tag{2.3}$$

the observer moving with respect to the source-detector system measures a longer time interval than the proper time measured by an observer sitting on the device.

Equation (2.3) is often written in the form

$$\Delta t = \Delta t_0 \gamma, \tag{2.4}$$

with the function γ (known as the *relativistic γ factor*) defined by

$$\gamma = \frac{1}{\sqrt{1 - \dfrac{V^2}{c^2}}} \geq 1. \tag{2.5}$$

An important experimental evidence (one of many): the elementary particle μ is unstable, with measured (proper) mean lifetime of 2.2 μs. A μ moving with velocity approaching that of light has an average path of 660 m. However, a large number of μ's is produced by interaction of cosmic rays with the upper layers of the atmosphere, i.e. at tens of km above sea level, and is detected close to the earth surface. Therefore they travel tens of km. This is possible because they move at a velocity close to that of light and an observer sitting on earth measures a strongly dilated time.

2.3.2   Length contraction

We consider a ruler of proper length L_0, with mirrors at both ends (see Fig. 2.4). We measure the time taken by a light signal to travel from mirror M_1 to mirror M_2 and back to mirror M_1.

For an observer sitting on the ruler

$$\Delta t_0 = 2L_0/c, \tag{2.6}$$
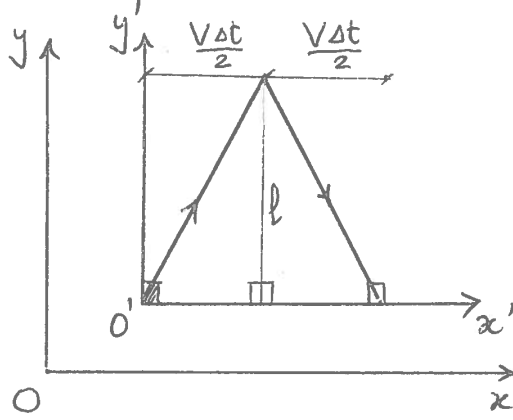
Figure 2.3: The primed frame moves towards the right hand side with velocity V. For an observer in S=(yOx) a light signal emitted in O' has to travel a path longer than $2l$ to reach the detector.

with Δt_0 a proper time.

For an observer moving with speed V the ruler length is L, and the time interval is

$$\Delta t = \Delta t_1 + \Delta t_2 = \frac{L}{c - V} + \frac{L}{c + V} = \frac{2cL}{c^2 - V^2} = \frac{2L/c}{1 - \dfrac{V^2}{c^2}}. \tag{2.7}$$

Time intervals Δt and Δt_0, in turn, are related by Eq. (2.3), and then

$$\Delta t = \frac{\Delta t_0}{\sqrt{1 - \dfrac{V^2}{c^2}}} = \frac{2L_0/c}{\sqrt{1 - \dfrac{V^2}{c^2}}}. \tag{2.8}$$

We find the relation between the lengths by equating the right hand sides of Eq. (2.7) and Eq. (2.8), which gives

$$L = L_0\sqrt{1 - \frac{V^2}{c^2}} = L_0/\gamma : \tag{2.9}$$

the ruler is shorter for the observer moving with respect to it.

2.4 Lorentz transformations

In special relativity, Lorentz transformations replace Galilean transformations. Here we consider the simple case of measurements performed by observers in
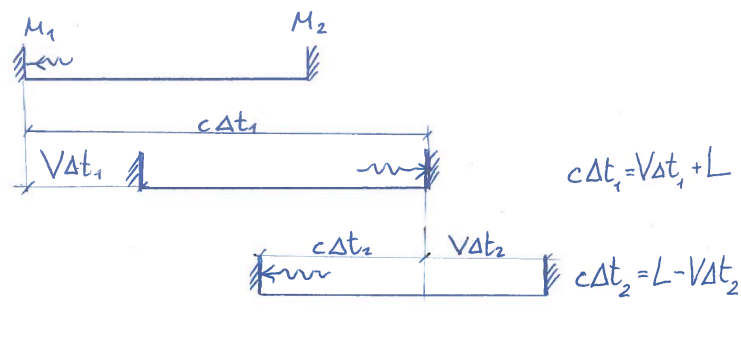
Figure 2.4: Experiment to evidence length contraction. The ruler with the mirrors moves towards the right hand side with velocity V. The figure shows the positions of the ruler at different times and the path travelled by light, as seen by an observer sitting on the foil.

inertial frames, translating with respect to each other, with velocity V, parallel to the x-axis (see Fig. 2.5). The relevant transformations, relating measurements performed in the S $(OXYZ)$ frame and in the S' frame $(X'O'Y'Z')$ are

$$x = \frac{x' + Vt'}{\sqrt{1 - \frac{V^2}{c^2}}}, \tag{2.10}$$

$$y = y', \tag{2.11}$$

$$z = z', \tag{2.12}$$

$$t = \frac{t' + \frac{V}{c^2}x'}{\sqrt{1 - \frac{V^2}{c^2}}}, \tag{2.13}$$

and, analogously,

$$x' = \frac{x - Vt}{\sqrt{1 - \frac{V^2}{c^2}}}, \tag{2.14}$$

$$y' = y, \tag{2.15}$$

$$z' = z, \tag{2.16}$$

$$t' = \frac{t - \frac{V}{c^2}x}{\sqrt{1 - \frac{V^2}{c^2}}}. \tag{2.17}$$

We immediately see that we recover the usual Galilean transformations ($x =$
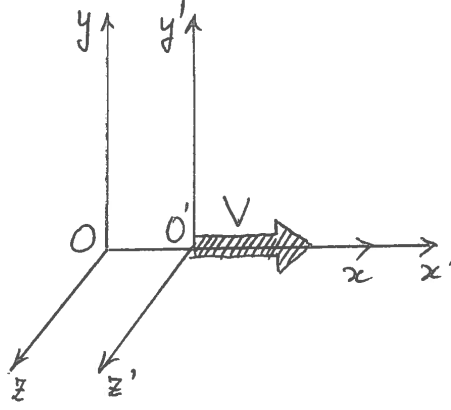
Figure 2.5: Reference frames $S = (yxz)$ and $S' = (x'y'z')$

$x' + Vt$; $t = t'$) as $V/c \to 0$.

2.4.1 Recovering time dilatation and length contraction

We now check that the expressions for time dilatation [Eq. (2.3)] and length contraction [Eq. (2.9)] derived earlier are recovered from the Lorentz transformations.

Time dilatation

We consider a phenomenon occurring in the origin of system S', i.e. at $x' = 0$. For an observer in S' it occurs in a time interval $\Delta t'$. An observer in S, moving with velocity V with respect to S', measures a time interval Δt given by Eq. (2.13) with $x' = 0$, i.e.

$$\Delta t = \frac{\Delta t'}{\sqrt{1 - \dfrac{V^2}{c^2}}}, \tag{2.18}$$

which is just Eq. (2.3).

Length contraction

We assume that an observer in frame S measures a given length Δx in a time interval $\Delta t = 0$. A length measured in S is related to a length measured in S' by Eq. (2.10), which we write compactly as

$$\Delta x = \gamma(\Delta x' + V\Delta t'). \tag{2.19}$$

To eliminate the dependence on $\Delta t'$ we rewrite Eq. (2.13) as

$$\Delta t' = \frac{\Delta t}{\gamma} - \frac{V\Delta x'}{c^2}, \tag{2.20}$$

and insert this expression into Eq. (2.19), thus obtaining

$$\Delta x = \gamma\Delta x' + \gamma V\left(\frac{\Delta t}{\gamma} - \frac{V\Delta x'}{c^2}\right) = \Delta x'\gamma\left(1 - \frac{V^2}{c^2}\right) + V\Delta t. \tag{2.21}$$

Setting $\Delta t = 0$ and using the definition of γ we eventually have

$$\Delta x = \Delta x'\sqrt{1 - \frac{V^2}{c^2}}, \tag{2.22}$$

which is just Eq. (2.9) for length contraction.

2.4.2 Transformation of velocities

Again, we assume that frame S' moves with velocity $\vec{V} = (V, 0, 0)$ with respect to frame S. In classical mechanics the x-components of the velocities in the two frames would be related by $v_x = v'_x + V$. We now obtain the expressions for relativistic transformation of velocities. The velocity components in the two frames are defined by

$$v_x \quad = \frac{dx}{dt}, \tag{2.23}$$

$$v_y \quad = \frac{dy}{dt}, \tag{2.24}$$

$$v_z \quad = \frac{dz}{dt}, \tag{2.25}$$

and

$$v'_x \quad = \frac{dx'}{dt'}, \tag{2.26}$$

$$v'_y \quad = \frac{dy'}{dt'}, \tag{2.27}$$

$$v'_z \quad = \frac{dz'}{dt'}. \tag{2.28}$$

Notice that, unlike the classical case, time now depends on the reference system. By differentiating the Lorentz transformations [Eqs. (2.10)–(2.13)] we obtain

$$dx \quad = \quad \gamma(dx' + V dt'), \tag{2.29}$$

$$dy \quad = \quad dy', \tag{2.30}$$

$$dz \quad = \quad dz', \tag{2.31}$$

$$dt \quad = \quad \gamma(dt' + \frac{V}{c^2}dx'), \tag{2.32}$$

and then we can write the velocity components in the S frame as

$$v_x = \frac{\gamma(dx' + V\,dt')}{\gamma(dt' + \dfrac{V}{c^2}dx')}, \tag{2.33}$$

$$v_y = \frac{dy'}{\gamma(dt' + \dfrac{V}{c^2}dx')}, \tag{2.34}$$

$$v_z = \frac{dz'}{\gamma(dt' + \dfrac{V}{c^2}dx')}, \tag{2.35}$$

$$\tag{2.36}$$

from which we obtain the desired velocity transformation by dividing numerators and denominators by dt':

$$v_x = \frac{v_x' + V}{1 + \dfrac{V}{c^2}v_x'}, \tag{2.37}$$

$$v_y = \frac{v_y'}{\gamma(1 + \dfrac{V}{c^2}v_x')}, \tag{2.38}$$

$$v_z = \frac{v_z'}{\gamma(1 + \dfrac{V}{c^2}v_x')}. \tag{2.39}$$

As for the Lorentz transformations, we immediately see that we recover Galilean transformations as $V/c \to 0$.

Let us now take $V = c$, i.e. assume that system S' moves with the speed of light. Equation (2.37) yields

$$v_x = \frac{v_x' + c}{1 + \dfrac{c}{c^2}v_x'} = \frac{v_x' + c}{\dfrac{c + v_x'}{c}} = c. \tag{2.40}$$

The observer in S measures a velocity $v_x = c$, for any value of v_x' (including $v_x' = c$).

2.4.3 Lorentz matrix

If we consider four-component space-time vectors

$$\underline{x} = (x_1, x_2, x_3, x_4) = (x, y, z, ct) = (\vec{x}, ct) \tag{2.41}$$

and analogously

$$\underline{x}' = (x_1', x_2', x_3', x_4') = (x', y', z', ct') = (\vec{x'}, ct'), \tag{2.42}$$

we can write the Lorentz transformations as

$$
\begin{align}
x_1' &= \gamma x_1 - \beta\gamma x_4, \tag{2.43}\\
x_2' &= x_2, \tag{2.44}\\
x_3' &= x_3, \tag{2.45}\\
x_4' &= -\beta\gamma x_1 + \gamma x_4, \tag{2.46}
\end{align}
$$

where $\beta = V/c$, or

$$
\begin{pmatrix} x_1' \\ x_2' \\ x_3' \\ x_4' \end{pmatrix}
=
\begin{pmatrix}
\gamma & 0 & 0 & -\beta\gamma \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
-\beta\gamma & 0 & 0 & \gamma
\end{pmatrix}
\begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{pmatrix}
\tag{2.47}
$$

In compact vector form

$$
(\underline{x}')^T = A\underline{x}^T, \quad \text{or } x_i' = \sum_{i,j} A_{i,j} x_j \tag{2.48}
$$

where

$$
A =
\begin{pmatrix}
\gamma & 0 & 0 & -\beta\gamma \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
-\beta\gamma & 0 & 0 & \gamma
\end{pmatrix}
\tag{2.49}
$$

is the **Lorentz matrix**. Analogously,

$$
\underline{x}^T = A^{-1}(\underline{x}')^T, \tag{2.50}
$$

where

$$
A^{-1} =
\begin{pmatrix}
\gamma & 0 & 0 & \beta\gamma \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
\beta\gamma & 0 & 0 & \gamma
\end{pmatrix}
\tag{2.51}
$$

is the inverse of matrix A.

2.4.4   Four-vectors

The four-component vectors $\underline{x}$ and $\underline{x}'$ introduced in the previous section are just two particular (and particularly important) relativistic four-component vectors (*4-vectors*, in short). In general, a 4-vector $\underline{a}$ is a four-component vector

$$
\underline{a} = (a_1, a_2, a_3, a_4) \tag{2.52}
$$

that transforms according to Lorentz transformations, $\underline{a}' = A\underline{a}$, where A is Lorentz matrix.

The inner product of two 4-vectors $\underline{a}$ and $\underline{b}$ is defined by

$$
\underline{a} \cdot \underline{b} = a_1 b_1 + a_2 b_2 + a_3 b_3 - a_4 b_4. \tag{2.53}
$$

(Note the minus sign!)

One can verify that the inner product of two 4-vectors is relativistically invariant, i.e. it takes the same value in any (inertial) frame. Hence, for instance,

$$(\vec{x}, ct)^2 = (\vec{x'}, ct')^2, \tag{2.54}$$

or

$$x^2 + y^2 + z^2 - c^2 t^2 = x'^2 + y'^2 + z'^2 - ct'^2. \tag{2.55}$$

2.5 Momentum, mass, energy

In classical mechanics the momentum of a particle of mass m and velocity v is $\vec{p} = m\vec{v}$. Total momentum of an isolated system is conserved. It can easily be shown that total momentum $(\sum m_j \vec{v}_j)$ is not conserved if the velocities follow the Lorentz transformations. Since we want total momentum to be conserved, we have to modify the expression of the momentum.

2.5.1 Momentum-energy 4-vector

In analogy with the space-time 4-vector $\underline{x} = (x, y, z, ct)$ we define the 4-vector

$$\underline{p} = (m_0 \frac{dx}{dt_0}, m_0 \frac{dy}{dt_0}, m_0 \frac{dz}{dt_0}, m_0 \frac{dct}{dt_0}) \tag{2.56}$$

where t_0 is the proper time, i.e. the time measured in the body's frame, and m_0 is the rest mass, i.e. the mass of the body in a system moving with the body itself. The reason for the name rest mass will be apparent soon. The 4-vector $\underline{p}$ can also be written as

$$\underline{p} = (m_0 \frac{dx}{dt} \frac{dt}{dt_0}, m_0 \frac{dy}{dt} \frac{dt}{dt_0}, m_0 \frac{dz}{dt} \frac{dt}{dt_0}, m_0 \frac{dct}{dt_0}) \tag{2.57}$$

$$= (m_0 v_x \frac{dt}{dt_0}, m_0 v_y \frac{dt}{dt_0}, m_0 v_z \frac{dt}{dt_0}, m_0 c \frac{dt}{dt_0}) \tag{2.58}$$

The relation between the time differentials dt and dt_0 is obtained from the Lorentz transformation, as $dt = dt_0/(\sqrt{1 - v^2/c^2})$ or $dt/dt_0 = \gamma$. We can then write

$$\underline{p} = (m_0 \gamma v_x, m_0 \gamma v_y, m_0 \gamma v_z, m_0 \gamma c), \tag{2.59}$$

or, in a form resembling the classical one (with spatial part equal to mass times velocity),

$$\underline{p} = (m v_x, m v_y, m v_z, mc) = (m\vec{v}, mc) = (\vec{p}, mc). \tag{2.60}$$

2.5.2 Momentum

We have then found that the expression of the momentum is just the same as in classical mechanics, i. e.

$$\vec{p} = m\vec{v}, \tag{2.61}$$

but with the mass m depending on velocity:

$$m = m_0\gamma = \frac{m_0}{\sqrt{1 - \dfrac{v^2}{c^2}}}. \tag{2.62}$$

The mass tends to infinity as the velocity approaches the speed of light c.

Note that, using the definitions of $\vec{\beta} = \vec{v}/c$ and of γ, the momentum is often written as

$$\vec{p} = m_0 c \gamma \vec{\beta}. \tag{2.63}$$

Both the spatial part and the temporal-part (fourth component) of the 4-vector are conserved simultaneously in an isolated system.

As for any 4-vector, the square of the modulus of the momentum-energy 4-vector is relativistically invariant; indeed

$$\begin{aligned}
|\underline{p}|^2 &= |m\vec{v}|^2 - m^2 c^2 = (m_0\gamma v)^2 - (m_0\gamma c)^2 = m_0^2 \gamma^2 (-v^2 + c^2) \\
&= -m_0^2 c^2 \gamma^2 \frac{1 - v^2}{c^2} = -m_0^2 c^2,
\end{aligned} \tag{2.64}$$

independent of the reference system.

2.5.3   Energy

We can find the relativistic expression of a particle energy by proceeding as follows. From the invariance of the momentum-energy 4-vector we have $d|\underline{p}|^2 = d(|\vec{p}|^2 - m^2 c^2) = 0$, or

$$2\vec{p} \cdot d\vec{p} - 2mc^2 dm = 0, \tag{2.65}$$

from which

$$\vec{v} \cdot d\vec{p} = c^2 dm. \tag{2.66}$$

In classical mechanics the increment of momentum equals the instantaneous impulse of the force $d\vec{p} = \vec{F}dt$. We assume this relation still holds relativistically, and then write Eq. (2.66) as

$$\vec{F} \cdot \vec{v}dt = c^2 dm. \tag{2.67}$$

The left hand side of this equation represents the work done on the particle, i.e., its energy increment. We can then write

$$dE = c^2 dm, \tag{2.68}$$

or

$$E = mc^2 = \frac{m_0 c^2}{\sqrt{1 - \dfrac{v^2}{c^2}}} = m_0 c^2 \gamma. \tag{2.69}$$

Equation (2.69) also tells us that an energy release is associated to any reduction of rest mass of a system of particles (viceversa energy is required to increase the mass), according to

$$E = \Delta m_0 c^2.$$

(2.70)

Hence mass conservation is replaced by mass-energy conservation.

Note that using Eq. (2.69) the 4-vector $\underline{p}$ can be written as

$$\underline{p} = (\vec{p}, \frac{E}{c}),$$

(2.71)

hence the name of momentum-energy 4-vector.

Finally, from the definition of modulus of a 4-vector we can write

$$|\underline{p}|^2 = (\vec{p})^2 - \frac{E^2}{c^2},$$

(2.72)

and using Eq. (2.64) we obtain an important relation between energy, momentum and rest mass, namely

$$E^2 = (pc)^2 + (m_0 c^2)^2.$$

(2.73)

Note that

> **for a photon** (with zero mass), $E = h\nu$, and $p = E/c = h\nu/c$.

2.5.4 Kinetic energy

We go back to the Eq. (2.67), $\vec{F} \cdot \vec{v} dt = c^2 dm$, and integrate assuming a body at rest at time $t = 0$, thus obtaining

$$L = E - E_0 = mc^2 - m_0 c^2,$$

(2.74)

where L is the work made by external forces on the body. On the other hand, according to the kinetic energy theorem, such a work is equal to the increment of the body's kinetic energy T. Hence

$$T = mc^2 - m_0 c^2 = m_0 c^2 (\gamma - 1).$$

(2.75)

For $v/c \ll 1$, we can Taylor expand

$$\gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \simeq 1 + \frac{1}{2} \left(\frac{v}{c}\right)^2 - \frac{3}{8} \left(\frac{v}{c}\right)^4,$$

(2.76)

and

$$T \simeq \frac{1}{2} m_0 v^2 - \frac{3}{8} m_0 \frac{v^4}{c^2}.$$

(2.77)

We see that the classical limit $T = (1/2) m_0 v^2$ is recovered when the velocity $v \ll c$. As $v \to c$, T grows indefinitely: see Fig. 2.6.
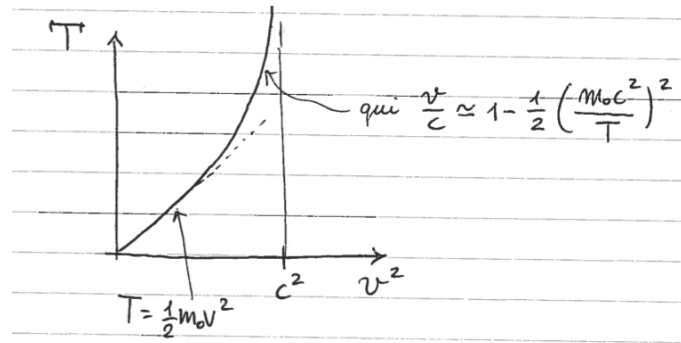
Figure 2.6: Kinetic energy T vs v^2.

Chapter 3

Particles, photons and Old Quantum Theory

3.1 Introduction and summary

Old quantum theory refers to quantum concepts introduced *ad-hoc* in order to overcome limitations of classical physics.

- The black body spectrum was recovered by Planck, introducing **quantization of oscillator energy** $[E(\nu) = nh\nu]$ and giving up the principle of equipartition of energy in favour of level **occupation according to the Boltzmann factor** $\exp(-E/k_{\mathrm{B}}T)$.

- The photoelectric effect was explained by Einstein assuming that electromagnetic waves carry energy in *packets* of finite quantity. Light is composed of particle-like **photons**, of zero mass, energy $E = h\nu$ and momentum $p = h\nu/c$. The concept of photon also explains Compton effect.

- Atom emission and absorption spectra are recovered by Bohr's atom model and its subsequent extensions. Bohr's model assumes that **orbital momentum is quantized** ($l = n\hbar = nh/2\pi$, with $n = 1, 2, \ldots$) and that **orbiting electrons do not irradiate**. The concepts of force and energy are just the classical one. The electron orbits and energies turn out to be quantized. In the Hydrogen atom the electrons with quantum number n move in a circular orbit of radius r_n and have total energy E_n,

$$
\begin{aligned}
r_n &= r_0 n^2, & (3.1) \\
E_n &= E_0/n^2, & (3.2)
\end{aligned}
$$

with

$$
\boxed{r_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_{\mathrm{e}} e^2} = 5.292 \times 10^{-11} \text{ m;} \quad \text{Bohr's radius}} \quad (3.3)
$$

and

$$E_0 = -\frac{1}{2}\frac{m_e e^4}{(4\pi\varepsilon_0)^2\hbar^2} = -13.60 \text{ eV} = -2.179 \times 10^{-18}\text{J}, \qquad (3.4)$$

with ε_0 the vacuum dielectric constant, m_e the electron mass, and $-e$ the electron charge. When excited electrons in level m return to a lower energy state n they emit a photon with frequency $\nu_{mn} = (E_m - E_n)/\hbar$.

Some notes on black body, photoelectric effect, Compton effect, and Bohr's atom, respectively, are presented in the next subsections.

3.2 Black body spectrum and energy quantization

3.2.1 The black body

Radiation incident on a body can be absorbed, reflected, transmitted. We call black body an ideal body that absorbs all incident radiation. Experience however shows that many real bodies behave in a manner not too much different from a black body. In turn, all bodies emit radiation.

In conditions of thermodynamic equilibrium a body must emit the same amount of radiation it absorbs, at any frequency. Thermodynamics also tells us that the black body spectral emissivity does not depend on the body shape and material. [The spectral emissivity is defined as $d\eta(\nu) = \eta(\nu)d\nu$, power emitted per unit surface in a frequency interval $d\nu$ around ν or, equivalently, $d\eta(\lambda) = \eta(\lambda)d\lambda$, power emitted per unit surface in a wavelength interval $d\lambda$ around λ.]

Experimental evidence:

- Total emissivity is proportional to the fourth power of the absolute temperature of the black body (Stefan-Boltzmann law)

$$\eta = \int_0^\infty \eta(\nu)d\nu = \sigma T^4 \qquad (3.5)$$

with the Stefan-Boltzmann constant $\sigma = 5.67 \times 10^{-8}$ W/(m^{2}K^4);

- The maximum of $\eta(\lambda)$ occurs at a wavelength inversely proportional to the black body temperature (Wien's displacement law, see Fig. 3.1)

$$\lambda_m = \frac{C}{T} \qquad (3.6)$$

where $C = 2.897 \times 10^{-3}$ m K;

- at low frequencies (long wavelengths) the spectral emissivity $\eta(\nu)$ is proportional to the square of the frequency (<u>Rayleigh-Jeans law</u>)

$$\eta(\nu) \propto \nu^2; \qquad (3.7)$$

- at any wavelength

$$\eta(\lambda, T_2) > \eta(\lambda, T_1), \quad \text{for any } T_2 > T_1; \qquad (3.8)$$

as shown by Fig. 3.1.
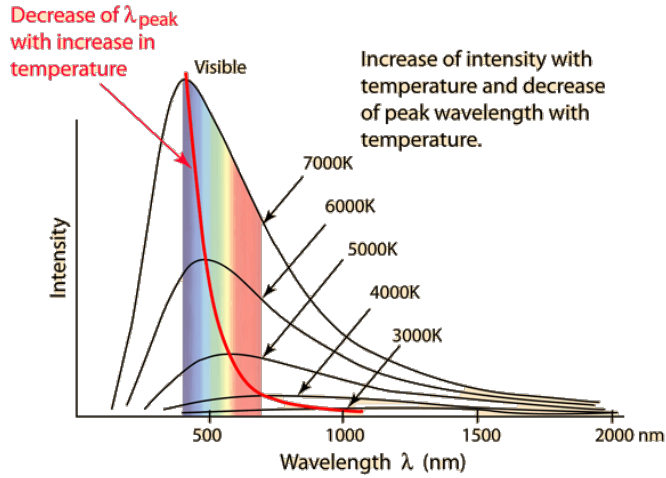
Figure 3.1: Black body spectral emission vs wavelength at different temperatures. From http://hyperphysics.phy-astr.gsu.edu/hbase/wien.html

3.2.2 Modelling the black body spectrum

Rather than considering an emitting surface, one can consider a cavity with a very small hole, so small that practically all incoming radiation enters in the cavity (see Fig. 3.3). Instead of computing the emissivity, one can compute the spectral energy density $u(\nu)$ of the equilibrium radiation inside the cavity. Indeed it can be shown[1] that in this case emissivity and energy density are related by

$$\eta(\nu) = \frac{cu(\nu)}{4} \qquad (3.9)$$

The analysis is made easier by choosing suitable cavity shape and material, since the black body properties do not depend on a specific shape and materials, but only on the temperature. We consider a parallelepiped with perfectly

---

[1] Note that in the case of a beam of collimated radiation, directed along the normal to the hole one would have $\eta = cu$; the factor $1/4$ arises from the isotropy of the radiation field.

Conceptual Black Body
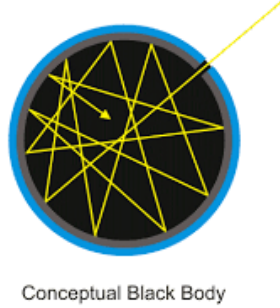
Figure 3.2: A conceptual realization of a black body is a cavity with a small hole, such that practically all incoming radiation is trapped inside the body. Adapted from http://www.electrical4u.com/black-body-radiation/

reflecting metallic surfaces, with lengths L_x, L_y and L_z, respectively. According to electromagnetism such a cavity will contain radiation in the form of standing waves (*modes* of oscillation) with nodes on the surfaces. We can then write the spectral energy density as

$$u(\nu)d\nu = \frac{\text{number of modes in } [\nu, \nu + d\nu]}{\text{cavity volume}} \times (\text{ average energy per mode}). \tag{3.10}$$

The number of standing waves (modes) in a frequency interval du is

$$dN(\nu) = 4\pi V \nu^2 d\nu. \tag{3.11}$$

A rigorous proof can be found in many textbooks on thermodynamics, statistical thermodynamics, or statistical mechanics. We present here a simple argument. Consider first a one-dimensional system, as a string which can support transverse oscillations. Standing waves will have wavelengths

$$\lambda = \frac{2L}{n}, \quad n = 1, 2, \dots \tag{3.12}$$

with n a positive integer number. Corresponding wavevectors will be $k = 2\pi/\lambda = n\pi/L$, so that we can write,

$$dN_{1D} = dn = \frac{L}{\pi} dk \tag{3.13}$$

for the number of modes in this 1D system. This result can be extended to a 3D cavity in a straightforward way:

$$dN = \frac{L_x}{\pi} \frac{L_y}{\pi} \frac{L_z}{\pi} dk_x dk_y dk_z = \frac{V}{\pi^3} dk_x dk_y dk_z, \tag{3.14}$$
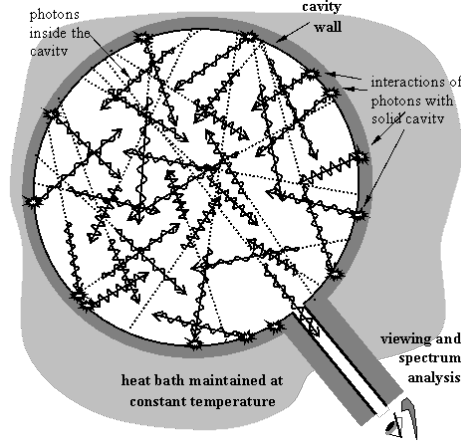
Figure 3.3: The spectral energy distribution of the radiation in equilibrium inside the cavity is determined by measuring the emitted spectrum. From http://claesjohnson.blogspot.it/2011/11/blackbody-as-bottle-with-peephole.html

where V is the volume of the cavity. Going from the discrete to the continuum, using spherical coordinates, assuming isotropy, and integrating over the angular we can write the volume element in k-space as $4\pi k^2 dk$; actually we have to take only $(1/8)$ of it because we have only to take positive values of the k components. Furthermore, we have to multiply the number of modes by 2, to account for two polarizations for each wavelength, thus obtaining

$$dN = \frac{V}{\pi^2}k^2 dk = V\frac{8\pi\nu^2}{c^3}d\nu, \qquad (3.15)$$

where we have used the relations $k = 2\pi/\lambda = 2\pi\nu/c$ and then $dk = 2\pi d\nu/c$, with c the speed of light.

We now turn to the average energy per mode. Attempts of classical interpretation rely on the equipartition principle: each mode of oscillation, with two degrees of freedom, has average energy $k_\mathrm{B}T$. This leads to

$$u(\nu)d\nu = \frac{8\pi\nu^2}{c^3}k_\mathrm{B}T d\nu, \qquad (3.16)$$

and then

$$\eta(\nu)d\nu = \frac{2\pi\nu^2}{c^2}k_\mathrm{B}T d\nu. \qquad (3.17)$$

This expression, known as Rayleigh-Jeans law, agrees with experimental data at low frequency, but clearly fails at high frequency, where it diverges, leading to infinite (frequency integrated) emissivity (see Fig. 3.4).

3.2.3   Planck's model and energy quantization

A result in excellent agreement with all experimental data is obtained by still using Eq. 3.10, but giving up with the equipartition principle. Planck showed that one should replace equipartition with the assumption that modes of frequency ν can only have energy

$$\boxed{\varepsilon = nh\nu, \quad n = 1, 2, \ldots,}$$ (3.18)

i.e. equal to an integer multiple of $h\nu$, where $h =$ is a constant, known as Planck constant: **energy levels are quantized**. The probability distribution of states as a function of their energy is proportional to the Boltzmann factor $\exp -\varepsilon/k_B T$, so that the average energy of modes with frequency ν is

$$\overline{\varepsilon} = \frac{\sum_0^\infty nh\nu e^{-nh\nu/k_B T}}{\sum_0^\infty e^{-nh\nu/k_B T}}.$$ (3.19)

With some algebra and calculus one finds [2]

$$\overline{\varepsilon} = \frac{h\nu}{e^{h\nu/k_B T} - 1}.$$ (3.22)

Note that in the low frequency limit (more properly, when $h\nu \ll k_B T$), Eq. (3.22) yields $\overline{\varepsilon} \simeq k_B T$, i.e the classical result. However, in the opposite limit $\overline{\varepsilon} \sim h\nu e^{-h\nu/k_B T} \ll kT_B$.

The final expression of the black body spectral radiation energy is then obtained by inserting Eqs. (3.22) and (3.17) into Eqs. (3.10):

$$\boxed{u(\nu)d\nu = \frac{8\pi}{c^3} \frac{h\nu^3}{e^{h\nu/k_B T} - 1} d\nu.}$$ (3.23)

and is found to agree accurately with experimental data. A plot of such Planck law is shown in Fig. 3.4. The Rayleigh-Jeans spectrum is also shown for comparison.

From the Planck spectral energy distribution, Eq. (3.23), one recovers Stefan-Boltzmann law, Wien law and Rayleigh-Jeans limit (see the suggested exercises).

3.2.4   Exercises

1. Show that Stefan-Bolzmann law for the black body emissivity is recovered from Planck distribution. Find the expression of the constant σ as

---

[2]Set $\beta = 1/k_B T$; then

$$\overline{\varepsilon} = \frac{\sum_0^\infty nh\nu e^{-\beta nh\nu}}{\sum_0^\infty e^{-\beta \nu}} = -\frac{d}{d\beta}\left[\ln \sum_0^\infty e^{-\beta nh\nu}\right]$$ (3.20)

$$= -\frac{d}{d\beta}\left[\ln \frac{1}{1 - e^{-\beta h\nu}}\right] = \frac{h\nu e^{-\beta h\nu}}{1 - e^{-\beta h\nu}} = \frac{h\nu}{e^{\beta h\nu} - 1}$$ (3.21)
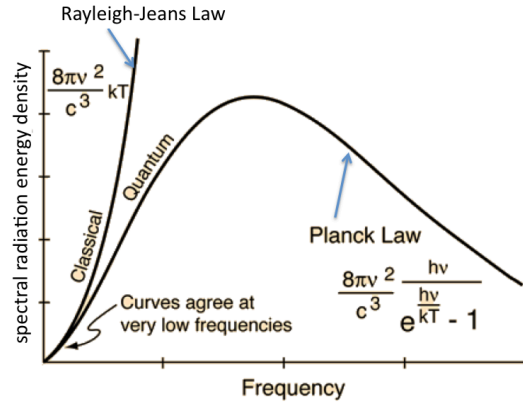
Figure 3.4: Black body spectrum (Adapted from http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod/bb7b.gif)

a function of fundamental constants. Hint: in integrating the spectral emissivity, set $x = h\nu/k_{\mathrm{B}}T$; also, use

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}. \tag{3.24}$$

2. Recover Wien displacement law.[3]

3. Show that $\eta(\nu, T_2) > \eta(\nu, T_1), \quad$ for any $T_2 > T_1$.

4. The Sun is a very powerful emitter of electromagnetic radiation. Estimate the power released by the Sun in the form of electromagnetic radiation knowing that a) the solar constant, i.e. the intensity of solar radiation (power per unit surface orthogonal to the direction of solar radiation) incident on the upper layers of the earth's atmosphere is 1350 W/m^2 and b) the average distance Sun-earth is 150 million of kilometers.

5. Using the result of the previous exercise, and assuming that the Sun radiates as a spherical black body of radius of 700 000 km, find the temperature of the surface of the Sun. Next, find the wavelength at the maximum of $\eta(\lambda)$. [Answer: about 5700 K, as also shown by the plot in Fig. 3.5)

6. After crossing the earth atmosphere the intensity of solar radiation is about 1000 W/m^2. On average, 25% of the incoming radiation is reflected by the earth surface. Find what would be the equilibrium temperature of the surface if the atmosphere were transparent to the radiation emitted

---

[3]At some point you have to solve the equation $x = 5(1 - e^{-x})$. It can easily be checked that $x \simeq 4.965$
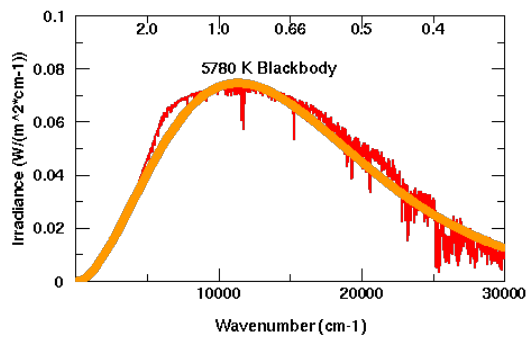
Figure 3.5: Sun irradiance compared with that of a blackbody at $T = 5800$ K. From https://www.quora.com/Why-is-the-Sun-considered-to-be-a-black-body)

by the earth. [Hint: balance absorbed solar radiation with the radiation emitted by the earth, assumed to behave as a black body].

3.3 Photoelectric effect

Photolectric effect: emission of electrons from an irradiated [metallic] surface (more generally, from atoms).

Consider monochromatic radiation (visible light, uv, X-rays) with frequency ν and intensity Φ hitting a metallic surface.

<u>Experiment</u> to find the relation between light properties and emitted electron current (Lennard, 1900)

M: metal foil
C: cap
A: amperometers
V: voltmeter
R: variable resistor
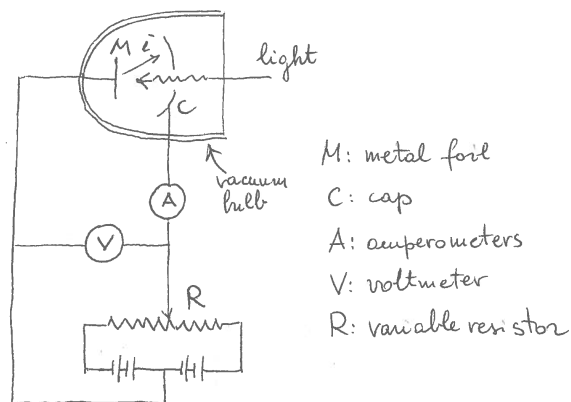
Fig. 1 Apparatus for the study of photoelectric effect.

Intensity and frequency of radiation are known.

By acting on the potentiometer (variable resistor) R, the potential difference ΔV between metallic foil and the cap can be varied (and be either positive or negative). For large positive ΔV, all emitted electrons reach the cap and contribute to the current I in the circuit. As ΔV decreases but remains positive, the fraction of collected electron decreases somewhat. When ΔV becomes negative electrons are repelled and only electrons with energy $E_e > -eV$ (with -e the electron charge) can reach the cap.

Measuring the current I we know the rate of electron emission.

Measuring the voltage ΔV_0 (stopping voltage) at which the current vanishes we know the maximum energy of the emitted electrons $E_e^{max} = -e \ \Delta V_0$

Experimental results
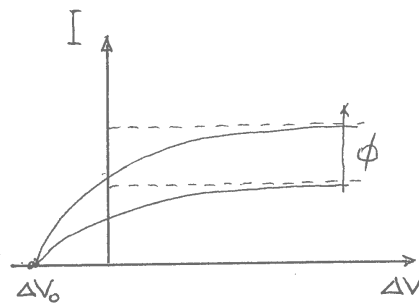
Fig. 2 : Current I vs $\Delta V = V_c - V_M$, for different values of light intensity ϕ and the same material and frequency ν
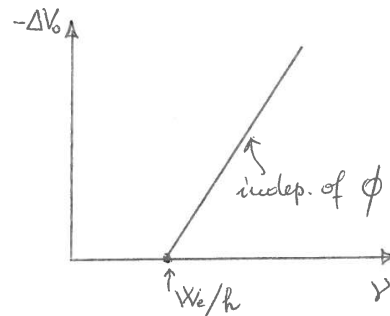
Fig. 3 : Stopping voltage vs light frequency for a given material

Fig. 2: if emission occurs, for given material and light frequency
  - ΔV_0 (hence the maximum energy of the emitted electrons) does not depend on light intensity
  - The rate of electron emission grows with light intensity

Fig. 3: again, for a given material,
  - The stopping voltage (hence the maximum energy of emitted electrons) varies linearly with frequency.
  - No electrons are emitted if the frequency is below a certain threshold (depending on the material, but not on light intensity)

Einstein's explanation (1905)

Light is quantized. It consists of photons, "particles" of zero mass, energy $\varepsilon = h\,\nu$ (and momentum $p = h\nu/c$, see the relation between energy and momentum in the chapter on special relativity); here h is Planck constant.

The extraction of an electron from the metal requires an energy W_e (sometimes called work function), which must provided by a single electron. Therefore photoemission can only occur if $h\nu > W_e$.

Emitted electrons can loose part of their energy in the path from the emission point to the metal surface its energy. Electrons which do not suffer any loss emerge from the surface with maximum energy

$E_e^{max} = -e\ \Delta V_0 = h\upsilon - W_e$, in excellent agreement with the experimental curve shown in Fig. 3.

3.4 Compton effect

λ' ← scattered X-rays

λ

X rays
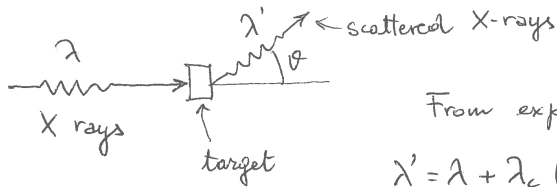
target

From experiments

$$\lambda' = \lambda + \lambda_c \left(1 - \cos\vartheta\right), \quad (1)$$

with $\lambda_c \simeq 2.5 \times 10^{-12}\, m$,
independent of target material

Interpretation (Compton, 1923):

   <u>elastic collision</u> between a <u>photon</u> and an <u>electron</u>

before

λ e^-, at rest

after λ'

e^-

- use conservation of energy and momentum
- neglect energy required to "extract" the electron
  from the atom (few-tens of eV vs keV of X-ray)
  = assume the electron is free

	before	after	
photon energy	$h\nu$	$h\nu'$	
momentum	$h\nu/c$	$h\nu'/c$	
electron energy	$m_e c^2$	E	for relativity
momentum	0	p	$E^2 = \left(m_e c^2\right)^2 + (pc)^2$

energy conservation $\qquad h\nu + m_e c^2 = h\nu' + E \qquad (3)$

momentum conservation
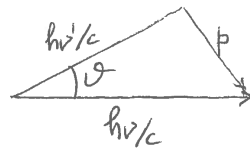
$$p^2 = \left(\frac{h\nu}{c}\right)^2 + \left(\frac{h\nu'}{c}\right)^2 - 2\left(\frac{h\nu}{c}\right)\left(\frac{h\nu'}{c}\right)\cos\vartheta \quad (4)$$

From Eq.(3): $\quad E^2 = \left(m_e c^2\right)^2 + \left(h\nu\right)^2 + \left(h\nu'\right)^2 + 2m_e c^2 h\nu - 2m_e c^2 h\nu' - 2h\nu h\nu'$

$$(5)$$

Now insert p^2 from Eq.(4) and E^2 from Eq.(5) into Eq.(2):

$$\cancel{\left(m_e c^2\right)^2} + \cancel{\left(h\nu\right)^2} + \cancel{\left(h\nu'\right)^2} + 2m_e c^2 h\nu - 2m_e c^2 h\nu' - 2h\nu h\nu' = \cancel{\left(m_e c^2\right)^2}$$

$$+ \cancel{\left(h\nu\right)^2} + \cancel{\left(h\nu'\right)^2} - 2\left(h\nu\right)\left(h\nu'\right)\cos\vartheta \ ;$$

$$\Rightarrow \qquad h\nu - h\nu' = \frac{h^2 \nu\nu' \left(1 - \cos\vartheta\right)}{m_e c^2}$$

and, using $\nu = c/\lambda$ and $\nu' = c/\lambda'$

$$\lambda' = \lambda + \frac{h}{m_e c}\left(1 - \cos\vartheta\right)$$

$$\hookrightarrow 2.5 \times 10^{-12} m$$

"Compton wavelength"

Einstein's interpretation of the photoelectric effect and Compton interpretation of the effect now named after him "finally convinced most physicists of the reality of light quanta" [1]

Notice however that as early as in 1927 it was shown that both effects can be explained without resorting to photon concepts. Experiments which can only be interpreted using photons were performed only in 1986. A clear and simple explanation can be found in Ref. [2].

[1] H. Bethe, Rev. Modern Phys. 71 (1999) S1.

[2] HRW, Physics, 2nd Vol. (see page 1 of these notes)

3.5 Bohr's atom

Experimental

- [obvious] the atom is stable

= Rutherford, Geiger & Mardsen

  • central nucleus,
    radius $\sim 10^{-5}$ atom radius
    positive charge
  • "rotating" electrons
    (cannot be static)
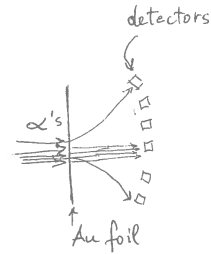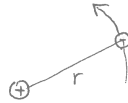
if dynamic $\Rightarrow$ electrons should irradiate
$P_{rad} \propto (\text{acceleration})^2$
$\Rightarrow$ • unstable atom (!!)
    • emission of radiation
      with continuous spectrum

    contrary to observations

- (instead) line spectra

for Hydrogen $\dfrac{1}{\lambda} = Ry \left(\dfrac{1}{n^2} - \dfrac{1}{m^2} \right)$, $m, n \geq 1$

(1)

integer

Rydberg constant $= 1.097 \times 10^{-7} m^{-1}$

detectors

α's

Au foil

r

Bohr's model (1913) of the Hydrogen atom

- use classical concepts of force and energy

- new postulates

> 1) Angular momentum is quantized

$$l = n \frac{h}{2\pi} = n\hbar \qquad (2)$$

$$n = 1, 2, \ldots$$

2) electron in stable orbits do not radiate

3) when a transition of an electron from one energy level (orbit) to another one occurs, a photon of frequency $\nu = \Delta E/h$ is emitted or absorbed

[ΔE = energy difference between the two levels]

⇒

- Electron equation of motion ($m\vec{a} = \vec{f}$):

$$m\vec{a} = \frac{q_1 q_2}{4\pi \mathcal{E}_0} \frac{\hat{r}}{r^2} \quad , \text{ with } q_1 = e$$
$$q_2 = -e$$

electron mass

circular motion $|\vec{a}| = v^2/r$

$$\Rightarrow \frac{mv^2}{r} = \frac{e^2}{4\pi \mathcal{E}_0 r^2} \longrightarrow mv^2 r = \frac{e^2}{4\pi \mathcal{E}_0} \qquad (3)$$

- From Eq.(2): $(n\hbar)^2 = (mvr)^2 = mv^2 r\,(mr) = \dfrac{e^2}{4\pi\varepsilon_0} mr$ (4)

                       ↑

               using (3)

  $\Rightarrow\ r_n = n^2\,\hbar^2\,\dfrac{4\pi\varepsilon_0}{e^2 m} = n^2 r_0$

  (5) $\boxed{r_n = n^2 r_0\,,}$ with $\boxed{r_0 = \dfrac{\hbar^2\,4\pi\varepsilon_0}{me^2} = 5.3\times10^{-11}\,m}$ (6)

         $n = 1, 2, ..$ ↑

                                        Bohr radius

- Total electron energy $\ E_{TOT} = E_{Kin} + U = \dfrac{1}{2}mv^2 - \dfrac{e^2}{4\pi\varepsilon_0}\cdot\dfrac{1}{r}$

                                ↑   ↑

                             Kinetic   potential

  and using Eq.(3): $\ E_{TOT} = -\dfrac{1}{8\pi\varepsilon_0}\dfrac{e^2}{r}\,,$

  where r can only take the values given by Eq.(5). Hence

  (7) $E_{TOT} = \boxed{E_n = -\dfrac{E_0}{n^2}}$ with $E_0 = \dfrac{1}{8\pi\varepsilon_0}\dfrac{e^2}{r_0} = 13.59\ eV$

                          ↑

                     energy of level "n"
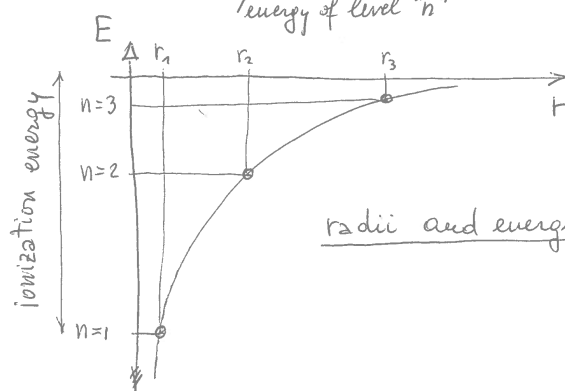
radii and energies are quantized

- Radiation emitted in a transition $m \to n$

  $(m > n \geqslant 1)$

$$h \nu_{mn} = E_m - E_n \quad \longrightarrow \quad \frac{1}{\lambda_{mn}} = \frac{E_m - E_n}{ch}$$

$$\frac{1}{\lambda_{mn}} \underset{\text{using Eq. (7)}}{=} \frac{E_0}{ch} \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \quad \equiv \quad Eq. (1)$$

$$\text{with } Ry = \frac{me^4}{8h^3 c \, \varepsilon_0}$$

- Bohr's model can be "extended" to apply to multi-electron atoms, and can be improved to account for the observed "splitting" of spectral lines. In any case, it is an ad-hoc model.

- Note: we assumed the proton at rest, i.e $m_p / m_e \to \infty$. However the rigorous treatment of the problem leads to the same eqs. as above, with the electron mass m replaced by the reduced mass $m_r = m m_p / (m + m_p)$ and the velocity replaced by the relative velocity.

Chapter 4

Material waves

4.1 de Broglie associated wave

Louis de Broglie suggested that just as light has both wave-like and particle-like properties, particles also have wave-like properties. The wavelength associated to a particle of momentum p is

$$\boxed{\lambda = \frac{h}{p}.}$$
(4.1)

Experiments on electrons, nuclei, nucleons, atoms, molecules have confirmed de Broglie's hypothesis.

4.1.1 Justification of de Broglie's hypothesis

The relation (4.1) between wavelength and momentum is just the same as that holding for photons

$$\lambda = \frac{c}{\nu} = h\frac{c}{h\nu} = \frac{h}{p}.$$
(4.2)

Another argument in support of Eq. (4.1) is as follows. We associate a wave packet to a particle, and impose that the group velocity (see Appendix A) of the wave packet coincides with the particle velocity. The kinetic energy of a non relativistic particle of mass m and velocity v can be written as $E = p^2/2m$, which can be differentiated to yield $dE = pdp/m = vdp$, and then

$$v = \frac{dE}{dp}.$$
(4.3)

On the other hand, as shown in Appendix A, the group velocity of a wave packet is $v_{\mathrm{g}} = d\omega/dk$. If we write the angular frequency as $\omega = 2\pi\nu = 2\pi E/h$ and the wavenumber as $k = 2\pi/\lambda$, we have

$$v_{\mathrm{g}} = -\frac{\lambda^2}{h}\frac{dE}{d\lambda}.$$
(4.4)

By imposing $v = v_{\mathrm{g}}$ we obtain

$$\frac{dE}{dp} = -\frac{\lambda^2}{h}\frac{dE}{d\lambda},\tag{4.5}$$

and then $-(h/\lambda^2)d\lambda = dp$, from which Eq. (4.1) is immediately obtained.

4.1.2   Experimental confirmation

de Broglie hypothesis has been verified by a number of experiments, concerning, e.g.

- electron diffraction by powders (Davidson & Germer, 1927), electron diffraction by crystals (Thomson & Reid, 1927);

- electron interference (Tomonura 1989), with a set-up analogous to that of Young's experiment with light;

- atom interference;

- neutron interference.

Elementary descriptions of the above experiments can be found in Halliday, Resnick, Krane, *Physics II*, 5th Ed., John Wiley & Sons(2002), Chapter 46, and in Feynmann, Leighton, Sands, *The Feynmann Lectures on Physics*, Addison-Wesley (1962), Ch. 38.[1]

4.1.3   Discussion

Just as for photons, either particle behaviour alone or wave behaviour alone cannot explain all experimental evidence. **Wave and corpuscular nature are complementary**.

In is interesting to observe that de Broglie assumption is, in a sense, consistent with Bohr's postulated quantization of the electron angular momentum l. For an electron moving with velocity v in a circular orbit of radius r, $l = mvr$. If we associate a standing wave to an electron orbit or radius r we have (see Fig. 4.1)

$$2\pi r = n\lambda = n\frac{h}{mv},\tag{4.6}$$

or

$$l = mvr = n\frac{h}{2\pi} = n\hbar,\tag{4.7}$$

which is just Bohr's postulate.

A few words are in order to discuss the analogy between interference experiments with light and with electrons (see Fig. 4.2). In experiments with light

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[1]Free on-line edition: http://www.feynmanlectures.caltech.edu/
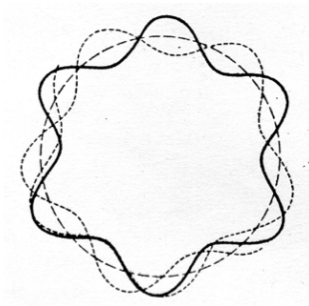
Figure 4.1: Bohr's electron orbit and standing de Broglie wavefunction.

the pattern shown in the figure represents the intensity of the electromagnetic wave, which is proportional to the square of the amplitude of the electric (and magnetic) field. In experiments with particles, we plot the number of counts, i.e. the number of particles reaching the detecting screen at a certain position. Therefore, we have an analogy between the density of counts and the square of the wave amplitude. This analogy somehow supports the physical interpretation of quantum mechanics wavefunctions, which will be discussed in Section 5.5.
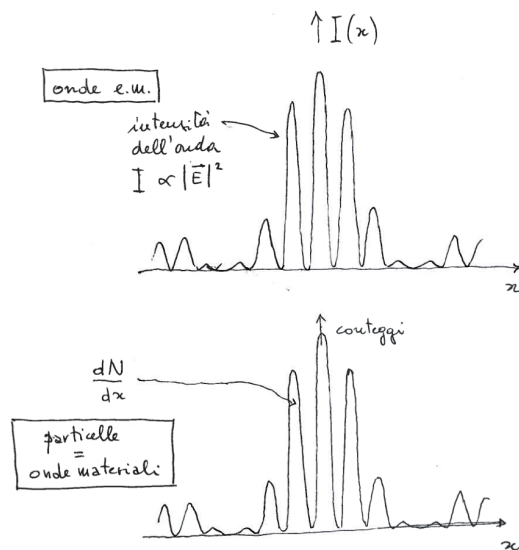
Figure 4.2: Interference patterns in experiments with light and with particles.

4.2   Heisenberg's uncertainty principle

The principle states that certain pairs of quantities cannot be measured simultaneously with arbitrary precision. Uncertainties are unavoidable, whatever the instrumental accuracy; the measurement of one quantity perturbs the status of the system, so that the accuracy of the measurement of the conjugated quantity is limited. In the following we indicate with Δf the uncertainty in the measurement of quantity f, defined as root mean square deviation of a sequence of measurements,

$$\Delta f = \sqrt{<f^2> - <f>^2},\tag{4.8}$$

where the brackets denote average values.

4.2.1   Position and momentum

In particular, the principle concerns measurements of a coordinate (e.g. x) and the homologous component of momentum (p_x). Heisenberg's uncertainty principle then states that in any case,

$$\boxed{\Delta x \ \Delta p_x \geq \frac{\hbar}{2}},\tag{4.9}$$

and analogously

$$\Delta y \ \Delta p_y \quad \geq \quad \frac{\hbar}{2},\tag{4.10}$$

$$\Delta z \ \Delta p_z \quad \geq \quad \frac{\hbar}{2},\tag{4.11}$$

where $\hbar = h/2\pi$ is the *reduced Planck constant* or, simply, *h bar*.

Justifications

The principle, as such, cannot be proved.[2] However it can be *justified* on the basis of arguments based on

1. the perturbation of the measurement of a quantity (e.g., p_x), induced by the measurement of the other quantity (x);

2. the localization of the wave-packet associated to a particle.

Such arguments lead to inequalities of the form $\Delta x \ \Delta p_x \approx h$ or $\Delta x \ \Delta p_x \approx \hbar$, qualitatively in agreement with Heisenberg's principle.

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[2]In Appendix C, we proof the principle using solutions of the Schrödinger equation. This requires having established (as a postulate) Schrödinger equation itself.

1. Uncertainties in a conceptual experiment
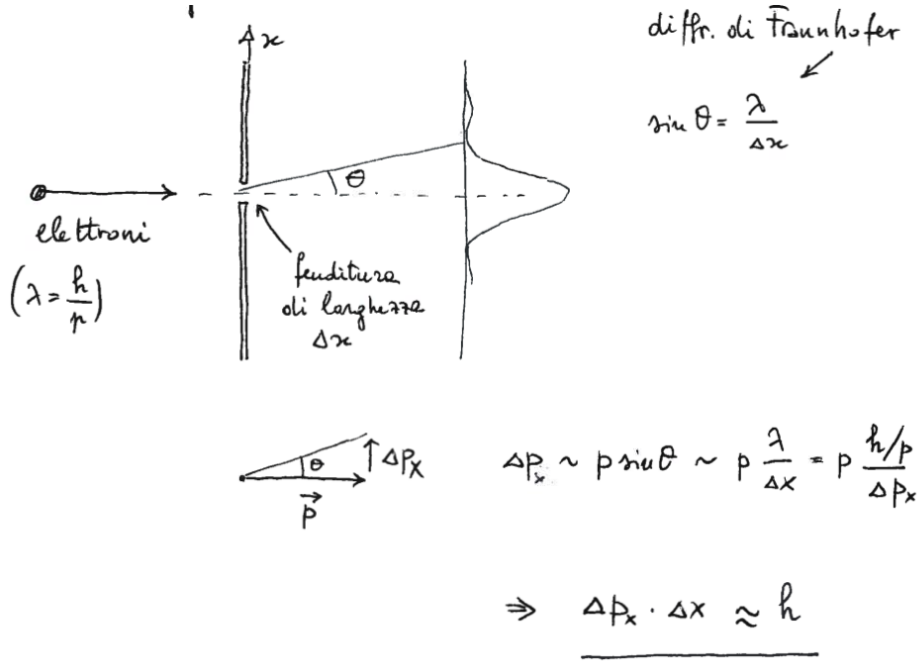
Figure 4.3: Uncertainties in a conceptual experiment for the measurement of position and momentum.

2. Wave packets and uncertainty
Let us consider a plane harmonic wave

$$\sim e^{i(kx-\omega t)}, \tag{4.12}$$

with wave number k and wavelength $\lambda = 2\pi/k$. Such a wave

- has exactly defined wavenumber and wavelength: $\Delta k = 0$

- occupies the whole space $-\infty \leq x \leq \infty$; hence $\Delta x = \infty$

A wave packet of reduced spatial extension (as a packet representing a particle), instead has a broad spectrum. Let us quantify the relation between spatial extension and spectral width. We can write such wave-packet as

$$\Psi(x,t) = \int_{-\infty}^{-\infty} g(k)e^{i(kx-\omega t)}dk, \tag{4.13}$$

with the k-spectrum $g(k)$ given by the Fourier transform of $\Psi(x,t)$ (actually,
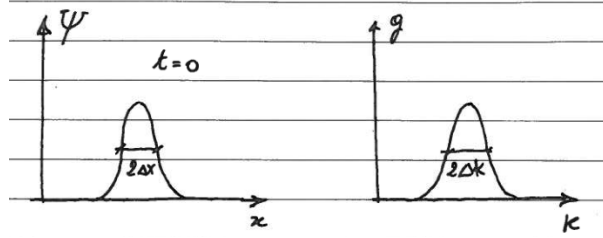
Figure 4.4: Wave-packet and its Fourier transform.

we take the transform at $t = 0$)

$$g(k) = \frac{1}{2\pi} \int_{-\infty}^{-\infty} \Psi(x,0)e^{-ikx}dx. \tag{4.14}$$

One can show that the widths of the two functions $\Psi(x,0)$ and $g(k)$ are related by $\Delta x \, \Delta k \geq 1$, with the equal sign applying when $\Psi(x,t)$ is Gaussian in x (see Appendix B). If we apply this inequality to a de Broglie wave, with $\lambda = h/p$ (and then $k = 2\pi p_x/h$, we find

$$\Delta x \, \Delta p_x \geq \hbar. \tag{4.15}$$

4.2.2   Energy and time

An uncertainty relation also applies to energy and time:

$$\boxed{\Delta E \, \Delta t \geq \hbar.} \tag{4.16}$$

In this case, however, E and t are not two variables to be measured simultaneously. Rather, Eq. (4.16) concerns the uncertainty of a measurement of energy and the characteristic time of change of the status of the system being measured. In principle such a time is the maximum length of the time interval during which we can perform the energy measurement.

Equation (4.16) is of great importance for all radioactive processes or, more in general, for all processes concerning excited states, with mean life τ. The energy of the excited level, and then the energy of the emitted particle or photon is affected by an uncertainty

$$\Delta E = \frac{\hbar}{\tau}. \tag{4.17}$$

This is the *natural width* of the emission line.

Chapter 5

Quantum Mechanics: Postulates and Schrödinger equation

Quantum mechanics is a coherent theory, incorporating a few concepts/principles that have been introduced in the previous chapters, namely

- **energy quantization**, $E = h\nu = \hbar\omega$;

- the principle of **complementarity** (particle - wave duality; $\vec{p} = \hbar\vec{k}$);

- the principle of **correspondence**:
  classical theory as the large quantum number limit of quantum theory;
  formal analogy between classical theory and quantum theory;

- the principle of **superposition**;

- following experiments on wave-like particles (e.g. electron diffraction) a **statistical interpretation** is required.

We now outline the process leading to the establishment of the Schrödinger equation as the fundamental equation of non-relativistic quantum mechanics.

5.1 Wavefunction and general properties of its evolution equation

- We **postulate** that a *physical system is fully described by its wavefunction.* For simplicity here we consider systems consisting of a single particle. Therefore the wavefunction will be a function $\Psi(\vec{r}, t)$ of particle position $\vec{r}$ and time t. In general, Ψ is a complex quantity.

- The equation describing the time-evolution of Ψ must be linear and homogeneous (for the superposition) and must be a differential equation of first order in t to guarantee the uniqueness of the solution for $t > t_0$, once $\Psi(\vec{r}, t_0)$ is known.

- We **postulate** that *we can associate a linear operator $\hat{A}$ acting on the wavefunction to any measurable physical quantity a (an observable).*

- For the principle of correspondence, the relations between quantum operators should be identical to the classical relations between the corresponding observables. For instance, if we indicate with $\hat{\vec{p}}$ and $\hat{E}$ the operators of momentum $\vec{p}$ and kinetic energy E, respectively, then

$$\hat{E} = \frac{\hat{p}^2}{2m}, \tag{5.1}$$

since classically $E = p^2/2m$.

5.2 Wave equation for a free particle

As a first step in the construction of an appropriate equation, we consider a wavefunction describing a free particle. In general, we should consider a wave packet of arbitrary shape, in three-dimensional space. However, to make treatment simpler (and relying, anyhow, on linearity, and hence on superposition), we consider a harmonic wavefunction in a one-dimensional space, i.e.

$$\Psi(x, t) = e^{i(kx - \omega t)}, \tag{5.2}$$

representing a free particle of momentum $p = \hbar k$ and energy $E = \hbar \omega$. We can therefore also write

$$\Psi(x, t) = e^{i(px - Et)/\hbar}. \tag{5.3}$$

Differentiating this expression with respect to x we obtain

$$\frac{\partial \Psi(x, t)}{\partial x} = i\frac{p}{\hbar} e^{i(px - Et)/\hbar} = i\frac{p}{\hbar} \Psi(x, t). \tag{5.4}$$

We can rewrite this last equation as

$$-i\hbar \frac{\partial \Psi(x, t)}{\partial x} = p\Psi(x, t), \tag{5.5}$$

which states that applying the operator $-i\hbar \frac{\partial}{\partial x}$ to Ψ we obtain the product of p times Ψ itself. Such a circumstance *suggests* us the expression of the operator of momentum. We **postulate**

$$\boxed{\hat{p}_x = -i\hbar \frac{\partial}{\partial x}.} \tag{5.6}$$

(We have added the index x because this is the operator of the x-component of the momentum.)

We now look for the evolution equation for the wavefunction of the considered free particle. We differentiate Eq. (5.4) again with respect to x:

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = -\frac{p^2}{\hbar^2} e^{i(px-Et)/\hbar} = -\frac{p^2}{\hbar^2} \Psi(x,t) = -\frac{2mE}{\hbar^2} \Psi(x,t). \tag{5.7}$$

On the other hand, by differentiating $\Psi(x,t)$ with respect to time we have

$$\frac{\partial \Psi(x,t)}{\partial t} = -i\frac{E}{\hbar} e^{i(px-Et)/\hbar} = -i\frac{E}{\hbar} \Psi(x,t). \tag{5.8}$$

By comparing Eq. (5.7) and Eq. (5.8) we obtain

$$i\hbar\frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2}. \tag{5.9}$$

We now observe that, for the correspondence principle and the definition of the momentum operator,

$$\hat{E} = \frac{\hat{p}_x^2}{2m} = \frac{1}{2m}\hat{p}_x(\hat{p}_x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}. \tag{5.10}$$

Equation (5.8) for the evolution of the wavefunction of a free particle can then be written as

$$i\hbar\frac{\partial \Psi(x,t)}{\partial t} = \hat{E}\Psi(x,t). \tag{5.11}$$

5.3 Time-dependent Schrödinger equation

In real problems, particles are subjected to (conservative) forces. In addition to kinetic energy we have to consider potential energy $V(x)$. We then **postulate** that *the evolution equation takes just the same form as Eq. (5.11), but with the kinetic energy operator replaced by the total energy operator* $\hat{H} = \hat{E} + \hat{V}$. We also **postulate** that the operator of the spatial coordinate x, is $\hat{x} = x$. We then write

$$\hat{H} = \frac{\hat{p}_x^{\,2}}{2m} + V(\hat{x}) = -\frac{h^2}{2m} \frac{\partial^2}{\partial x^2} + V(x). \tag{5.12}$$

The **time-dependent Schrödinger equation**, ruling the evolution of the wavefuntion $\Psi = \Psi(x,t)$ is then

$$\boxed{i\hbar\frac{\partial \Psi(x,t)}{\partial t} = \left[-\frac{h^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)\right]\Psi(x,t),} \tag{5.13}$$

or, more compactly,

$$\boxed{\boxed{i\hbar\frac{\partial \Psi}{\partial t} = \hat{H}\Psi(x,t).}} \tag{5.14}$$

5.4 Time-independent Schrödinger equation

For a particle in a stationary state, i.e. when the energy E is time-independent, the wavefunction $\Psi(x,t)$ has a well defined, time independent, angular frequency $\omega = E/\hbar$. We can then factorize the wavefunction as the product of the spatial part and of the time-dependent part, by writing

$$\Psi(x,t) = \psi(x)e^{-i\omega t} = \psi(x)e^{-iEt/\hbar}. \tag{5.15}$$

Inserting this expression into the time-dependent Schrödinger equation (5.14) we obtain

$$i\hbar\psi(x)\left(-i\frac{E}{\hbar}\right)e^{-iEt/\hbar} = \hat{H}\psi(x)e^{-iEt/\hbar}, \tag{5.16}$$

and then

$$\boxed{\hat{H}\psi = E\psi,} \tag{5.17}$$

or, writing the operator and the independent variable explicitly,

$$\boxed{\left[-\frac{h^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x) = E\psi(x).} \tag{5.18}$$

Equations (5.17) and (5.18) are two equivalent forms of the **1-D time-independent Schrödinger equation**.

Both time-dependent and time-independent Schrödinger equation are easily extended to three dimension, by the following replacements

$$\frac{\partial}{\partial x} \quad \rightarrow \quad \nabla = \left(\frac{\partial}{\partial x}; \frac{\partial}{\partial y}; \frac{\partial}{\partial z}\right) \tag{5.19}$$

$$\frac{\partial^2}{\partial x^2} \quad \rightarrow \quad \nabla^2 = \left(\frac{\partial^2}{\partial x^2}; \frac{\partial^2}{\partial y^2}; \frac{\partial^2}{\partial z^2}\right) \tag{5.20}$$

$$\Psi(x,t) \quad \rightarrow \quad \Psi(x,y,z,t) = \Psi(\vec{r},t) \tag{5.21}$$

$$\psi(x) \quad \rightarrow \quad \psi(x,y,z) = \psi(\vec{r}) \tag{5.22}$$

5.5 Interpretation of the wavefunction

So far, we have discussed the equation that rules the behaviour of the wavefunction, but we have not yet assigned any meaning to the wavefunction.

An interpretative *postulate* tells us that the quantity

$$|\Psi(x,y,z,t)^*\Psi(x,y,z,t)| \qquad (5.23)$$

is proportional to the probability density of the particle at time t, i.e. $|\Psi^*\Psi|dxdydz$ is proportional to the probability of finding the particle in an infinitesimal volume $dxdydz$ around (x,y,z) at time t.

In the following we will only consider time-independent problems. In such cases the probability density is proportional to

$$|\psi(x,y,z)^*\psi(x,y,z)|, \qquad (5.24)$$

independent of time.

5.6 Wavefunction normalization

Solution of the Schrödinger equation does not allow to determine a multiplying front factor. Such a factor is determined as follows. When the wavefunction represents a particle the probability to find the particle everywhere in space must be equal to 1. Therefore **the wavefunction is normalized** by requiring

$$\iiint_{\text{whole space}} |\psi(x,y,z)^*\psi(x,y,z)|dxdydz = 1. \qquad (5.25)$$

When the wavefunction is normalized the probability density $p(P)$ at point P(x,y,z) is

$$p(x,y,z,t) = |\Psi(x,y,z,t)^*\Psi(x,y,z,t)| \qquad (5.26)$$

If, instead, the wavefunction $\psi(x) = Ae^{ikx}$ represents a parallel beam of particles of mass m, with density n and velocity v, and hence current $J = nv$ (actually, current density, i.e. particles per unit surface per unit time)[1]

$$|A| = \sqrt{\frac{mJ}{\hbar k}}, \qquad (5.28)$$

as obtained by observing that $n = |\psi^*\psi| = A^2$, and $v = p/m = \hbar k/m$.

5.7 Eigenvalues and eigenfunctions

The time-independent Schrödinger equation is an eigenvalue equation: it admits solutions [eigenfunctions $\psi(\vec{r})$, corresponding to physical eigenstates] for certain

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[1]In general, the quantum mechanics probability current is

$$\vec{J} = -\frac{i\hbar}{2m}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right) \qquad (5.27)$$

values (eigenvalues) of E. Whether the eigenvalues have a continuous or a discrete spectrum depends on the form of the potential and on the boundary conditions. Typically, particles in finite size systems (such as electrons in atoms and nucleons in nuclei) are characterized by a discrete spectrum.

> One can show that the result of a measurement of an observable A can only be an eigenvalue a, satisfying the eigenvalue equation
>
> $$\hat{A}\psi(\vec{r}) = a\psi(\vec{r}). \tag{5.29}$$
>
> If a system is in an eigenstate ψ_n than the result of the measurement will be the corresponding eigenvalue a_n. If it is not in an eigenstate, the average value of a series of measurements is given by
>
> $$<A> = \frac{\iiint \Psi^* \hat{A}\Psi dx dy dz}{\iiint \Psi^* \Psi dx dy dz}. \tag{5.30}$$
>
> If the wavefunction is normalized, then
>
> $$<A> = \iiint \Psi^* \hat{A}\Psi dx dy dz. \tag{5.31}$$

5.8   Operators and commutators

We have already encountered the definitions of the operators of the x-components of position and momentum. The definitions of the other components are, of course, analogous, e.g.

$$\hat{y} = y \tag{5.32}$$

$$\hat{p}_y = -i\hbar \frac{\partial}{\partial y}. \tag{5.33}$$

The operators of all other quantities are constructed using the correspondence principle. We have already followed such a principle to write the kinetic energy and total energy operators. Another example is given by the operator of the z-component of the angular momentum:

$$\hat{l}_z = (\hat{\vec{r}} \times \hat{\vec{p}})_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right). \tag{5.34}$$

We have seen that according to the Heisenberg's uncertainty principle certain pairs of variables, such as, e.g., x and p_x, cannot be measured simultaneously with arbitrary precision. One can show that the operators of two observables, $\hat{A}$ and $\hat{B}$ which cannot be measured simultaneously do not commute, i.e.

$$\hat{A}(\hat{B}\psi) \neq \hat{B}(\hat{A}\psi)$$

or, in compact notation

$$[\hat{A}, \hat{B}] \neq 0,$$

where $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$. For instance,

$$[\hat{x}, \hat{p}_x] = i\hbar. \tag{5.35}$$

In general, in quantum mechanics one can measure simultaneously only observables with commuting operators.

One can easily verify that

$$[\hat{l}^2, \hat{l}_z] = [\hat{l}^2, \hat{H}] = [\hat{l}_z, \hat{H}] = [\hat{x}, \hat{H}] = 0, \tag{5.36}$$

while

$$[\hat{l}_x, \hat{l}_y] = i\hbar\hat{l}_z; \quad [\hat{l}_y, \hat{l}_z] = i\hbar\hat{l}_x; \quad [\hat{l}_z, \hat{l}_x] = i\hbar\hat{l}_y. \tag{5.37}$$

It is therefore possible to measure simultaneously energy and position, energy and single component of the angular momentum, energy and the modulus of the angular momentum. Instead, it is not possible to measure simultaneously two or three components of the angular momentum (unless they are all zero).

Chapter 6

Quantum Mechanics: One-dimensional problems

In this Chapter we will consider (time-independent) problems in one spatial dimension. We will only consider cases in which the potential energy $V(x)$ is piecewise constant. In such cases Schrödinger equation becomes

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\psi(x) = 0. \tag{6.1}$$

In the portion of the x domain where the potential energy takes the constant value V, the solutions of Eq. (6.1) take the form

$$\psi(x) = \begin{cases} A\sin kx + B\cos kx, & E > V, \\ A'e^{kx} + B'e^{-kx}, & E < V, \end{cases} \tag{6.2}$$

with

$$k = \sqrt{\frac{2m}{\hbar^2}|E - V|}. \tag{6.3}$$

The values of the constants appearing in Eq. (6.2) are determined according to the following *rules*:

- $\psi(x)$ must be everywhere finite, because $|\psi^*\psi| \propto$ probability density;

- $\psi(x)$ must be continuous, because the probability density must be continuous;

- $\psi'(x) = d\psi(x)/dx$ must be continuous, because otherwise ψ'', appearing in Eq. (5.18), would be undefined;

- $\psi = 0$ where $V = \infty$, because the product $V\psi$ must be finite everywhere.

In addition, the wavefunction has to be normalized as discussed in Sec. 5.6. In the next sections we shall use the above rules to deal with a few simple problems of great physical interest.

6.1   Infinite potential well
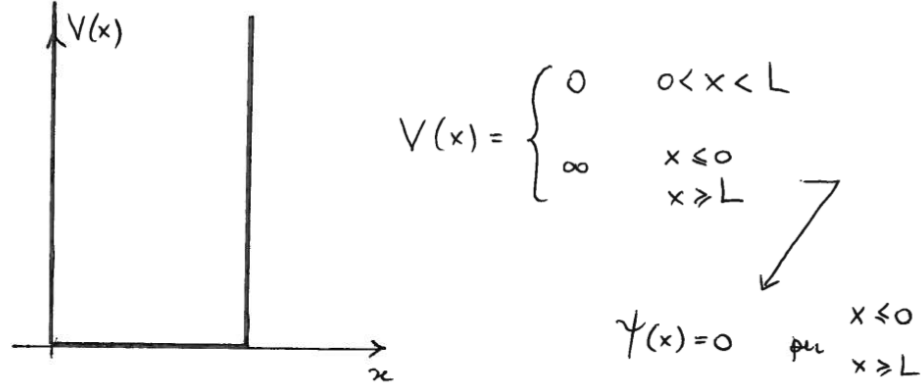
Figure 6.1: Infinite potential well of width L.

As a first problem we consider the so-called infinite well, in which potential energy is zero in a region $0 \leq x \leq L$ and is infinite elsewhere. Inside the well, $0 \leq x \leq L$, Schröedinger equation (6.1) becomes

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} E \psi(x) = 0, \tag{6.4}$$

to be solved with the boundary conditions

$$\psi(0) = \psi(L) = 0. \tag{6.5}$$

The general solution of Eq. (6.4) is

$$\psi(x) = A \sin kx + B \cos kx, \quad 0 \leq x \leq L, \tag{6.6}$$

with

$$k = \sqrt{\frac{2m}{\hbar^2} E}. \tag{6.7}$$

By imposing the boundary condition (6.5) at $x = 0$ we have $A \sin 0 + B \cos 0 = 0$, hence $B = 0$. The condition at $x = L$ reads

$$A \sin kL = 0, \tag{6.8}$$

which admits non-trivial solutions if kL is a integral multiple of π, i.e. $kL = n\pi$, with $n = 1, 2, \ldots$. It follows that k can only take values

$$k_n = n \frac{\pi}{L}, \tag{6.9}$$

with **quantum number** $n = 1, 2, \ldots$. The corresponding values of energy are

$$E_n = \frac{\hbar^2 k^2}{2m} = n^2 \frac{\pi^2 \hbar^2}{2mL^2}, \tag{6.10}$$

and the corresponding wavefunctions (eigenfunctions) are

$$\psi_n(x) = A_n \sin \frac{n\pi}{L} x. \tag{6.11}$$

Note that such eigenfunctions are just the standing waves on the interval $[0, L]$. (In fact the previous energy eigenvalues could have been simply found by imposing that the wavefunctions are standing waves with wavelength $\lambda_n = 2L/n$ and with momentum given by the de Broglie relation.)

The above result on the energy eigenvalues can be used for a rough estimate of atomic and nuclear energies. For an electron in an atom we set $m = m_e$ and L of the order of the Bohr radius r_0, for a nucleon in a nucleus, $m = m_p = 1836 m_e$ and L of the order of the nuclear radius $r_{\mathrm{n}} \approx 3 \times 10^{-5} r_0$. We then have nucleon energies of the order of MeV and

$$\frac{E_{nucleon}}{E_{electron}} \approx \frac{m_e r_0^2}{m_p r_{\mathrm{n}}^2} \approx 6 \times 10^5. \tag{6.12}$$

The normalization constant A_n in Eq. (6.11) is determined by imposing the normalization condition (5.25), i.e.

$$1 = \int_0^\infty |\psi^*(x)\psi(x)| dx = \int_0^L A_n^2 sin^2(k_n x) dx = A_n^2 \left(\frac{L}{n\pi}\right) \int_0^{n\pi} sin^2 y \, dy. \tag{6.13}$$

Using

$$\int_0^{n\pi} sin^2 y \, dy = \frac{n}{2} \int_0^{2\pi} sin^2 y \, dy = n\frac{\pi}{2}, \tag{6.14}$$

we obtain

$$A_n = \sqrt{\frac{2}{L}}, \tag{6.15}$$

independent of n. The shapes of the wavefunctions for $n = 1$–4 are shown in the left column of Fig. 6.2. The figure also shows the corresponding shapes of the probability density. It is apparent that the probability density is not uniform. The probability of finding the particle is an interval $[x, x + \Delta x]$ is therefore not uniform. However, as the quantum number n tends to infinite, then the probability of finding the particle in an interval Δx of finite size tends to a constant value, as in the classical case.
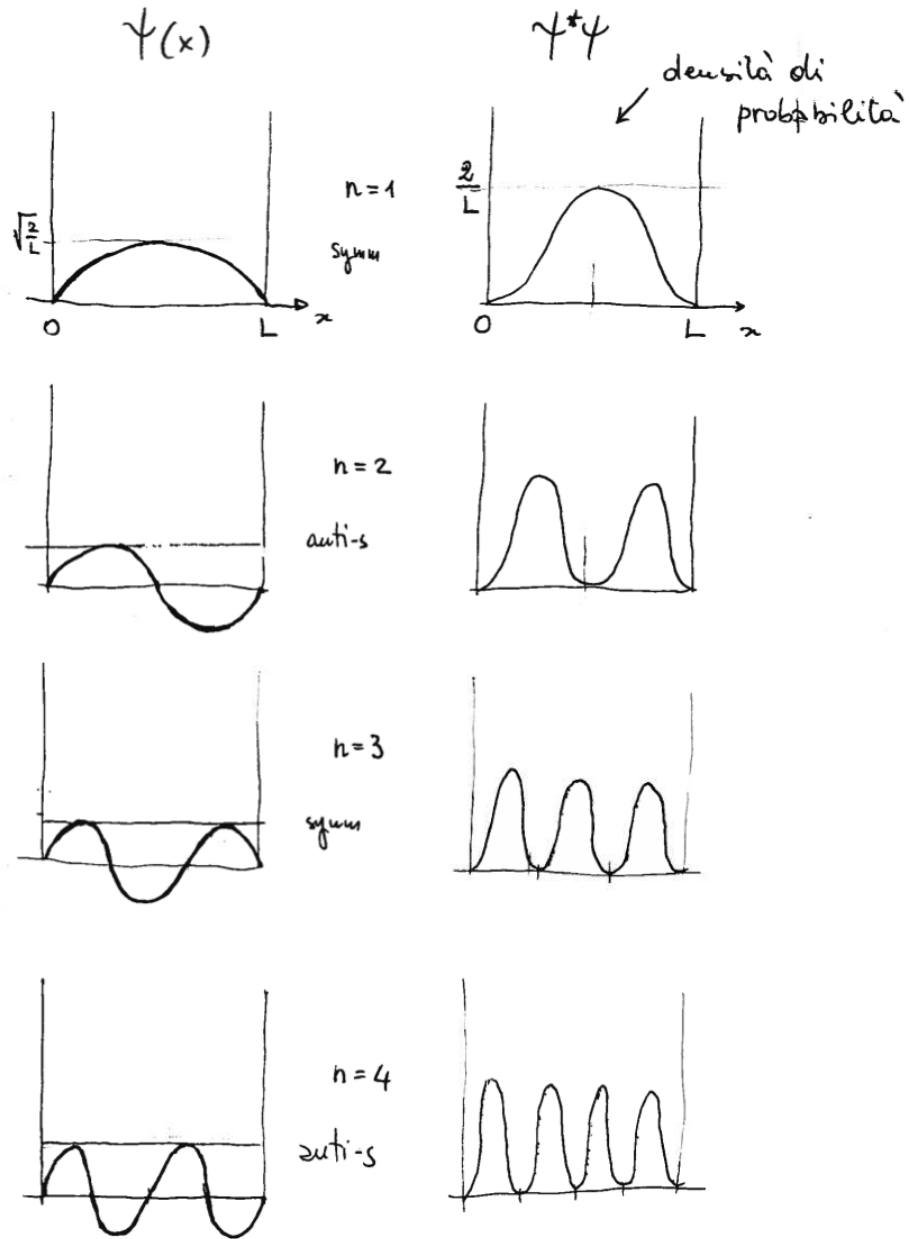
Figure 6.2: Infinite potential well: wavefunctions and probability density for the first four quantum numbers.

6.2 Finite potential well

We now refer to the symmetric potential well illustrated in Fig. 6.3, namely,

$$U(x) = \begin{cases} U_1 & x \leq 0 & \text{region 1} \\ 0 & 0 < x < L & \text{region 2} \\ U_1 & x \geq 0 & \text{region 3} \end{cases} \tag{6.16}$$
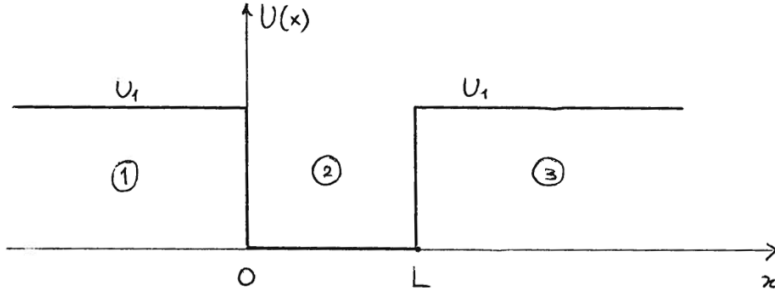
Figure 6.3: Finite, symmetric potential well.

We only consider the case $E < U_1$. In regions 1 and 3, Schrödinger equation can be written in the form

$$\frac{\partial^2 \psi(x)}{\partial x^2} - \chi^2 \psi(x) = 0, \tag{6.17}$$

with

$$\chi = \sqrt{\frac{2m(U_1 - E)}{\hbar^2}}, \tag{6.18}$$

and has solutions of the form

$$\psi(x) \sim e^{\pm \chi x} \tag{6.19}$$

Analogously, in region 2, the relevant equation becomes

$$\frac{\partial^2 \psi(x)}{\partial x^2} + k^2 \psi(x) = 0, \tag{6.20}$$

with

$$k = \sqrt{\frac{2mE}{\hbar^2}}, \tag{6.21}$$

and has solutions of the form

$$\psi(x) \sim \sin(kx + \delta). \tag{6.22}$$

By imposing that $\psi(x)$ be finite for any value of x we can write the general solution as

$$\psi(x) = \begin{cases} \psi_1(x) = A_1 e^{\chi x} & x \leq 0 \\ \psi_2(x) = A_2 \sin(kx + \delta) & 0 \leq x \leq L \\ \psi_3(x) = A_3 e^{-\chi x} & x \geq L. \end{cases} \tag{6.23}$$

Next, we impose continuity of the wavefunction and of its first derivative in $x = 0$ and in $x = L$:

$$\begin{array}{ccccccc} \psi_1(0) & = & \psi_2(0) & \rightarrow & A_1 & = & A_2 \sin \delta, \\ \psi_1'(0) & = & \psi_2'(0) & \rightarrow & A_1 \chi & = & A_2 k \cos \delta, \\ \psi_2(L) & = & \psi_3(L) & \rightarrow & A_2 \sin(kL + \delta) & = & A_3 e^{-\chi L}, \\ \psi_2'(L) & = & \psi_3'(L) & \rightarrow & A_2 k \cos(kL + \delta) & = & -A_3 \chi e^{-\chi L}. \end{array} \tag{6.24}$$

From the first two equations we obtain $\tan \delta = k/\chi$, or

$$\delta = \arctan \frac{k}{\chi} + m_1 \pi, \tag{6.25}$$

where m_1 is an integer number. Analogously, from the third and fourth equation (6.24), $\tan(kL + \delta) = -k/\chi$, and then

$$\delta = -kL - \arctan \frac{k}{\chi} + m_2 \pi, \tag{6.26}$$

with m_2 integer. By equating the right hand sides of Eq. (6.25) and Eq. (6.26), and setting $m_2 - m_1 = n$, we can write

$$n\pi - kL = 2 \arctan \frac{k}{\chi}, \tag{6.27}$$

with n an integer number. It is now convenient to express k and χ as functions of two new quantities, K and ξ

$$K = \sqrt{\frac{2mU_1}{\hbar^2}}, \tag{6.28}$$

$$\xi = \sqrt{\frac{E}{U_1}}, \tag{6.29}$$

so that

$$k = K\xi, \tag{6.30}$$

$$\chi = K\sqrt{1 - \xi^2}, \tag{6.31}$$

with $0 < \xi < 1$. We then have

$$\frac{k}{\chi} = \frac{\xi}{\sqrt{1 - \xi^2}}, \tag{6.32}$$
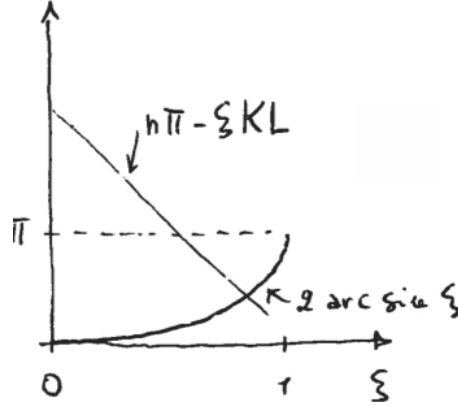
Figure 6.4: Graphical solution of Eq. (6.33).

and Eq. (6.27) becomes

$$n\pi - K\xi L = 2\arctan\frac{\xi}{\sqrt{1-\xi^2}} = 2\arcsin\xi. \tag{6.33}$$

We observe (see Fig. 6.4) that $2\arcsin\xi$ is an increasing function of ξ, with maximum value $\xi_{\max} = 1$; the quantity $n\pi - K\xi L$, instead, is a decreasing function of ξ. It follows that there are solutions $\xi_n = \xi(n)$ for integers n such that $n\pi - \xi_{\max}KL \le \pi$, i.e.

$$n = 0, 1, \dots, n_{\max} = \lfloor\frac{KL}{\pi} + 1\rfloor, \tag{6.34}$$

with corresponding energy eigenvalues

$$E_n = \xi_n^2 U_1; \qquad n = 0, 1, \dots, n_{\max} \tag{6.35}$$

Energy levels are quantized just as in the case of an infinite well, but **the number of *bound states* is finite**.

As an example, we consider an electron in a well with $U_1 = 250$ eV and $L = 0.1$ nm. In this case $K = 8.13 \times 10^{10}$ m^{-1}, $KL = 8.13$ and $n_{\max} = \lfloor\frac{KL}{\pi}+1\rfloor = 3$. The three values of ξ are the solutions of the equation

$$n\pi - 8.13\xi = 2\arcsin\xi,$$

which are easily found by the graphic construction shown in Fig. 6.5 or by a straightforward numerical solution. The figure also shows the three eigen-functions $\psi_n(x)$, ($n = 1, 2, 3$), obtained as follows. First, the unnormalized eigenfunction corresponding to the eigenvalue n (and then to ξ_n) is obtained by

using the continuity conditions (6.24). We have

$$
\begin{aligned}
\delta_n &= \arcsin \xi_n && (6.36)\\
A_{2,n} &= A_{1,n}/\sin \delta_n && (6.37)\\
A_{3,n} &= A_{2,n}e^{\chi_n L}\sin(k_n L + \delta_n) && (6.38)
\end{aligned}
$$

and then

$$
\psi_n(x) = \begin{cases}
A_{1,n}e^{\chi_n x} & x \leq 0 \\
[A_{1,n}/\sin \delta_n]\sin(k_n x + \delta_n) & 0 \leq x \leq L \\
[A_{1,n}\sin(k_n L + \delta_n)/\sin \delta_n]\,e^{-\chi_n(x-L)} & x \geq L
\end{cases} \qquad (6.39)
$$

Finally, each eigenfunction is normalized (and the coefficient $A_{1,n}$ is determined) by imposing the normalization condition

$$
\int_{-\infty}^{\infty} |\psi_n^*(x)\psi_n(x)|dx. \qquad (6.40)
$$

A new feature, in contrast with classical physics, is apparent from Eqs. (6.23) and (6.39): in regions 1 and 3, where the energy of the particle is smaller than the potential energy U_1 the wavefunction is different from zero, and therefore the probability density is not zero. The particle can therefore be found outside the well, with a probability

$$
p_{\text{out}} = 2\int_{-\infty}^{0} |\psi_n^*(x)\psi_n(x)|dx. \qquad (6.41)
$$

With lengthy but simple algebra, one finds

$$
p_{\text{out,n}} = \frac{\xi_n^3}{\xi_n^3 + (1 - \xi_n^2)^{1/2}\frac{1}{2}KL\xi_n + \frac{1}{4}\sin(KL\xi_n)}. \qquad (6.42)
$$

In the case of Fig. 6.6)we obtain $p_{\text{out,n}} = 0.0224; 0.089; 0.289$, for $n = 1; 2; 3$, respectively. The greater the eigenvalue, the greater the particle energy, the larger is the probability of finding the particle outside the potential well.

$$n\pi - 8.13\,\xi = 2\,\text{arc}\,\sin\xi$$

n	ξ_n	ξ_n^2	E
1	0.309	0.095	23.8 eV
2	0.61	0.37	93 eV
3	0.89	0.79	198 eV
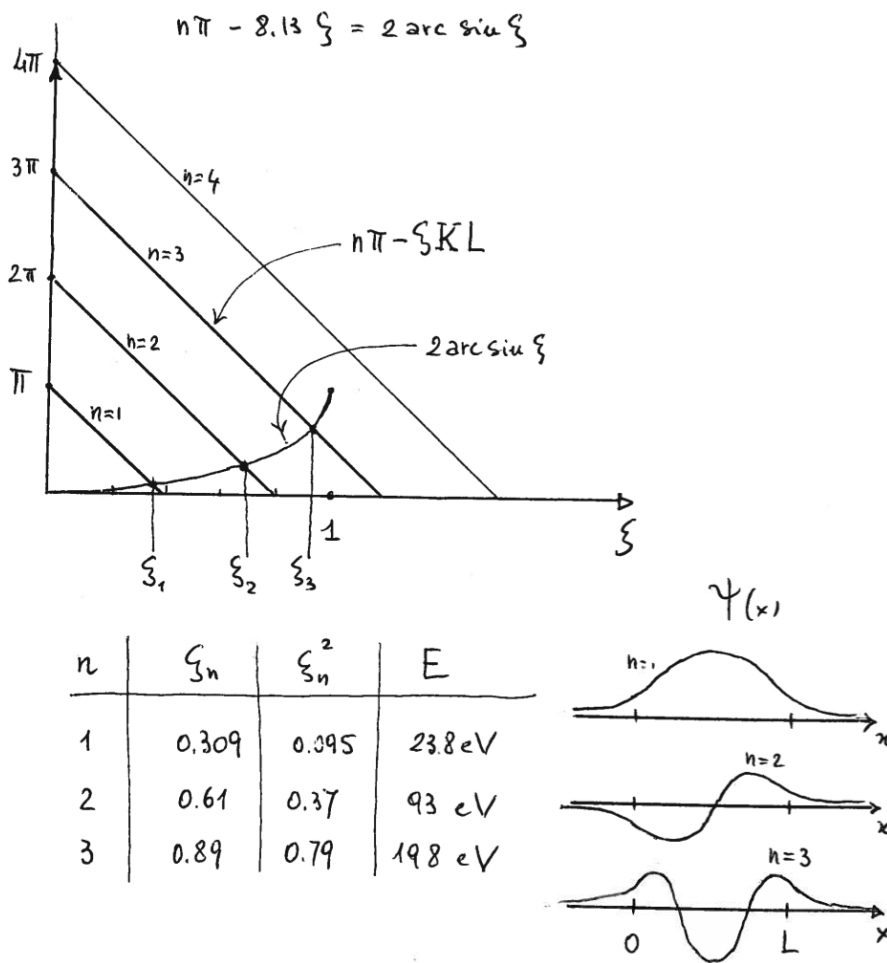
Figure 6.5: Example of a finite potential well: eigenvalues; quantized energy levels, wavefunctions.
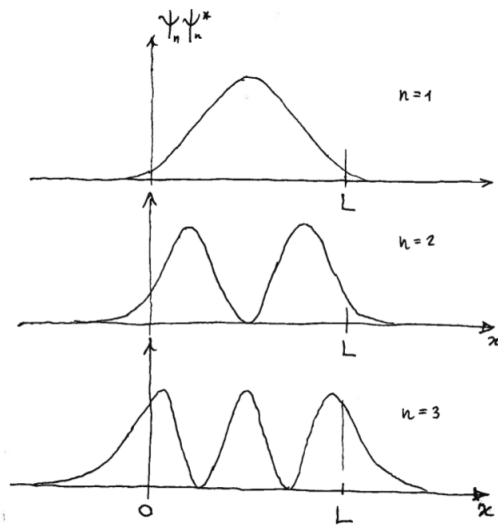
Figure 6.6: Probability densities for the three bound states of Fig. 6.5.

6.3   Potential step
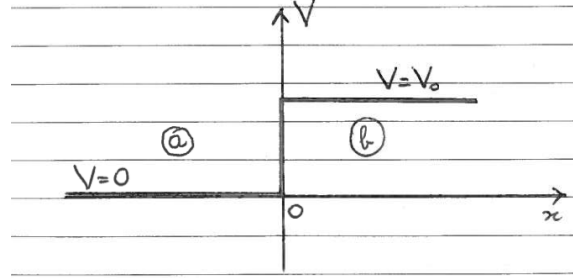
Figure 6.7: Potential step.

We now consider a potential step, as shown in Fig. 6.7. This is of course an idealized situation, describing particles which move everywhere freely, and are subjected to a force ($F = -dU/dx$) directed toward the left only near $x = 0$. We assume that particles approach the step coming from the left. Classically particles with energy $E = (1/2)mv^2 > V_0$ will proceed to the right hand side of the step, with lower velocity v_1, since, for energy conservation $(1/2)mv_1^2 = E - V_0$. Particles with energy $E < V_0$, instead do not have sufficient energy to overcome the step, and are reflected. So, classically we have total transmission for $E > V_0$ and total reflection for $E < V_0$.

In the quantum case, we have to solve Schrödinger equation

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m[E - V]}{\hbar^2}\psi(x) = 0 \tag{6.43}$$

in the two regions $x < 0$ (a), and $x > 0$ (b) and to properly match the solutions. The solutions in each region will be oscillating if $E > V$, exponential if $E < V$.

Notice that, unlike the previous problems, concerning particles inside a well, we are now dealing with beam of particles. In particular, incident particles (i.e. particles coming from the left hand side) are represented by progressive plane waves $\Psi(x, t) = \text{const} \times e^{i(kx - \omega t)}$. Since we are only considering time-independent problems, we are simply interested in the spatial part, and then we write

$$\text{incident wave}: \quad \psi(x) \quad \propto \quad e^{ikx}; \tag{6.44}$$

$$\text{reflected wave}: \quad \psi(x) \quad \propto \quad e^{-ikx}. \tag{6.45}$$

We now consider separately the cases $E > V_0$ and $E < V_0$.
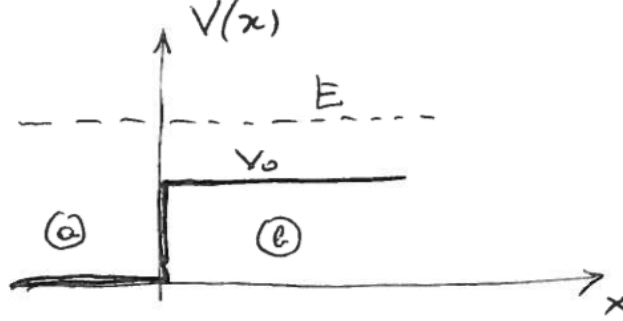
Figure 6.8: Potential step; case $E > V_0$.

6.3.1 $E > V_0$

In this case the solution is oscillating in both regions (a) and (b). The general solution has the form

$$
\begin{aligned}
\psi(x) = \psi_a(x) &= A e^{ik_a x} + B e^{-ik_a x}, \quad x < 0 \qquad (6.46)\\
\psi(x) = \psi_b(x) &= C e^{ik_b x} + D e^{-ik_b x}, \quad x > 0 \qquad (6.47)
\end{aligned}
$$

with

$$
k_a = \sqrt{\frac{2mE}{\hbar^2}} \qquad (6.48)
$$

$$
k_b = \sqrt{\frac{2m(E - V_0)}{\hbar^2}} = k_a \sqrt{1 - \frac{V_0}{E}}. \qquad (6.49)
$$

Since we are considering a wave-particle coming from $x < 0$, there cannot be a wave coming from the region $x > 0$, and then $D = 0$. The other three constants are related by the matching conditions at $x = 0$:

$$
\begin{aligned}
\psi_a(0) &= \psi_b(0) &&\rightarrow & A + B &= C, \\
\psi'_a(0) &= \psi'_b(0) &&\rightarrow & (A - B)k_a &= C k_b,
\end{aligned} \qquad (6.50)
$$

and then

$$
\frac{B}{A} = \frac{k_a - k_b}{k_a + k_b} = \frac{1 - k_b/k_a}{1 + k_b/k_a}, \qquad (6.51)
$$

$$
\frac{C}{A} = 1 + \frac{B}{A} = \frac{2}{1 + k_b/k_a}. \qquad (6.52)
$$

Surprisingly (at least if we were expecting the classical result), the incoming wave is partially reflected ($B \neq 0$) even when $E > V_0$: transmission is incomplete. Note, however, that the classical limit is approached as $E \gg V_0$. Indeed, in this limit $k_b/k_a \rightarrow 1$, and then $B \rightarrow 0$ and $C \rightarrow 1$.

Figure 6.9: Potential step; case $E > V_0$. Incoming and transmitted wavefunctions.

One may also be surprised that $C/A > 1$, i. e. the amplitude of the transmitted wave exceeds that of the incident wave, However, we have to recall that the wavefunctions in this case represent free particles, and the relevant physical quantity in our problems are particle currents. According to Eq. (5.28), incident and transmitted currents, are

$$J_a = A^2 \hbar k_a / m, \qquad (6.53)$$
$$J_c = C^2 \hbar k_b / m, \qquad (6.54)$$

respectively. The ratio of transmitted to incident current is then given by

$$\frac{J_c}{J_a} = \frac{4 k_b / k_a}{\left(1 + \dfrac{k_b}{k_a}\right)^2}, \qquad 0 < \frac{k_b}{k_a} < 1, \qquad (6.55)$$

which is always smaller than 1. Asymptotically, it approaches 1 in the classical limit.

Another limiting case is of particular interest, again with a surprising result. Let us consider a negative potential energy $V_0 < 0$ and incident particles with $E \ll |V_0|$ (see Fig. 6.10), i.e. a slow particle approaching a strongly attractive potential. In this case, $k_a \ll k_b$ and then, according to Eqs. (6.51 and (6.52)) we have

$$B \rightarrow -1 \qquad (6.56)$$
$$C \rightarrow 0 \qquad (6.57)$$

Contrary to classical physics, we have total reflection! Note that this highly idealized problem qualitatively describes the scattering of a low energy neutron by a nucleus.
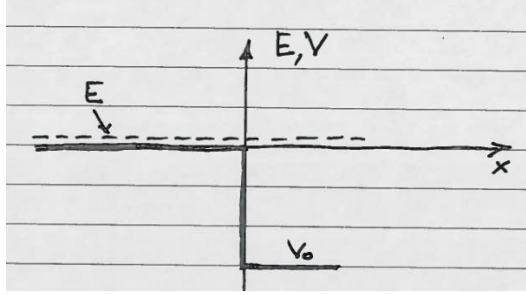
Figure 6.10: Potential step; case $E > V_0$, with $V_0 < 0$ and $E \ll -V_0$
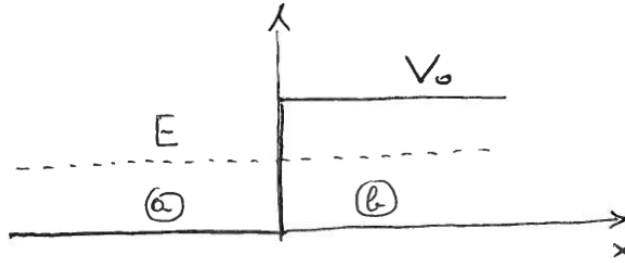
Figure 6.11: Potential step: case $E < V_0$

6.3.2 $E < V_0$

We proceed just as in the previous case. However, since now $E - V_0 < 0$ the general solution in region (b) is a combination of exponentials. We can write

$$\psi(x) = \psi_a(x) \quad = \quad Ae^{ik_a x} + Be^{-ik_a x}, \quad x < 0 \tag{6.58}$$
$$\psi(x) = \psi_b(x) \quad = \quad Ce^{-\chi x} + De^{\chi x}, \quad x > 0 \tag{6.59}$$

with

$$k_a \quad = \quad \sqrt{\frac{2mE}{\hbar^2}}, \tag{6.60}$$

$$\chi \quad = \quad \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}. \tag{6.61}$$

The coefficient $D = 0$ because $\psi(x)$ must be everywhere finite.

As usual, we impose the conditions of continuity of ψ and ψ' at $x = 0$:

$$\begin{array}{rclcrcl}
\psi_a(0) & = & \psi_b(0) & \rightarrow & A + B & = & C, \\
\psi_a'(0) & = & \psi_b'(0) & \rightarrow & i(A - B)k_a & = & -C\chi,
\end{array} \tag{6.62}$$
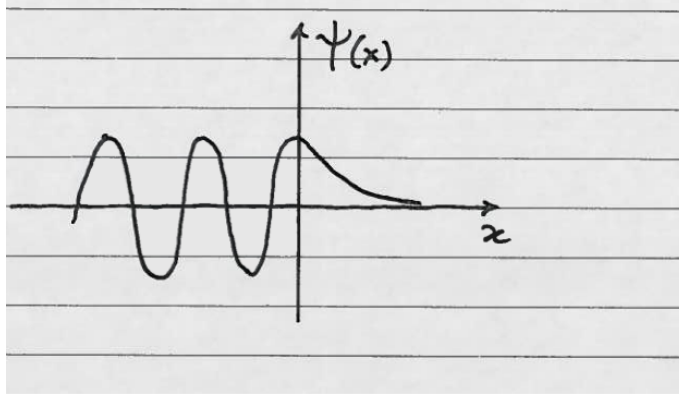
Figure 6.12: Wavefunction for the potential step, when $E < V_0$.

from which we obtain

$$\frac{B}{A} = \frac{1 - i\chi/k_a}{1 + i\chi/k_a}, \tag{6.63}$$

$$\frac{C}{A} = 1 + \frac{B}{A} = \frac{2}{1 + i\chi/k_a}. \tag{6.64}$$

We see that there is a finite probability P of finding the particle at $x > 0$ in the classically forbidden region (b). Indeed

$$\frac{P(x > 0)}{P(x = 0)} = \frac{|\psi^*(x)\psi(x)|}{|\psi^*(0)\psi(0)|} = \frac{|Ce^{-\chi x}|^2}{|A + B|^2} = e^{-2\chi x}. \tag{6.65}$$

6.4 Potential barrier and tunnel effect

We now consider a potential barrier of uniform height V and thickness L. According to the results of the previous section we expect that a particle coming from the left can be found at $x = L$ even if $E < V$, and can then propagate freely again in the region at the right hand side of the barrier. In quantum mechanics jargon we say the particle *tunnels* the barrier. The rigorous calculation of the probability of tunneling T, or penetrability of the barrier, requires solving the Schrödinger equation, matching the general solutions obtained in the regions on the left of the barrier, inside the barrier and at the right hand side of the barrier. The case $E < V_0$ is dealt with in Appendix F. The full treatment can be found in several textbooks.[1] However, when $\chi L \gg 1$ [with χ defined by

---

[1]see, e.g., Messiah, *Quantum Mechanics*, Wiley, (1966) or *Quantum Mechanics - Two volumes bound as one*, Dover Publ., (1999). The relevant solution also shows that even when the energy E is slightly greater than V_0 there is a finite probability of reflection. Of course, the classical limits, of full transparency and full reflection are recovered as $E \gg V_0$ and $E \ll V_0$ respectively.
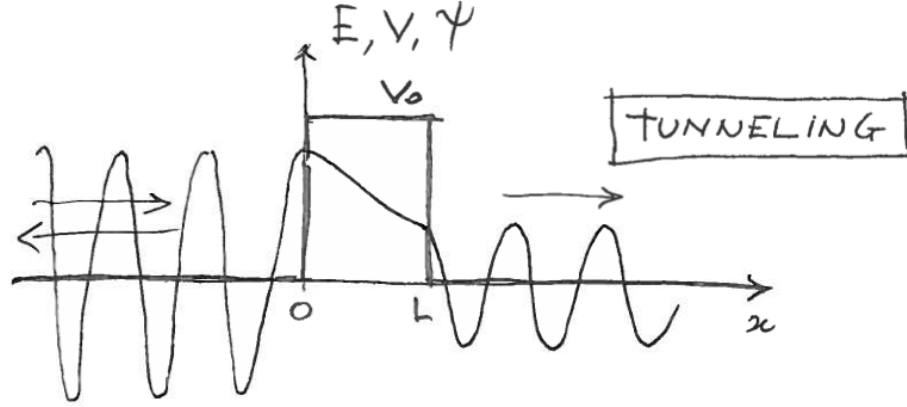
Figure 6.13: Potential barrier, with sketch of the wavefunction.

Eq. (6.61)], a reasonably accurate approximation is simply obtained by the ratio of the probability densities found for the potential step in the previous section at $x = L$ and $x = 0$, respectively,

$$T \simeq \left.\frac{P(x = L)}{P(x = 0)}\right|_{\text{step}} = \exp\left[-2\left(\frac{2m}{\hbar^2}\right)^{1/2}(V_0 - E)^{1/2}L\right] \qquad (6.66)$$

As an example, let us consider a barrier of $V_0 = 20$ MeV and width $L = 2.5 \times 10^{-14}$ m. The probability that an alpha-particle with energy $E = 5$ MeV is transmitted through the barrier is $e^{-85.3} \approx \times 10^{-38}$.

In practical cases the potential is varies in space, $V = V(r)$. In this case, theory shows that a good approximation of the barrier penetrability is obtained by still using Eq. (6.65), and replacing the argument of the exponential with an integral, according to[2]

$$-2\left(\frac{2m}{\hbar^2}\right)^{1/2}(V_0 - E)^{1/2}L \rightarrow -2\left(\frac{2m}{\hbar^2}\right)^{1/2}\int_{x_1}^{x_2}[V(x) - E]^{1/2}dx \qquad (6.67)$$

where x_1 and x_2 are lower and upper bound of the region to be tunneled.

The tunnel effect plays a central role in alpha decay and fusion reactions, and is at the basis of devices such as tunnel diode and Scanning Tunneling Microscope.

---

[2]This is the so-called WKB approximation, discussed in many books on mathematical physics or on quantum mechanics. A nice presentation, with both historical and pedagogical references, can be found in Wikipedia: http://en.wikipedia.org/wiki/WKB_approximation

Chapter 7

Elementary atomic physics

7.1 Operators in spherical coordinates

Atomic physics problems are most easily dealt with by using spherical coordinate systems. Such coordinates are indeed convenient when the potential has a central symmetry, i.e. is in the form $V(r)$, with r the distance from the centre of symmetry, as is the case of Coulomb potential. The use of spherical coordinates (r, θ, ϕ) is also convenient to deal with angular momentum. Spherical coordi-
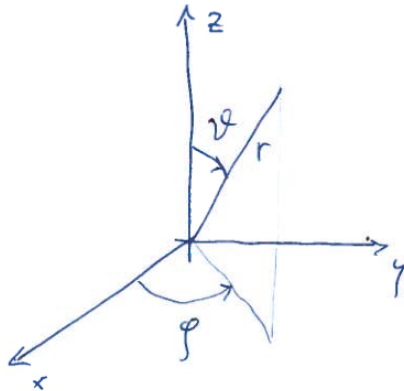
Figure 7.1: Sperical and Cartesian coordinates.

nates (r, θ, ϕ) are related to Cartesian coordinates (x, y, z) by (see Fig. 7.1)

$$
\begin{align}
r &= \sqrt{x^2 + y^2 + z^2}, \tag{7.1}\\
\theta &= \arctan \frac{\sqrt{x^2 + y^2}}{z}, \tag{7.2}\\
\phi &= \arctan \frac{y}{x}, \tag{7.3}
\end{align}
$$

and

$$x \;=\; r \sin\theta \cos\phi, \tag{7.4}$$
$$y \;=\; r \sin\theta \sin\phi, \tag{7.5}$$
$$z \;=\; r \cos\theta. \tag{7.6}$$

The expressions of the operators in spherical coordinates are obtained from those in Cartesian coordinates by using Eqs. (7.4)-(7.6) and writing the derivatives using chain rules as

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z}\frac{\partial}{\partial \phi}. \tag{7.7}$$

Before solving Schrödinger equation with a Coulomb potential, we consider angular momentum. Expressions of the angular momentum operators in spherical coordinates are derived in Appendix D.

7.2   Angular momentum, z-component

Let us consider the operator of the $z-$component of angular momentum

$$\hat{l}_z = (\hat{\vec{r}} \times \hat{\vec{p}})_z = \hat{x} \times \hat{p_y} - \hat{y} \times \hat{p_x} = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}). \tag{7.8}$$

Its expression in spherical coordinates is

$$\hat{l}_z = -i\hbar\frac{\partial}{\partial \phi}, \tag{7.9}$$

as shown in Appendix D.

The possible values of the z-component of the angular momentum are obtained by solving the operator equation

$$\hat{l}_z\psi(r,\theta,\phi) = l_z\psi(r,\theta,\phi), \tag{7.10}$$

or

$$-i\hbar\frac{\partial\psi(\phi)}{\partial\phi} = l_z\psi(\phi), \tag{7.11}$$

which has solutions

$$\psi(\phi) = \text{const } e^{i(l_z/\hbar)\phi}. \tag{7.12}$$

Imposing the the boundary condition

$$\psi(\phi) = \psi(\phi + 2\pi), \tag{7.13}$$

we find that $l_z/\hbar$ must be an integer.[1] Therefore the z-**component of the angular momentum is quantized**. It can take the values

$$l_z = \hbar m, \quad m = 0, \pm 1, \pm 2, \ldots . \tag{7.16}$$

For historical reasons, this quantum number m is called *magnetic quantum number*. The corresponding eigenfunctions are

$$\psi(\phi) = \text{const } e^{im\phi}. \tag{7.17}$$

7.3 Total angular momentum

We have seen in Sec. 5.8 that we cannot measure two components of the angular momentum simultaneously. Instead, we can measure one component (e.g. the $z-$component) and the square of the modulus, which has operator

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_z^2 + \hat{l}_z^2, \tag{7.18}$$

or, in spherical coordinates,

$$\hat{l}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]. \tag{7.19}$$

We then have to solve the eigenvalue equation

$$\hat{l}^2 Y(\theta, \phi) = l^2 Y(\theta, \phi), \tag{7.20}$$

with eigenvalues l^2 and eigenfunctions Y. We solve Eq. (7.20) by separation of variables, i.e. we factorize the wavefunction as the product of a function of θ and a function of ϕ

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi). \tag{7.21}$$

We substitute this last expression into Eq. (7.20) and multiply by $-\sin^2\theta/(\Theta(\theta)\Phi(\phi))$. We also set

$$l^2 = \hbar^2 \beta, \tag{7.22}$$

where β is a dimensionless quantity, and obtain

$$\underbrace{\frac{\sin\theta}{\Theta(\theta)} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta(\theta)}{\partial\theta} \right) + \beta \sin^2\theta}_{\text{function of } \theta \text{ only}} = - \underbrace{\frac{1}{\Phi(\phi)} \frac{\partial^2\Phi(\phi)}{\partial\phi^2}}_{\text{function of } \phi \text{ only}} . \tag{7.23}$$

---

[1]Equation (7.13) can be written

$$e^{i(l_z/\hbar)\phi} = e^{i(l_z/\hbar)(\phi+2\pi)}. \tag{7.14}$$

Dividing both members by $e^{i(l_z/\hbar)\phi}$, we obtain

$$1 = e^{2\pi i(l_z/\hbar)}, \tag{7.15}$$

which is satisfied if $l_z/\hbar$ is $0, \pm 1, \pm 2, \ldots$

We observe that the left hand side of this equation depends only on θ, while the right hand side only on ϕ. Since the equality holds for any value of θ and ϕ, the two sides have both to be constant, and then equal to the same constant, which we call $(m^*)^2$. We can then write two separate ordinary differential equations

$$-\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2} \;\; = \;\; (m^*)^2, \tag{7.24}$$

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right) + \beta\sin^2\theta \;\; = \;\; (m^*)^2. \tag{7.25}$$

We first consider Eq. (7.24), which has solution

$$\Phi(\phi) = \text{const }e^{im^*\phi}. \tag{7.26}$$

This is just the same solution found in the previous section for the wavefunction of the z-component of the angular momentum [Eq. (7.17)]. We recognize that $m^* = m$, with m the magnetic quantum number, and then

$$\Phi(\phi) = \text{const }e^{im\phi} \tag{7.27}$$

We now consider the equation for Θ. Multiplying Eq. (7.25) by $\Theta(\theta)/\sin^2\theta$ we have

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right) + \beta\Theta(\theta) - \frac{m^2\Theta(\theta)}{\sin^2\theta} = 0. \tag{7.28}$$

Next, we set $w = \cos\theta$ and call $\Theta(\theta) = P(w)$ and obtain

$$\frac{d}{dw}\left[(1-w^2)\frac{dP(w)}{dw}\right] + \left(\beta - \frac{m^2}{1-w^2}\right)P(w) = 0. \tag{7.29}$$

The solution of this equation is rather long and requires considerable manipulations. It can be found in most textbooks on quantum mechanics. Here we simply report and discuss the solution.[2]. It is found that the solution $P(w)$ is everywhere finite only for

$$\beta = l(l+1), \quad l = 0, 1, 2, \ldots \quad \text{and } l \geq |m|. \tag{7.30}$$

The eigenvalues of $\hat{l}^2$ are then $\hbar^2 l(l+1)$, and the angular momentum is quantized:

$$\boxed{|\vec{l}| = \hbar\sqrt{l(l+1)}} \tag{7.31}$$

The relation between angular momentum and the possible values of its z-component are illustrated by the diagram of Fig. 7.2.

The angular momentum eigenfunctions are the associated Legendre polynomials $P_l^{|m|}(w)$ defined by

$$P_l^{|m|}(w) = (1-w^2)^{|m|/2}\left(\frac{d}{dw}\right)^{|m|}P_l(w), \tag{7.32}$$

---

[2]The solution procedure is analogous to that for the radial equation of the Hydrogen atom, which we will describe in detail later
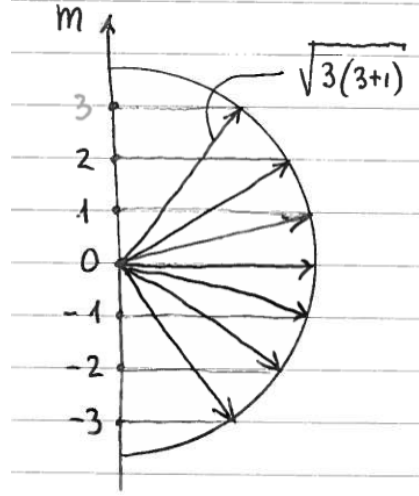
Figure 7.2: The *angular momentum diagram* for angular quantum number $l = 3$

where P_l is the Legendre Polynomial of order l,

$$P_l(w) = \frac{1}{2^l l!} \left(\frac{d}{dw}\right)^l (w^2 - 1)^l. \tag{7.33}$$

The normalized angular momentum wavefunctions turn out to be

$$Y(\theta, \phi) = Y_l^m(\theta, \phi) = \Theta_l(\theta)\Phi(\phi) = A_{l,m} P_l^{|m|}(\cos\theta)e^{im\phi}, \tag{7.34}$$

with normalization constants

$$A_{l,m} = i^l \left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} \times \begin{cases} (-1)^m & m > 0 \\ 1 & m \leq 0 \end{cases} \tag{7.35}$$

Note that when $m = 0$, $P_l^m(w) = P_l^0(w) = P_l(w)$. The expressions of the first four Legendre polynmials are as follows

$$P_0 \quad = \quad 1 \tag{7.36}$$
$$P_1 \quad = \quad \cos\theta \tag{7.37}$$
$$P_2 \quad = \quad \frac{1}{2}(3\cos^2\theta - 1) \tag{7.38}$$
$$P_3 \quad = \quad \frac{1}{2}(5\cos^3\theta - 3\cos\theta) \tag{7.39}$$

The $l = 0$ eigenfunction is therefore spherically symmetric.

7.4   Angular momentum and parity

Electron wavefunctions in atoms, as well as nucleon wafefunctions in nuclei, are also characterized by their *parity*, a property which has no classical analogue. Parity concerns coordinate reflection about the origin

$$x \to x' = -x; \quad y \to y' = -y; \quad , z \to z' = -z. \tag{7.40}$$

One can show that when the potential is not changed by such a reflection of coordinates [as in the case of a spherical potential $V(r)$, or a 1-D potential for which $V(x) = V(-x)$] then the solutions (eigenfunctions) of the Schrödinger equation are either symmetric $\psi(\vec{x}) = \psi(\vec{x}')$ or anti-symmetric $\psi(\vec{x}) = -\psi(-\vec{x}')$. In the first case we say that the eigenfunction has positive parity ($\Pi = 1$), in the second case it has negative parity ($\Pi = -1$).

Parity is an important property because **the total parity of a system** (i.e. the product of the parities of all its components) **is conserved in electromagnetic and strong nuclear interactions**. (It is not necessarily conserved in the weak interactions responsible, e.g. of beta-deacy.)

It is useful to consider the parity Π_l of angular momentum wavefunctions, because it enters in the determination of the so-called selection rules, ruling possible (and forbidden) atomic transitions. It is found that Π_l is only determined by the angular quantum number l:[3]

$$\boxed{\Pi_l = (-1)^l.} \tag{7.45}$$

---

[3]The proof is the following. When the coordinates are reflected according to Eq. (7.40), the polar coordinates change as

$$r \to r' = r; \quad \theta \to \theta' = \pi - \theta; \quad \phi \to \phi' = \phi + \pi. \tag{7.41}$$

Then, aside from normalization constants,

$$
\begin{aligned}
Y(\theta', \phi') = Y_l^m(\theta', \phi') &= P_l^{|m|}(\cos(\pi - \theta)e^{im(\phi+\pi)} \tag{7.42} \\
&= \left[(-1)^{|m|-l} P_l^{|m|}(-\cos\theta) \right] e^{im\phi}(-1)^l \tag{7.43}
\end{aligned}
$$

We also observe that the associate Legendre polynomials $P_l^m(x)$ appearing in the angular momentum eigenfunctions Y_l^m (see Eq. [7.34]) are polynomials of even powers of x (and then symmetric in x) if $l - |m|$ is even, while are polynomials of odd powers of x (and then antisymmetric in x) if $l - |m|$ is odd. Hence the term in square brackets is simply equal to $P_l^{|m|}(\cos\theta)$. It follows that

$$Y_l^m(\theta', \phi') = (-1)^l P_l^{|m|}(\cos\theta)e^{im\phi} = (-1)^l Y_l^m(\theta, \phi). \tag{7.44}$$

7.5 Schrödinger equation for the hydrogen atom

We now consider a Hydrogen atom, i.e. the motion an electron in the field of a proton. We determine the energy levels by solving Schrödinger equation

$$\nabla^2 \psi(r,\theta,\phi) + \frac{2\mu}{\hbar^2}\left[E - V(r)\right]\psi(r,\theta,\phi) = 0, \tag{7.46}$$

where

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{7.47}$$

and

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}, \tag{7.48}$$

Here r is the distance of the electron from the nucleus, μ is the reduced mass of the electron in the Hydrogen atom, $\mu = m_e m_p/(m_e + m_p)$, and m_e and m_p are the electron and proton mass, respectively.

Observing that the term in square brackets in Eq. (7.47) is just equal to $-\hat{l}^2/\hbar^2$ [see Eq. (7.19)], we can write Eq. (7.46)] as [4]

$$\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{r^2}\frac{\hat{l}^2}{\hbar^2} + \frac{2\mu}{\hbar^2}\left[E - V(r)\right]\right\}\psi(r,\theta,\phi) = 0. \tag{7.49}$$

Furthermore, in the previous section we have found that

$$\hat{l}^2 Y(\theta,\phi) = \hbar^2 l(l+1)Y(\theta,\phi). \tag{7.50}$$

We also notice that while the angular momentum term depends on θ and ϕ, the other terms only depend on the radial variable r. This suggests to factorize

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi), \tag{7.51}$$

where $R(r)$ is a function depending on r only, and $Y(\theta,\phi)$ is the momentum eigenfunction discussed in the previous section. Substituting Eq. (7.51) and Eq. (7.50) in Eq. (7.49), and multiplying by r^2/Y we have

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) + \frac{2\mu r^2}{\hbar^2}\left[E - V(r)\right]R(r) - l(l+1)R(r) = 0. \tag{7.52}$$

Since we have obtained an equation in the single variable r we can replace partial derivatives with ordinary derivatives. To proceed further, we note that

$$\frac{d}{dr}\left(r^2\frac{d}{dr}\right) = r^2\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right). \tag{7.53}$$

---

[4]Note that ∇^2 can be written in a slightly different form, using the identity

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = \frac{1}{r}\frac{\partial^2(r\psi)}{\partial r^2}$$

We substitute this expression into Eq. (7.52) and divide by r^2, to obtain

$$\left\{\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + \frac{2\mu}{\hbar^2}\left[E - V(r)\right] - \frac{l(l+1)}{r^2}\right\} R(r) = 0 \qquad (7.54)$$

Note that this last equation can also be written as

$$\left\{\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + \frac{2\mu}{\hbar^2}\left[E - V_{\text{eff}}(r)\right]\right\} R(r) = 0 \qquad (7.55)$$

with an effective potential equal to the sum of the potential of the central force and a centrifugal potential due to the angular momentum.[5]

$$V_{\text{eff}}(r) = V(r) + \frac{l(l+1)\hbar^2}{2\mu r^2} \qquad (7.58)$$

We write r in units of Bohr radius r_0 [Eq. (3.3)] and E in units of first Bohr's energy level E_0 [Eq. (3.4)], i.e.

$$r = \rho r_0, \qquad r_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}, \qquad (7.59)$$

$$E = \varepsilon E_0, \qquad E_0 = -\frac{1}{2}\frac{\mu e^4}{(4\pi\varepsilon_0)^2\hbar^2}, \qquad (7.60)$$

and use Eq. (7.48) for the potential energy. Equation (7.54) becomes

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} - \varepsilon + \frac{2}{\rho} - \frac{l(l+1)}{\rho^2}\right] R(r) = 0, \qquad (7.61)$$

which cannot be solved in closed form.

However, we can easily study the limiting cases for $\rho \to \infty$ and $\rho \to 0$, respectively. As $\rho \to \infty$ Eq. (7.61) reduces to

$$\left(\frac{d^2}{d\rho^2} - \varepsilon\right) R(r) = 0, \qquad (7.62)$$

which has solutions $R \sim e^{\pm\rho\sqrt{\varepsilon}}$. The solution with the plus sign has to be discarded because it diverges for large ρ. We are then left with

$$R(\rho) \sim e^{-\rho\sqrt{\varepsilon}} = R_{(\infty)}(\rho), \qquad (7.63)$$

---

[5]It is also interesting to observe that at large distance from the nucleus, where one can neglect both the Coulomb potential and the centrifugal potential, Schrödinger equation becomes

$$\frac{\partial^2}{\partial r^2}(rR) + \frac{2\mu E}{\hbar^2}rR = 0, \qquad (7.56)$$

with solutions

$$R(r) \sim \frac{e^{\pm ikr}}{r}, \qquad k = (2\mu E/\hbar)^{1/2} \qquad (7.57)$$

i. e. a combination of in-going and out-going spherical waves.

In the limit $\rho \to 0$, we instead have

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} - \frac{l(l+1)}{\rho^2} \right] R(r) = 0. \tag{7.64}$$

We look for a solution of the form $R \sim \rho^b$. By Substituting this last expression into Eq. (7.64) we have

$$b(b+1) = l(l+1),$$

which has solutions $b = l$ and $b = -l - 1$. Discarding the solution ρ^{-l-1}, that diverges in the origin, we are left with

$$R(\rho) \sim \rho^l = R_{(0)}(\rho). \tag{7.65}$$

Now, we notice that the product of the solutions $R_{(0)}(\rho)R_{(\infty)}(\rho)$ still has the correct behaviour in both limits. We therefore search a solution, valid everywhere, in the form

$$R(\rho) = R_{(0)}(\rho)R_{(\infty)}(\rho)f(\rho) = \rho^l e^{-\rho\sqrt{\varepsilon}} f(\rho), \tag{7.66}$$

where $f(\rho)$ is a function to be determined.

We substitute Eq. (7.66) for R in Eq. (7.61). Lengthy, but elementary algebra (detailed in Appendix E) leads to the equation

$$\frac{d^2 f}{d\rho^2} + \left[\frac{2(l+1)}{\rho} - 2\sqrt{\varepsilon} \right] \frac{df}{d\rho} + \frac{2}{\rho} \left[1 - \sqrt{\varepsilon}(l+1) \right] f = 0 \tag{7.67}$$

We assume $f(\rho)$ can be written as a series of powers of ρ or, better, of $x = 2\sqrt{\varepsilon}\rho$,

$$f(\rho) = \sum_{i=0}^{\infty} a_i x^i, \tag{7.68}$$

and then substitute

$$R(\rho) = e^{-x/2} R(x/2\sqrt{\varepsilon}) \sum_{i=0}^{\infty} a_i x^i, \tag{7.69}$$

into Eq. (7.61). Again with lengthy algebra (see Appendix E), we find that the coefficients a_i satisfy the recurrence relation

$$a_{i+1} = a_i \frac{i + l + 1 - (1/\sqrt{\varepsilon})}{(i+1)(i+2l+1)}. \tag{7.70}$$

The series so obtained diverges, because $a_{i+1} \to a_i/i$, for large i, and then $f(\rho) \sim e^\rho$. Since the solution has to remain finite, the series must terminate, i.e. $f(\rho)$ must be a polynomial of finite order σ, which occurs if $a_{\sigma+1} = 0$. From Eq. (7.70) we see that this requires

$$\sigma + l + 1 - \frac{1}{\sqrt{\varepsilon}} = 0, \tag{7.71}$$

with σ and l non negative integers ($\sigma = 0, 1, 2, \ldots$) It follows that $1/\sqrt{\varepsilon}$ **must be a positive integer** $n = 1, 2, \ldots$ (the **principal quantum number**). The electron energy $E = \varepsilon E_0$ can then only take the discrete values

$$\boxed{E(n) = E_n = \frac{E_0}{n^2}, \quad n = 1, 2, \ldots} \tag{7.72}$$

in agreement with Bohr's model. Notice that the energy levels only depend on n.[6]

From Eq. (7.71), which can now be written as $\sigma + l + 1 - n = 0$, we also see that $l = n - \sigma - 1$, and then

$$\boxed{l = 0, 1, 2, \ldots, n - 1.} \tag{7.73}$$

The radial eigenfunction then is

$$R_{nl}(\rho) = \rho^l e^{-\rho/n} \sum_{i=0}^{\sigma} a_i \left(\frac{2}{n}\right)^i \rho^i, \tag{7.74}$$

with $l = 0, 1, \ldots, n - 1$ and $\sigma = n - l - 1 = 0, 1, \ldots$, and the wavefunction is

$$\boxed{\Psi(r, \theta, \phi) = \Psi_{nlm} = A_{nlm} R_{nl}(\rho) P_l^{|m|}(\cos\theta) e^{im\phi}}. \tag{7.75}$$

For the fundamental state of the hydrogen atom, $n = 1$ (and then $l = \sigma = m = 0$), we have

$$\psi(r, \theta, \phi) = \psi(r) = A_{n00} e^{-\rho} = \text{const } e^{-r/r_0} \tag{7.76}$$

Exercise: For the fundamental state of the Hydrogen atom $(n, l, m) = (1, 0, 0)$, find the normalization constant and the radius $r_{\max}$ at which the probability density of finding the electron is maximum. [Answers: $A_{1,0,0} = 1/\sqrt{\pi a_0^3}$ and $r_{\max} = a_0$, with a_0 the Bohr's radius.]

The spatial distributions of the probability density of the (electron in the) hydrogen atom are shown in Fig. 7.3.

---

[6]This is the case for Hydrogen only, and in absence of a magnetic field. The energy levels of all other atoms also depend on the angular momentum.
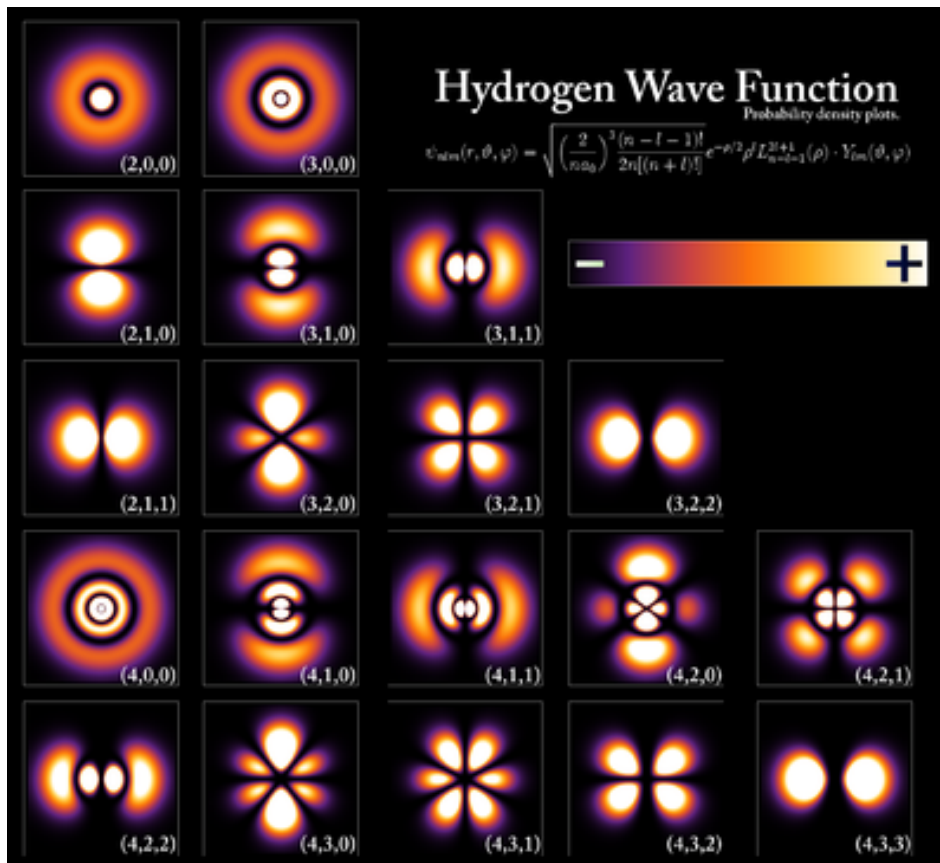
Figure 7.3: False colour probability density plots of the Hydrogen wavefunctions; from http://en.wikipedia.org/wiki/Wave_function

7.6 Spin and *Exclusion principle*

In addition to (rest) mass and electric charge, elementary particles possess another intrinsic property: spin or intrinsic angular momentum. Spin is represented by vector **S**, of magnitude

$$S = \sqrt{s(s+1)}\hbar, \tag{7.77}$$

where s, usually simply referred to as *spin*, is a non-negative, integer or semi-integer number. The projection S_z of the vector **S** along an axis z is

$$S_z = m_s\hbar, \tag{7.78}$$

with m_s the spin quantum number, which can take $2s + 1$ (integer or semi-integer) values $-s, -s + 1, \ldots, s - 1, s$. In particular

$$
\begin{aligned}
s = 0 \quad &=> \quad m_s = 0 \\
s = \frac{1}{2} \quad &=> \quad m_s = -\frac{1}{2}; \frac{1}{2} \\
s = 1 \quad &=> \quad m_s = -1; 0; 1 \\
s = \frac{3}{2} \quad &=> \quad m_s = -\frac{3}{2}; -\frac{1}{2}; \frac{1}{2}; \frac{3}{2}
\end{aligned}
$$

Particles with **semi-integer spin** are called **fermions** [7]

Particles with **integer spin** are called **bosons** [8]

Fermions

- electron, proton, neutron, neutrino (all with $s = 1/2$)

- ...

- systems with an odd number of fermions (e.g. Deuterium atom, consisting of one electron, and a nucleus with one proton and one neutron)

Bosons

- photon $(s = 1)$

- mesons, ...

- systems with an even number of fermions (e.g. Hydrogen atom, consisting of one electron and a nucleus with one proton)

---

[7]After E. Fermi, who studied their energy distribution function (Fermi-Dirac statistics)
[8]After S.N. Bose, who studied their energy distribution function (Bose-Einstein statistics)

Fermions obey **Pauli exclusion principle**,[9] stating that

No two fermions in a system can have the same quantum numbers
<div align="center">or</div>
A quantum state can be occupied by at most one fermion.

For electrons in an atom, Pauli exclusion principle is often stated in a slightly different way, taking into account that electron spin quantum number can take two values ($m_s = \pm 1/2$, or, simply *spin up* and *spin down*) and an orbital is defined by the quantum numbers n, l, and m. The principle then states that an orbital can be occupied at most by two electrons, with opposite spin quantum numbers.

Bosons are not subject to the Pauli exclusion principle: **any number of identical bosons can occupy the same quantum state.**

---

[9]stated by W. Pauli for electrons in 1925, and extended to all fermions in 1940

7.7   Electrons in the atom

From the previous sections:
electrons in the atom are characterized by four quantum numbers:

- principal quantum number: $n = 0, 1, 2, \ldots$

- angular quantum number: $l = 0, 1, \ldots, n-1$

- azimuthal or magnetic quantum number: $m = 0, \pm 1, \ldots, \pm l$

- spin quantum number: $m_s = \pm\frac{1}{2}$

The disposition of electrons in the atom follows from the above numbers and Pauli's exclusion principle. The structure of the periodic table of the elements then follows. (We do not deal wit this topic, which is part of any basic course of Chemistry).

We only recall some notation frequently used in atomic spectroscopy.

- The electron *shells* with principal quantum numbers $n = 1, 2, 3$, and 4 are also called K, L, M, and N shells, respectively.

- The orbitals with angular quantum numbers $l = 0, 1, 2, 3$ are identified by lower case letters s, p, d, and f, respectively.

7.8 Indistinguishability

We have already seen that the development of quantum mechanics relies on a few postulates which do not have a classical analogue. An additional postulate concerns the indistinguishability of identical particles: as a consequence

Systems obtained from each other by exchanging particles are indistinguishable, i.e. are the same system

This principle finds application, e.g. in the computation of thermodynamic multiplicity (and hence of entropy of quantum systems), as well as when studying collisions between identical particles.

Chapter 8

Quantum statistics

In questo capitolo descriviamo il procedimento per ottenere le funzioni di distribuzione di equilibrio per particelle che obbediscono alle leggi della meccanica quantistica. Ricaveremo le espressioni della funzione di distribuzione di Bose-Einstein, che si applica ai *bosoni*, cioè alle particelle con spin intero (fra cui i fotoni, gli atomi di elio e le coppie di elettroni nei superconduttori), e della funzione di distribuzione di Fermi-Dirac, che si applica ai *fermioni*, cioè alle particelle con spin semintero (fra cui gli elettroni). Vedremo inoltre in quale limite la distribuzione (classica) di Boltzmann approssima le distribuzioni quantistiche.

Le configurazioni di un qualsiasi sistema in equilibrio macroscopico in effetti variano nel tempo, *fluttuando* in prossimità della configurazione più probabile. Si verifica comunque che, poiché i sistemi considerati sono costituiti da un grandissimo numero di particelle, le fluttuazioni (relative alla configurazione più probabile) sono estremamente piccole. Le proprietà fisiche medie di un sistema macroscopico si possono allora descrivere, con ottima precisione, tramite le proprietà della configurazione più probabile. Ciò giustifica il procedimento che seguiremo, con cui anzichè determinare la distribuzione media, determineremo la più probabile.

Per quanto riguarda quest'ultima, abbiamo visto (cfr. Mencuccini-Silvestrini, Vol. I, § XVII.4 e XVII.5; Sette-Alippi, vol. I, § 17.12), che un sistema termodinamicos isolato tende a raggiungere, all'equilibrio, lo stato che corrisponde al valore massimo della probabilità termodinamica W, definita come numero di microstati distinguibili con cui può essere realizzato un dato stato macroscopico. In condizioni di equilibrio termodinamico, la probabilità termodinamica è legata all'entropia tramite la relazione

$$S = k_\mathrm{B} \ln W, \qquad (8.1)$$

dove $k_\mathrm{B} = 1.3807 \times 10^{-23}$ J/K è la costante di Boltzmann.

8.1   Descrizione del sistema

Il primo passo nello studio del sistema di cui si vuole determinare la funzione di distribuzione consiste nella descrizione dei livelli energetici e della loro occupazione da parte delle *particelle* (particelle nel senso classico o fotoni) che costituiscono il sistema stesso. Osserviamo che i sistemi oggetto di studio sono costituiti da un grandissimo numero di particelle, distribuite su un gran numero di livelli energetici (o *stati*). Ai fini del calcolo della funzione di distribuzione, piuttosto che considerare i singoli livelli, conviene considerare (vedi la Fig. 8.1) raggruppamenti di livelli (o *shell*), abbastanza grandi da contenere un elevato numero di stati, con energie molto prossime fra loro, e un elevato numero di particelle. Inoltre, le energie dei vari stati della shell possono essere considerate coincidenti. Indichiamo con il pedice s la generica shell, con g_s il suo numero di stati (o *peso*), con ε_s l'energia di ciascuno degli stati e con n_s il numero di particelle contenute nella shell. Il numero totale di particelle N e l'energia totale E del sistema possono allora essere espresse rispettivamente come

$$N \;=\; \sum_s n_s, \tag{8.2}$$

$$E \;=\; \sum_s n_s \varepsilon_s, \tag{8.3}$$

dove le sommatorie sono estese a tutte le shell del sistema. I passi successivi del procedimento consistono nella determinazione del peso e della probabilità termodinamica di ciascuna shell. Scopo finale è ottenere il valore più probabile della popolazione $n_s(g_s)$ di ciascuna shell e quindi la funzione di distribuzione

$$f(\varepsilon_s) = \frac{n_s}{g_s} \tag{8.4}$$

Si può dimostrare (non lo facciamo qui) che il risultato ottenuto è indipendente dal modo in cui si raccolgono i livelli nelle shell; il procedimento fornisce quindi la funzione di distribuzione $f(\varepsilon)$ per qualsiasi valore di ε.

8.2   Statistica di Bose-Einstein

In questa sezione descriviamo la statistica di Bose-Einstein. Iniziamo considerando un sistema costituito da fotoni, in numero non assegnato e non vincolato, in equilibrio alla temperatura T.

8.2.1   Statistica di Bose-Einstein per i fotoni

Consideriamo particelle (fotoni) indistinguibili, con energia e quantità di moto legate alla frequenza tramite le relazioni

$$\varepsilon \;=\; h\nu, \tag{8.5}$$

$$p \;=\; \frac{h\nu}{c}, \tag{8.6}$$
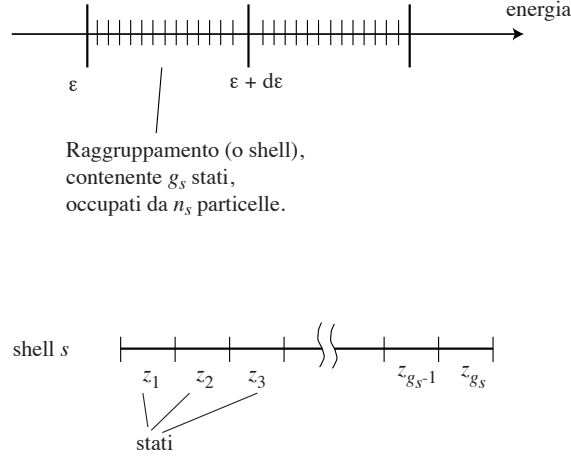
Figure 8.1: Stati e raggruppamenti.

dove h è la costante di Planck e c è la velocità della luce.

Pesi - Modi di vibrazione

Per esprimere il peso g_s della shell s sfruttiamo un risultato che abbiamo già utilizzato nella trattazione classica del corpo nero. Abbiamo infatti visto che in una cavità di volume V il numero di modi di vibrazione indipendenti con frequenza compresa fra ν e $\nu + d\nu$, per ciascuna delle due possibili polarizzazioni delle onde elettromagnetiche, è dato da (Mencuccini-Silvestrini, Vol. II, Eq. XII.11; Sette-Alippi, Vol. I, § 16.5 e 21.15)

$$d\mathcal{N}(\nu) = \mathcal{N}(\nu)d\nu = \frac{4\pi V}{c^3}\nu^2 d\nu. \tag{8.7}$$

Il peso g_s della shell relativa a fotoni con energia compresa fra $\varepsilon = h\nu$ e $\varepsilon + d\varepsilon = h(\nu + d\nu)$ è allora

$$g_s = 2\mathcal{N}(\nu)d\nu = \frac{8\pi V}{c^3}\nu^2 d\nu \tag{8.8}$$

Probabilità termodinamica

Calcoliamo ora la probabilità termodinamica W.[1] Ricordiamo che per i postulati della meccanica quantistica i fotoni sono indistinguibili; inoltre, non c'è limite al numero di fotoni che possono occupare un dato stato.

Consideriamo la s-sima shell, che ha peso g_s e contiene n_s particelle. Indichiamo gli stati con

$$z_1, z_2, z_3, \ldots, z_{g_s} \tag{8.9}$$

---

[1]Seguiamo l'elegante e semplice presentazione di M. Born, Atomic Physics, 8th Ed., Dover, New York, 1989, Cap. 7; trad. it.: Fisica Atomica, 2ª Ed., Bollati Boringhieri, Torino, 1976.

e le particelle con

$$a_1, a_2, a_3, \ldots, a_{n_s}. \tag{8.10}$$

Per valutare il numero di configurazioni possibili, procediamo nel modo seguente. Indichiamo una possibile configurazione con una stringa costituita da sequenze stato-particelle nello stato. Per esempio, con

$$z_1 \, a_1 \, a_2 \, z_2 \, a_3 \, z_3 \, a_4 \, a_5 \, a_6 \, z_4 \, z_5 \, a_7 \, \ldots . \, z_{g_s-1} \, z_{g_s} \, a_{n_s-1} \, a_{n_s} \tag{8.11}$$

rappresentiamo la configurazione della Fig. 8.2, in cui lo stato z_1 contiene le particelle a_1 e a_2, lo stato z_2 contiene la particella a_3, lo stato z_3 le particelle a_4, a_5 e a_6, lo stato z_4 non contiene nessuna particella, lo stato z_5 contiene la particella a_7 .... , lo stato z_{g_s-1} non contiene nessuna particella e lo stato z_{g_s} contiene le particelle $a_{a_n s-1}$ e a_{n_s}. Osserviamo che tutte le possibili stringhe

$$z_1 \, a_1 \, a_2 \, z_2 \, a_3 \, a_4 \, a_5 \, a_6 \, z_4 \, z_5 \, a_7 \, \ldots z_{g_s-1} \, z_{g_s} \, a_{n_s-1} \, a_{n_s}$$
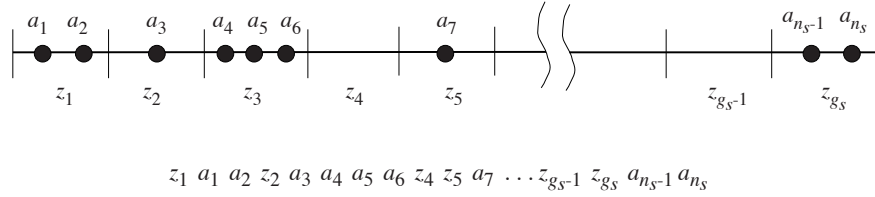
Figure 8.2: Esempio di configurazione di una shell e stringa che la rappresenta.

che descrivono la shell considerata sono costituite da $g_s + n_s$ elementi. Il primo elemento è sempre una z, e può quindi essere scelto in g_s modi diversi. Una volta scelto il primo elemento, gli altri $g_s + n_s - 1$ possono essere ordinati in $(g_s + n_s - 1)!$ modi diversi. Tuttavia, per i postulati della meccanica quantistica, le configurazioni ottenute l'una dall'altra per permutazione degli stati o per permutazione delle particelle sono indistinguibili. Poiché il numero di queste permutazioni è $g_s! n_s!$, il numero di configurazioni distinguibili di una shell risulta

$$W_s = \frac{g_s(g_s + n_s - 1)!}{g_s! n_s!} = \frac{(g_s + n_s - 1)!}{(g_s - 1)! n_s!}. \tag{8.12}$$

Inoltre, essendo per ipotesi $n_s \gg 1$ e $g_s \gg 1$, possiamo scrivere

$$W_s \simeq \frac{(g_s + n_s)!}{g_s! n_s!}. \tag{8.13}$$

Il numero di configurazioni possibili dell'intero sistema è pari al prodotto del numero di configurazioni di tutte le shell, ovvero

$$W = \prod_s W_s \simeq \prod_s \frac{(g_s + n_s)!}{g_s! n_s!}, \tag{8.14}$$

e quindi si ha

$$\ln W \simeq \sum_s [\ln(g_s + n_s)! - \ln g_s! - \ln n_s!]. \tag{8.15}$$

Usando la formula di Stirling, $\ln n! \simeq n \ln n - n$, possiamo infine scrivere

$$\ln W \simeq \sum_s [(g_s + n_s) \ln(g_s + n_s) - g_s \ln g_s - n_s \ln n_s]. \qquad (8.16)$$

Configurazione più probabile e funzione di distribuzione

Cerchiamo ora la configurazione che rende massima la funzione $\ln W$, con il vincolo, imposto dalla conservazione dell'energia,

$$\sum_s n_s \varepsilon_s = E, \qquad (8.17)$$

ovvero

$$E - \sum_s n_s \varepsilon_s = 0. \qquad (8.18)$$

A tale scopo usiamo il metodo dei moltiplicatori di Lagrange (vedi Appedice G). Cerchiamo cioè i massimi non condizionati della funzione

$$F = \ln W + \beta(E - \sum_s n_s \varepsilon_s), \qquad (8.19)$$

dove β è un moltiplicatore di Lagrange. Riscriviamo l'Eq. (8.19) esprimendo $\ln W$ tramite l'Eq. (8.16), ottenendo

$$
\begin{aligned}
F &= \sum_s [(g_s + n_s) \ln(g_s + n_s) - g_s \ln g_s - n_s \ln n_s] + \beta(E - \sum_s n_s \varepsilon_s) \\
&= \sum_s [(g_s + n_s) \ln(g_s + n_s) - g_s \ln g_s - n_s \ln n_s - \beta n_s \varepsilon_s] + \beta E.
\end{aligned}
$$
$$(8.20)$$

Il massimo di F si ottiene imponendo che si annullino le derivate parziali rispetto a tutte le n_s:

$$\frac{\partial F}{\partial n_s} = \ln(g_s + n_s) + 1 - 0 - \ln n_s - 1 - \beta \varepsilon_s = 0, \qquad (8.21)$$

da cui si ha

$$\ln \frac{g_s + n_s}{n_s} = \beta \varepsilon_s, \qquad (8.22)$$

e quindi

$$\frac{n_s}{g_s} = \frac{1}{e^{\beta \varepsilon_s} - 1}. \qquad (8.23)$$

$\beta = 1/k_{\mathrm{B}}T$

La relazione fra il moltiplicatore di Lagrange β e i parametri macroscopici del sistema (in realtà un solo parametro, come si vedrà fra poco) si trova nel modo

seguente. Consideriamo una variazione infinitesima dell'energia del sistema attorno all'equilibrio. Differenziando la condizione

$$\sum_s n_s \varepsilon_s = E \tag{8.24}$$

otteniamo

$$\sum_s n_s \delta\varepsilon_s + \sum_s \delta n_s \varepsilon_s = \delta E. \tag{8.25}$$

Il primo addendo a primo membro di questa equazione rappresenta il lavoro $-\delta L$ compiuto sul sistema a seguito dello scostamento dall'equilibrio. Infatti, se i livelli energetici non dipendono dalla temperatura (come ragionevole pensando ai modi di vibrazione in una cavità), si ha

$$\sum_s n_s \delta\varepsilon_s = \sum_s n_s \frac{\partial \varepsilon_s}{\partial V}\delta V = -p\delta V = -\delta L. \tag{8.26}$$

Allora, per il primo principio della termodinamica, applicato a una trasformazione infinitesima reversibile ($\delta E = \delta Q - \delta L$), il secondo addendo a primo membro dell'Eq. (8.25) rappresenta il calore δQ scambiato dal sistema:

$$\sum_s \varepsilon_s \delta n_s = \delta Q \tag{8.27}$$

D'altra parte, nell'intorno di uno stato di equilibrio $\delta F = 0$, quindi, utilizzando l'Eq. (8.19), possiamo scrivere

$$\delta \ln W = \beta \sum_s \varepsilon_s \delta n_s \tag{8.28}$$

e ancora, confrontando le equazioni (8.27) e (8.28)

$$\delta \ln W = \beta \delta Q. \tag{8.29}$$

Esprimendo la probabilità termodinamica W tramite l'Eq. (8.1), $S = k_{\mathrm{B}} \ln W$, e la quantità di calore scambiata nella trasformazione infinitesima tramite la definizione di entropia ($\delta S = \delta Q/T$), si ha

$$\beta = \frac{1}{k_{\mathrm{B}} T}. \tag{8.30}$$

Introducendo quest'ultima relazione e la condizione di quantizzazione [Eq. (8.5)] nell'Eq. (8.23) otteniamo la **funzione di distribuzione di Bose-Eintein per i fotoni**

$$\boxed{\frac{n_s}{g_s} = \frac{1}{e^{h\nu/k_{\mathrm{B}}T} - 1}}, \tag{8.31}$$

dove abbiamo scritto la frequenza ν omettendo il pedice s.

Lo spettro del corpo nero

Ricordiamo che nelle formule precedenti il pedice s si riferisce all'intervallo di energia $[\varepsilon, \varepsilon + d\varepsilon]$ (e frequenza $[\nu, \nu + d\nu]$); quindi n_s rappresenta il numero di fotoni con frequenza compresa fra ν e $\nu + d\nu$, mentre g_s, espressa dall'Eq. (8.8), rappresenta il numero di stati compresi nello stesso intervallo. La densità di energia (energia per unità di volume) dei fotoni con frequenza fra ν e $\nu + d\nu$ è quindi data da[2]

$$u(\nu)d\nu = \frac{n_s h\nu}{V} = \frac{1}{V}\frac{g_s}{e^{h\nu/k_\mathrm{B}T} - 1} = \frac{8\pi h\nu^3 d\nu}{e^{h\nu/k_\mathrm{B}T} - 1}, \tag{8.32}$$

che fornisce il noto spettro del corpo nero. Utilizzeremo questa espressione nel seguito del corso anche per studiare il laser e il rumore termico nei componenti circuitali ohmici.

8.2.2 Statistica di Bose-Einstein per un sistema di N particelle

La dimostrazione illustrata nella sezione precedente si riferisce a una popolazione di fotoni, di numero non assegnato. L'espressione della funzione di distribuzione nel caso sia assegnato il numero totale N di particelle (bosoni), si ottiene procedendo in modo del tutto analogo, ma imponendo il vincolo aggiuntivo che $N = \sum_s n_s$ sia costante. In questo caso la funzione da massimizzare è

$$F = \ln W + \alpha(N - \sum_s n_s) + \beta(E - \sum_s n_s \varepsilon_s), \tag{8.33}$$

dove α è un altro moltiplicatore di Lagrange[3]. Eseguendo calcoli analoghi a quelli della precedente sezione si giunge all'espressione della **funzione di distribuzione di Bose-Einstein**:

$$f(\varepsilon) = \frac{n_s}{g_s} = \frac{1}{e^{\alpha}e^{\varepsilon/k_\mathrm{B}T} - 1}. \tag{8.34}$$

In questo caso il peso g_s va calcolato tenendo conto che [vedi Eq. (2), pag. 50] il volume minimo di una cella nello spazio delle fasi $d^3x\, d^3p$ è pari a h^3. Si ha quindi

$$g_s = \frac{4\pi V p^2 dp}{h^3}. \tag{8.35}$$

La quantità $\alpha = \alpha(N/V, T)$ si determina imponendo la condizione di conservazione del numero totale di particelle; vedi più sotto.

---

[2]cfr. Mencuccini-Silvestrini, vol. II, Eq. XII.20, dove si usa il simbolo f in luogo di u.

[3]Si noti che alcuni testi definiscono α con segno opposto a quello usato in questo capitolo.

8.3   Statistica di Fermi-Dirac

Mentre per i fotoni (e, più in generale per tutti i bosoni, cioè le particelle con numero quantico di spin intero) non esistono limiti alla popolazione degli stati quantici, per gli elettroni (e, più in generale per tutti i fermioni, cioè le particelle con numero quantico di spin semi-intero) vale il *principio di esclusione*. Quindi due fermioni con uguali numeri quantici non possono occupare uno stesso stato.

La funzione di distribuzione dei fermioni si ricava in modo del tutto analogo a quella dei bosoni, ma tenendo conto del principio di esclusione. In questo caso la probabilità termodinamica della s-sima shell, cioè il numero di modi in cui si possono disporre n_s particelle nei g_s stati della shell stessa, è pari al numero di disposizioni di g_s oggetti in gruppi di n_s oggetti, ovvero

$$W_s = \frac{g_s!}{n_s!(g_s - n_s)!}. \tag{8.36}$$

Utilizzando la formula di Stirling possiamo scrivere

$$\ln W_s \simeq g_s \ln g_s - n_s \ln n_s - (g_s - n_s) \ln(g_s - n_s). \tag{8.37}$$

Procedendo come nel caso della statistica di Bose-Einstein, applichiamo il metodo dei moltiplicatori di Lagrange per determinare il massimo della W, con i vincoli posti dalla costanza del numero totale di particelle e dalla conservazione dell'energia. Cerchiamo quindi i massimi della funzione

$$
\begin{aligned}
F &= \sum_s [g_s \ln g_s - n_s \ln n_s - (g_s - n_s) \ln(g_s - n_s)] \\
&\quad + \alpha(N - \sum_s n_s) + \beta(E - \sum_s n_s \varepsilon_s).
\end{aligned} \tag{8.38}
$$

Derivando rispetto a ciascuna n_s otteniamo

$$
\begin{aligned}
\frac{\partial F}{\partial n_s} &= -\ln n_s - 1 + \ln(g_s - n_s) + \frac{g_s - n_s}{g_s - n_s} - \alpha - \beta \varepsilon_s \\
&= \ln \frac{g_s - n_s}{n_s} - \alpha - \beta \varepsilon_s.
\end{aligned} \tag{8.39}
$$

Imponendo l'annullamento di ciascuna derivata, $\partial F/\partial n_s = 0$, si ha

$$\ln \frac{g_s - n_s}{n_s} = \alpha + \beta \varepsilon_s, \tag{8.40}$$

da cui è immediato ricavare l'espressione della funzione di distribuzione:

$$f(\varepsilon) = \frac{n_s}{g_s} = \frac{1}{e^{\alpha + \beta \varepsilon_s} + 1}. \tag{8.41}$$

Rimuovendo il pedice s e utilizzando la relazione $\beta = 1/k_B T$ (che si dimostra valere anche in questo caso), possiamo finalmente scrivere della **funzione di distribuzione di Fermi-Dirac**:

$$\boxed{f(\varepsilon) = \frac{n_s}{g_s} = \frac{1}{e^{\alpha} e^{\varepsilon/k_B T} + 1},} \tag{8.42}$$

8.4 Limite classico: statistica di Boltzmann

L'espressione (8.42) differisce da quella relativa alla distribuzione di Bose-Einstein solo per il segno che precede l'unità nel denominatore. Possiamo riassumere le espressioni delle funzioni di distribuzione quantistiche tramite la relazione

$$f(\varepsilon) = \frac{n_s}{g_s} = \frac{1}{e^{\alpha} e^{\varepsilon/k_{\mathrm{B}} T} \pm 1}, \tag{8.43}$$

dove il segno $+$ si riferisce alla statistica di Fermi-Dirac e il segno $-$ alla statistica di Bose-Einstein. Nel caso di una popolazione di fotoni di numero non vincolato, $\alpha = 0$. Altrimenti, α si determina imponendo la conservazione del numero di particelle, $N = \sum_s n_s = f(\varepsilon) g_s$. Per esplicitare questa relazione sostituiamo la sommatoria sulle shell con un integrale sull'energia e scriviamo il peso g_s in funzione di ε, ottenendo

$$N = \int_0^{\infty} \frac{g(\varepsilon)}{e^{[\alpha + (\varepsilon/k_{\mathrm{B}} T)]} \pm 1} d\varepsilon, \tag{8.44}$$

con $g(\varepsilon) d\varepsilon$ dato dall' Eq. (3), pag. 50.

L'equazione (8.44) definisce implicitamente $\alpha = \alpha(N/V, T)$. Si dimostra che essa può essere posta nella forma

$$\alpha = -\varepsilon_0/k_{\mathrm{B}} T, \tag{8.45}$$

dove ε_0 è un'energia caratteristica, che dipende dalla densità di particelle N/V e, molto debolmente, dalla temperatura. Si ha allora

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_0)/k_{\mathrm{B}} T} \pm 1}. \tag{8.46}$$

Nel caso della statistica di Fermi-Dirac, ε_0 prende il nome di *energia di Fermi* e si indica usualmente con il simbolo ε_{F}. La statistica di Fermi verrà discussa e utilizzata nel seguito del corso per studiare alcune proprietà di metalli e semiconduttori (vedi Sette-Bertolotti, Vol. II, § 16.3–16.5 e Mencuccini-Silvestrini, Vol. II, § XII.9.2).

Quando il termine $\exp[\alpha + (\varepsilon/k_{\mathrm{B}} T)]$ nel denominatore dell'Eq. (8.43) è molto maggiore dell'unità, l'Eq. (8.43) stessa può essere scritta

$$\boxed{f(\varepsilon) \simeq e^{-\alpha} e^{-\varepsilon/k_{\mathrm{B}} T}.} \tag{8.47}$$

Ritroviamo così la **funzione di distribuzione di Boltzmann**, che quindi costituisce un'ottima approssimazione delle distribuzioni quantistiche quando l'occupazione dei livelli energetici è molto bassa; vedi la Fig. 8.3.

Osserviamo che all'Eq. (8.47) si giunge anche applicando il procedimento variazionale seguito per ricavare le espressioni delle funzioni di distribuzioni quantistiche. In questo caso nel calcolare la probabilità termodinamica W si deve tenere conto della distinguibilità delle particelle. Si scrive quindi

$$W = N! \prod_s \frac{g_s^{n_s}}{n_s!}. \tag{8.48}$$
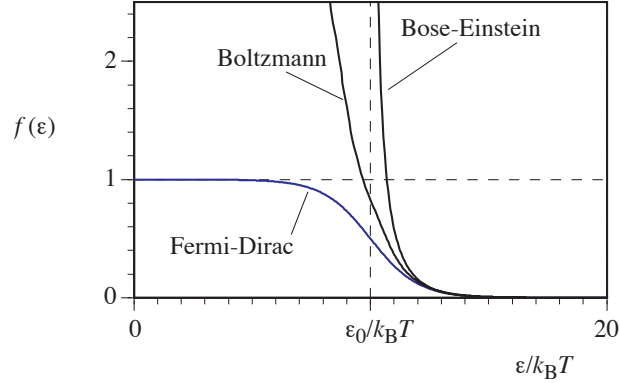
Figure 8.3: Confronto fra le funzioni di distribuzione di Fermi-Dirac, Bose-Einstein e Boltzmann, per $\varepsilon_0 = 10k_\mathrm{B}T$.

Nell'Eq. (8.48) fattore $N!$ rappresenta le permutazioni delle N particelle; il fattore $g_s^{n_s}$ i modi diversi in cui n_s particelle contenute in una shell possono essere distribuite nei g_s stati della shell stessa, il fattoriale $n_s!$ a denominatore tiene conto dell'equivalenza delle configurazioni realizzate permutando le particelle contenute in una stessa shell. Per calcolare la distribuzione più probabile si massimizza quindi la funzione $\ln W$ rispetto alle occupazioni n_s, imponendo la conservazione del numero totale di particelle e dell'energia totale. Utilizzando, come in precedenza, il metodo dei moltiplicatori di Lagrange, si massimizza il funzionale

$$F = \ln W + \alpha(N - \sum_s n_s) + \beta(E - \sum_s n_s\varepsilon_s),. \tag{8.49}$$

Inserendo l'espressione (8.48) nell'Eq. (8.49), usando la formula di Stirling per i logaritmi dei fattoriali e uguagliando a zero la derivata rispetto a n_s, si ottiene, per ogni s,

$$\ln \frac{g_s}{n_s} - \alpha - \beta\varepsilon_s = 0 \tag{8.50}$$

e quindi l'espressione della funzione di distribuzione

$$f(\varepsilon_s) = \frac{n_s}{g_s} = e^{-\alpha}e^{-\beta\varepsilon_s} = e^{-\alpha}e^{-\varepsilon_s/k_\mathrm{B}T}. \tag{8.51}$$

Chapter 9

s-wave scattering

In this Chapter we present a few basic elements of scattering theory. General scattering theory is extremely complex and outside the scope of the present introductory course. The goal of our treatment is to recover qualitative features of important nuclear reaction cross sections. Indeed, we shall find the nearly constant behaviour of potential scattering (e.g. elastic scattering far away from resonances), the Breit-Wigner resonant cross-section, and the $1/v$ behaviour of many absorption cross-sections.

9.1 Partial wave expansion
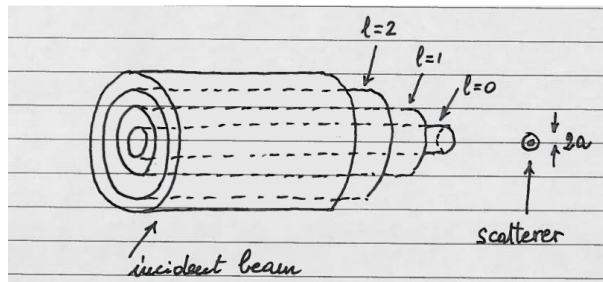
Figure 9.1: Geometrical interpretation of partial wave expansion.

We consider a beam of particles with momentum $p = \hbar k$ interacting with a particle (a scatterer) at rest in the origin of a coordinate system. Particles in the beam with impact parameter b have angular moment $L = pb = \hbar k b$. According to quantum mechanics angular momentum can only take values $L = \hbar\sqrt{l(l+1)} \simeq \hbar l$, with $l = 0, 1, \ldots$. Therefore, in a semi-classical picture (see Fig. 9.1), particles with angular quantum number between l and $l+1$ have impact parameters $l/k \leq b \leq (l+1)/k$. If we indicate with a the distance

from the scatterer at which the interaction potential vanishes (i.e. $V(r) = 0$ for $r > 0$) particles with $b > a$, i.e. with $l > ka$ are not affected by the potential and do not suffer any scatter (nor other reactions). It follows that if $ka \ll 1$ even particles with $l = 1$ are unaffected by the potential: only $l = 0$ particles matter. We can then consider the interaction as due only to such particles, i.e. to waves with $l = 0$ (angular momentum s-waves).
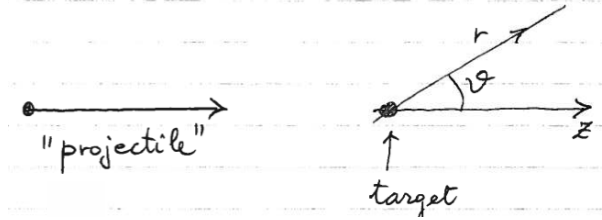
Figure 9.2: We study scattering in a reference frame centred on the scatterer.

We start by observing that the beam of incident particles is represented by a plane wave $\psi_0(z) = Ae^{ikz}$ or, in the spherical coordinate system centred around the scatterer, $\psi_0(r, \theta) = Ae^{ikr\cos\theta}$. This wavefunction can be expanded in a series of angular momentum wavefunctions [1] [2]

$$\psi_0 = Ae^{ikr\cos\theta} = A\sum_{l=0}^{\infty}(2l+1)i^l j_l(kr)P_l(\cos\theta). \tag{9.1}$$

Here P_l is the Legendre polynomial of order l [Eq. (7.33)] and j_l is the spherical Bessel function of order l, which asymptotically, for $kr \gg 1$ approaches

$$j_l(kr) \simeq \frac{\sin(kr - l\pi/2)}{kr}. \tag{9.2}$$

Each term of the expansion, i.e. each *partial wave* corresponds to a specific angular momentum l. Following the discussion above, we only retain the first term ($l = 0$, or s-wave) of the expansion. We then have

$$\psi_0(r) = -\frac{Ae^{-ikr}}{2ikr} + \frac{Ae^{ikr}}{2ikr}, \tag{9.3}$$

where the first term on the right hand side represents an entering spherical wave, and the second one an outgoing spherical wave.

9.2   General expression of the cross-sections

After the interaction with the particle in the origin, the s-wave component at large distance from the scatterer will again be given by the sum of an entering

---

[1] See, e.g. K. S. Krane, *Introduction to Nuclear Physics*, Wiley (1988), Sec. 11.8.

[2] The dependence on the other angle ϕ is omitted, assuming cylindrical symmetry around the z-axis.
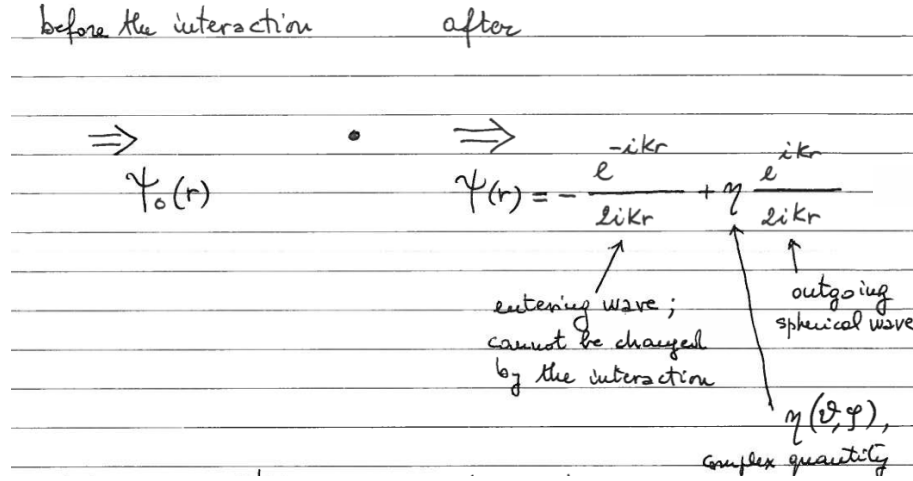
Figure 9.3: The wavefunction at large distance from the scatterer is the sum of an entering spherical wave and an outgoing one.

spherical wave (left unchanged by the interaction) and and an outgoing spherical wave,[3] and can then be written as

$$\psi(r) = -A\frac{e^{-ikr}}{2ikr} + A\eta\frac{e^{ikr}}{2ikr}, \tag{9.4}$$

where η is a complex quantity. While in general η depends on θ and ϕ, in the $l = 0$ approximation η is a (complex) constant. It is useful to write such a wave in a slightly different way, i.e.

$$\psi(r) = \underbrace{A\frac{e^{ikr} - e^{-ikr}}{2ikr}}_{\psi_0(r)} + \underbrace{A(\eta - 1)\frac{e^{ikr}}{2ikr}}_{\text{scattered or absorbed}}, \tag{9.5}$$

which highlights the difference between incoming wave and scattered wave.

The knowledge of η is sufficient to compute both the scattering cross-section and the reaction cross-section. In general, scattering is fully characterized by the differential cross-section $\sigma(\theta) = d\sigma/d\Omega$, with the (integrated) scattering cross-section given by $\sigma_{\rm sc} = \int_\Omega d\Omega\sigma(\theta)$. However s-wave scattering is symmetric in the centre-of-mass system, and then we simply have $\sigma_{\rm sc} = 4\pi\sigma(\theta)$. By definition

$$\sigma_{\rm sc} = \frac{\text{particles scattered per unit time}}{\text{incident particles per unit time and area}} = \frac{(dN/dt)_{\rm sc}}{J_{\rm inc}}, \tag{9.6}$$

where the current of the incident beam is (see Eq. (5.28)

$$J_{\rm inc} = \frac{\hbar k}{m}|A|^2. \tag{9.7}$$

---

[3]See footnote 2 of Sec. 7.5.

The scattering rate can instead be written by observing that the same number of particles will cross any sphere centred in the origin. Therefore the scattering rate is equal to the product of the particle density (i.e. the square of the modulus of the wavefunction) at distance r multiplied by the volume V spanned by the particles in the unit of time, i.e. $V = 4\pi r^2 \times v \times 1$, where $v = p/m = \hbar k/m$ is the particle velocity. We can then write

$$\left(\frac{dN}{dt}\right)_{\text{sc}} = \left|(\eta - 1)A\frac{e^{ikr}}{2ikr}\right|^2 \times 4\pi r^2 \times \frac{\hbar k}{m} = \tag{9.8}$$

$$= A^2|\eta - 1|^2\frac{1}{4k^2r^2}4\pi r^2\frac{\hbar k}{m} \tag{9.9}$$

$$= A^2|\eta - 1|^2\pi\frac{\hbar}{mk}, \tag{9.10}$$

and finally

$$\boxed{\sigma_{\text{sc}} = \pi\lambdabar^{\,2}|\eta - 1|^2,} \tag{9.11}$$

where we have introduced $\lambdabar = \lambda/2\pi = 1/k$.

So far we have considered elastically scattered particles. Particles can also be absorbed or scattered inelastically. Such processes are taken into account by the reaction cross-section σ_{reaction}. It can be shown that

$$\boxed{\sigma_{\text{reaction}} = \pi\lambdabar^2(1 - |\eta|^2),} \tag{9.12}$$

and the total cross-section is

$$\boxed{\sigma_{\text{tot}} = \sigma_{\text{sc}} + \sigma_{\text{reaction}} = 2\pi\lambdabar^2[1 - \Re(\eta)].} \tag{9.13}$$

9.3 Scattering from a hard sphere

9.3 Scattering from a hard sphere of radius R

or "Potential scattering"

scattering length
& nuclear radius

$\psi(r=R)$ must be zero $\quad(\psi \to 0$ as $V \to \infty)$
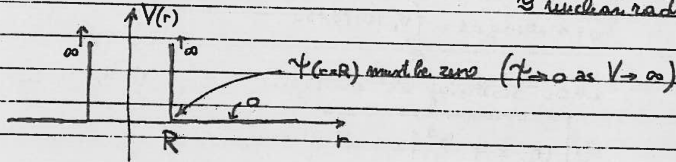
- scattering : no particles are lost $\Rightarrow |\eta| = 1$.

We can then write $\quad \eta = e^{2i\delta} \quad \left(\text{and} \quad \eta - 1 = 2i e^{i\delta} \sin\delta\right)$,

We impose $\quad \psi(r=R) = 0 \quad$, i.e.

$$\left[-\frac{e^{-ikr}}{2ikr} + e^{2i\delta}\frac{e^{ikr}}{2ikr} \right]_{r=R} = 0$$

$$\Rightarrow -e^{-ikR} + e^{i(2\delta + kR)} = 0$$

$$-1 + e^{2i(\delta + kR)} = 0 \qquad \Rightarrow \quad \underline{\delta = -kR} \quad ,$$

and the scattering cross section $\sigma_{sc} = \pi \lambda^2 |\eta - 1|^2$ becomes

$$\sigma_{sc} = \pi \lambda^2 \left| 2i e^{-ikR} \sin kR \right|^2 = 4\pi \lambda^2 \sin^2 kR . \qquad (*)$$

For $kR \ll 1 \quad (\text{i.e. } R \ll \lambda) \quad \sin^2 kR \approx k^2 R^2$,

s-wave $\qquad \boxed{\sigma_{sc} \approx 4\pi R^2} \quad (**) \quad$ Notice the front factor 4 !

$\Rightarrow$ **Exercise:** when is (i.e. for which energy) is $\lambda \gg R$ for a neutron interacting with a nucleus of mass $A m_u$?

9.4   Potential scattering and Breit-Wigner cross-section

Let us consider a more physical case, allowing to discuss both scattering and reactions.

"out" ↗
"in"
R
NUCLEUS
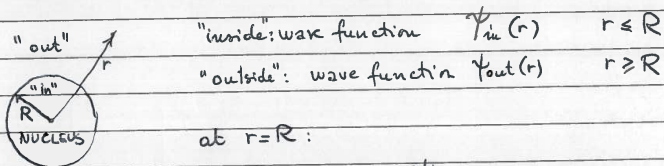
"inside": wave function $\psi_{in}(r)$ $r \leq R$

"outside": wave function $\psi_{out}(r)$ $r \geq R$

at $r = R$:

• continuity of ψ

• continuity of $d\psi/dr$

Setting $\psi(r) = u(r)/r$ we can write the matching conditions at $r = R$ as a single condition

$$\left. \frac{r \frac{du_{out}}{dr}}{u_{out}} \right|_{r=R} = \left. \frac{r \frac{du_{in}}{dr}}{u_{in}} \right|_{r=R} \doteq f$$

definition of f
(it is a complex quantity)

We know $u_{out}(r) = r\psi(r) = \frac{1}{2i}\left[e^{-ikr} + \eta e^{ikr} \right]$

[see eq. (9.4)]

$$\Rightarrow f = ikR \frac{e^{-ikR} + \eta e^{ikR}}{-e^{-ikR} + \eta e^{ikR}} \ ,$$

which can be solved for η:

$$\eta = \frac{f + ikR}{f - ikR} e^{-2ikR}$$

Since f is a complex quantity, we can write

$$f = f_R + i f_i,$$

and then

$$\eta = \frac{f_R + i(f_i + KR)}{f_R - i(f_i - KR)} e^{-2ikR}. \qquad (x)$$

We can then write scattering and reaction cross sections as functions of f_R and f_i.

For the scattering cross section, $\sigma_{sc} = \pi \lambda^2 |1-\eta|^2$ we need to compute $1-\eta$:

$$1 - \eta = e^{-2ikR} \left[e^{2ikR} - \frac{f_R + i(f_i + kR)}{f_R + i(f_i - kR)} \right] =$$

$$= e^{-2ikR} \left[e^{ikR} \left(e^{ikR} - e^{-ikR} \right) + 1 * \qquad \right]$$

$$\underbrace{}_{\substack{\text{we have subtracted} \\ \text{and added "1"}}}$$

$$\cdots\cdots$$

$$= 2i e^{-2ikR} \left[e^{ikR} \sin kR + \frac{kR}{i(kR - f_i) - f_R} \right],$$

and then

$$\sigma_{sc} = 4\pi \lambda^2 \left| e^{ikR} \sin kR + \frac{kR}{i(kR - f_i) - f_R} \right|^2. \qquad (\#)$$

Analogously (algebra omitted):

$$\sigma_{reas} = \pi \lambda^2 \left(1 - |\eta|^2\right) = \pi \lambda^2 \frac{-4 f_i KR}{f_R^2 + (kR - f_i)^2} \quad . \quad (*)$$

We immediately see that if $f_i = 0$, $\sigma_{reas} = 0$

$$\Rightarrow \text{ pure } \underline{\text{scattering}}$$

For pure scattering, therefore, Eq. [(#), previous page] becomes

$$\sigma_{sc} = 4\pi \lambda^2 \left| e^{ikR} \sin kR + \frac{KR}{ikR - f_R} \right|^2,$$

and we consider two limiting cases

a) $\left| \dfrac{KR}{ikR - f_R} \right|^2 \ll \sin^2 KR \quad \Rightarrow \quad \sigma_s \cong 4\pi \lambda^2 \sin^2 KR$

    we have recovered Eq. (*), page 4

   and then

   $$\boxed{\sigma_{sc} \simeq 4\pi R^2} \quad \text{for } KR \ll 1$$

   see Eq. (**), Sec. (9.3)

   POTENTIAL SCATTERING

b) $\left| \dfrac{KR}{ikR - f_R} \right|^2 \gg \sin^2 kR$

   $$\sigma_{sc} = 4\pi \lambda^2 \frac{k^2 R^2}{k^2 R^2 + f_R^2}$$

   σ_{sc} is maximum when $f_R = 0$. $\left[f_R(E_0) = 0 \right]$

We then expand $f_R(E)$ in proximity of $E = E_0$ as

$$f_R(E) = \underbrace{f_R(E_0)}_{\equiv 0} + f_R'(E_0)(E - E_0) + \dots \;\bcancel{\;} \quad , \text{ thus}$$

obtaining

$$\sigma_{sc} = 4\pi \lambda^2 \; \frac{4k^2R^2 / (f_R'(E_0))^2}{(E - E_0)^2 + \dfrac{k^2 R^2}{\left[f_R'(E_0)\right]^2}}.$$

We set $\Gamma_s \doteq \dfrac{2KR}{f_R'(E_0)}$ and write the cross section

in the form

$$\boxed{\; \sigma_{sc} = \pi \lambda^2 \; \frac{\Gamma_s^2}{(E - E_0)^2 + \dfrac{\Gamma_s^2}{4}} \;}$$

$$\Big\Uparrow$$

BREIT- WIGNER CROSS SECTION
FOR SCATTERING CLOSE TO A RESONANCE

It can be shown (see e.g. Segrè, Nuclei and Particles, p. 460)
that under similar assumptions

$$\sigma_{reas} = \pi \lambda^2 \; \frac{\Gamma_s \Gamma_r}{(E - E_0)^2 + \dfrac{(\Gamma_r + \Gamma_s)^2}{4}} \quad , \text{ with } \begin{array}{l} \Gamma_s \sim k \propto v \\[4pt] \lambda^2 \sim \dfrac{1}{k^2} \propto v^{-2} \end{array}$$

Hence, for absorption reactions with nearly constant $\Gamma_r \gg \Gamma_s$,
if $\Gamma_r \gg (E - E_0)$ or $E \ll E_0$, so that the denominator
is approximately constant, we have

$$\sigma_{reas} \sim \pi \lambda^2 \, \Gamma_s \Gamma_r^{-1} \propto 1/v.$$

We shall recover this last result by proceeding in a more
physical way in the next section.

9.5   Absorption cross-section

Inside the nucleus, we only have the incoming wave

$$\Psi_{in} \propto \frac{e^{-iKr}}{r}, \quad \text{i.e.} \quad u_{in} = r\Psi_{in} \propto e^{-iKR},$$

where K is the wave-number of the nucleon inside the nucleus;
$K \approx 1.6 \; fm^{-1}$ if $E_{nucleon} \approx 50 \; MeV$.

We can then compute $f = R \left. \frac{du/dr}{u(r)} \right|_{r=R}$ using $u = u_{in}$:

$$f = -RiK \frac{e^{-iKR}}{e^{-iKR}} = -iKR.$$

Inserting this last expression into Eq.[(x), Sec. 9.4], we obtain

$$\eta = \frac{-iKR + ikR}{iKR - ikR} e^{-2ikR} = \frac{K-k}{K+k} e^{-2ikR}.$$

and then the (absorption) reaction cross section

$$\sigma_{reac} = \pi \lambda^2 \left[1 - |\eta|^2 \right] = \pi \lambda^2 \left[1 - \left(\frac{K-k}{K+k} \right)^2 \right] = \pi \lambda^2 \frac{4Kk}{(K+k)^2},$$

where k is the wave number of the incoming neutron,

$$k = 1/\lambda \propto \sqrt{E} \propto v.$$

For a "low" energy neutron $k \ll K$, and then

$$\sigma_{reac} \approx \frac{4\pi}{k^2} \frac{k}{K} = \frac{4\pi}{kK} \propto \frac{1}{v}$$

$$\boxed{\sigma_{reac} \propto \frac{1}{v}} \quad \Longleftarrow \quad \text{"1/v" law}$$

Appendices

Appendix A

Wave packets and group velocity

Consideriamo il pacchetto d'onde descritto dalla funzione

$$u(x,t) = \int a(k)\, e^{i(kx-\omega t)}\, dk \;, \qquad \text{con } \omega = \omega(k)$$

Supponiamo $a(k)$ sia "centrata" attorno a k_0 e sia "stretta"

$$k = k_0 + k_1 \longrightarrow$$
$$\omega = \omega_0 + \omega_1$$
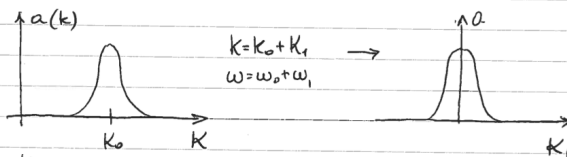
Quindi

$$u(x,t) = \int a(k_0+k_1)\, e^{i\left[(k_0+k_1)x - (\omega_0+\omega_1)t\right]}\, dk_1 =$$

$$= e^{i(k_0 x - \omega_0 t)} \underbrace{\int a(k_0+k_1)\, e^{i(k_1 x - \omega_1 t)}\, dk_1}_{A(x,t)}$$

$\Rightarrow$ pacchetto $\approx$ onda con numero d'onda k_0, pulsazione ω_0 e ampiezza $A(x,t)$ che varia da punto a punto e da istante a istante.

Chiamiamo <u>velocità di gruppo</u> la velocità di un punto del pacchetto con data A, per es. del punto di massimo. Quest'ultimo si trova imponendo

$$\frac{d\,A(x,t)}{dt} = 0 \quad,$$

$$\frac{\partial A(x,t)}{\partial x}\left(\frac{dx}{dt}\right) + \frac{\partial A(x,t)}{\partial t} = 0 \quad,$$

vel. di gruppo: $\quad U = \left.\frac{dx}{dt}\right|_{A=\text{cost}} \quad \Rightarrow \quad U = -\frac{\partial A/\partial t}{\partial A/\partial x}.$

$$\frac{\partial A}{\partial t} = -i \int \omega_1\, a(k_0+k_1)\, e^{i(k_1 x - \omega_1 t)}\, dk_1 \;; \qquad (*)$$

$$\frac{\partial A}{\partial x} = i \int k_1\, a(k_0+k_1)\, e^{i(k_1 x - \omega_1 t)}\, dk_1 \;; \qquad (**)$$

dove, per l'ipotesi di pacchetto "stretto", possiamo scrivere

$$\omega_1(k_1) = \omega(k) - \omega_0 = \left[\omega_0 + \left.\frac{d\omega}{dk}\right|_{\omega_0}(k-k_0) + \dots\right] - \omega_0$$

$$\approx \left.\frac{d\omega}{dk}\right|_{k_0}(k-k_0) = \left.\frac{d\omega}{dk}\right|_{k_0} k_1.$$

Sostituendo quest'ultima espressione nelle eq. (*) e (**) si ha quindi

$$U = -\frac{\partial A/\partial t}{\partial A/\partial x} = \frac{d\omega}{dk}.$$

Appendix B

Fourier transform of a Gaussian

We show that the Fourier transform of a Gaussian is still a Gaussian and that the product of the standard deviation of a Gaussian and of its Fourier transform is 1. We consider the Fourier-transform $F(\omega)$

$$F(\omega) = \int_{-\infty}^{\infty} f(t)e^{-i\omega t}dt \tag{B.1}$$

of a function $f(t)$, which can be recovered by anti-transforming $F(\omega)$, according to

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega)e^{i\omega t}d\omega. \tag{B.2}$$

Let us assume that $F(\omega)$ is given by

$$F(\omega) = e^{-\omega^2}, \tag{B.3}$$

i.e. it is a Gaussian $\exp\left(-\omega^2/2\sigma_\omega^2\right)$, with standard deviation $\sigma_\omega = 1/\sqrt{2}$. We now use Eq. (B.2) to obtain $f(t)$;

$$
\begin{aligned}
f(t) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-\omega^2 + i\omega t}d\omega = \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-(\omega - it/2)^2 - t^2/4}d\omega = \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-x^2 - t^2/4}dx = \frac{e^{-t^2/4}}{2\pi}\sqrt{\pi} \\
&= \frac{1}{2\sqrt{\pi}}e^{-t^2/4},
\end{aligned} \tag{B.4}
$$

which is a Gaussian in t, with standard deviation $\sigma_t = \sqrt{2}$, so that $\sigma_t \, \sigma_\omega = 1$.

Appendix C

A proof of the uncertainty relations

- pacchetto d'onde gaussiano $\quad f(x) = A e^{-x^2/a^2}$

  "istantanea" ad un certo istante "t_0".

- per il postulato interpretativo P3 la varianza di una misura di posizione (coordinata x) è data da

$$\overline{\Delta x^2} = \frac{\int_{-\infty}^{\infty} x^2 f^2(x)\, dx}{\int_{-\infty}^{\infty} f^2(x)\, dx} = \frac{\int x^2 e^{-2x^2/a^2}\, dx}{\int e^{-2x^2/a^2}\, dx}$$

  poniamo $\quad y^2 = 2x^2/a^2$:

$$\overline{\Delta x^2} = \frac{a^2}{2} \frac{\int_{-\infty}^{\infty} y^2 e^{-y^2}\, dy}{\int_{-\infty}^{\infty} e^{-y^2}\, dy} = \frac{a^2}{2} \cdot \frac{1}{2} = \frac{a^2}{4} \qquad (*)$$

  Se definiamo $\quad \Delta x \doteq \sqrt{\overline{\Delta x^2}}$, abbiamo $\quad \boxed{\Delta x = \dfrac{a}{2}}$

- La trasformata di Fourier $\phi(k)$ della $f(x)$ [cioè la $\phi(k)$ tale che $f(x) = \int_{-\infty}^{\infty} \phi(k) e^{+ikx}\, dk$] è

$$\phi(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(x) \cdot e^{-ikx}\, dx = \frac{A}{2\pi} \int_{-\infty}^{\infty} e^{-\left(\frac{x^2}{a^2} + ikx\right)}\, dx$$

$\overline{(*)} \quad \int y^2 e^{-y^2}\, dy = \frac{1}{2}\left[-y e^{-y^2} + \int e^{-y^2}\, dy\right]$

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Calcoliamo quest'ultimo integrale

$$\phi(k) = \frac{A}{2\pi} \int_{-\infty}^{\infty} e^{-\left(\frac{x^2}{a^2} + ikx\right)} \, dx =$$

$$= \frac{A}{2\pi} \int_{-\infty}^{\infty} \exp\left[-\left[\underbrace{\left(\frac{x}{a}\right)^2 + i\frac{ka}{2}\frac{x}{2} - \frac{k^2a^2}{4}}_{\left(\frac{x}{a} + ik\frac{a}{2}\right)^2} + \frac{k^2a^2}{4}\right]\right] dx =$$

$$= \frac{A}{2\pi} e^{-\frac{k^2a^2}{4}} \int_{-\infty}^{\infty} e^{-\left(\frac{x}{a} + ik\frac{a}{2}\right)^2} dx = \frac{Aa}{2\pi} e^{-\frac{k^2a^2}{4}} \cdot \underbrace{\int_{-\infty}^{\infty} e^{-y^2} dy}_{\sqrt{\pi}} =$$

$$\underset{y = \frac{x}{a} + ik\frac{a}{2}}{}$$

$$\phi(k) = \frac{Aa}{2\sqrt{\pi}} e^{-k^2a^2/4} \underset{\uparrow}{=} \frac{Aa}{2\sqrt{\pi}} e^{-k^2/b^2}$$

$$\text{def. } b = \frac{2}{a}$$

$$\Rightarrow \boxed{\Delta k = \frac{b}{2} = \frac{1}{a} = \frac{1}{2\Delta x}}$$

$\cdot$ ma $\quad k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} \quad \longrightarrow \quad p = k\frac{h}{2\pi} = k\hbar$

$\cdot$ quindi $\quad \Delta p = \hbar \, \Delta k = \frac{\hbar}{2\Delta x}$

$$\Downarrow$$

$$\boxed{\Delta p \cdot \Delta x = \frac{\hbar}{2}}$$

Appendix D

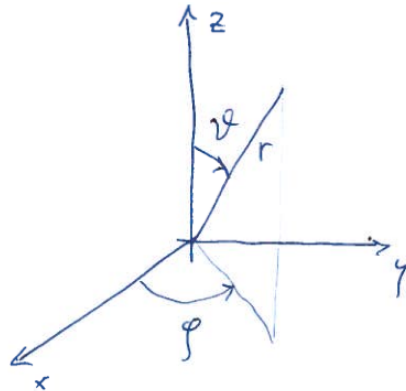# Angular momentum operators in spherical coordinates

Figure D.1: Spherical and Cartesian coordinates.

We introduce spherical coordinates r, θ, ϕ, related to the Cartesian coordinates x, y, z by

$$r = \sqrt{x^2 + y^2 + z^2} \tag{D.1}$$

$$\theta = \arctan \frac{\sqrt{x^2 + y^2}}{z} \tag{D.2}$$

$$z = \arctan \frac{y}{x} \tag{D.3}$$

$$x = r\sin\theta\cos\phi \tag{D.4}$$
$$y = r\sin\theta\sin\phi \tag{D.5}$$
$$z = r\cos\theta \tag{D.6}$$

We want to obtain the expressions of the angular momentum operators

$$\hat{l}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}) \tag{D.7}$$

$$\hat{l}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}) \tag{D.8}$$

$$\hat{l}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}) \tag{D.9}$$

in spherical coordinates. To express derivatives with respect to Cartesian coordinates in terms of derivatives with respect to spherical coordinates we have to use expressions such as

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial z}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial z}\frac{\partial}{\partial\phi}. \tag{D.10}$$

As an example, we detail the derivation of the expression of $\hat{l}_z$:

$$\hat{l}_z = -i\hbar\left[x\left(\frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial y}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial y}\frac{\partial}{\partial\phi}\right) + \right.$$
$$\left. -y\left(\frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}\right)\right], \tag{D.11}$$

and reordering the terms on the right hand side,

$$\hat{l}_z = -i\hbar\left[\left(x\frac{\partial r}{\partial y} - y\frac{\partial r}{\partial x}\right)\frac{\partial}{\partial r}\right.$$
$$+ \left(x\frac{\partial\theta}{\partial y} - y\frac{\partial\theta}{\partial x}\right)\frac{\partial}{\partial\theta}$$
$$\left. + \left(x\frac{\partial\phi}{\partial y} - y\frac{\partial\phi}{\partial x}\right)\frac{\partial}{\partial\phi}\right], \tag{D.12}$$

where, using Eqs. (D.4)–(D.6), we can write

$$\frac{\partial r}{\partial y} = \frac{1}{2\sqrt{x^2 + y^2 + z^2}} 2y = \frac{y}{r} \tag{D.13}$$

$$\frac{\partial r}{\partial x} = \frac{x}{r} \tag{D.14}$$

$$\frac{\partial \theta}{\partial y} = \frac{1}{1 + \frac{x^2 + y^2}{z^2}} \frac{1}{z} \frac{1}{2\sqrt{x^2 + y^2}} 2y = \frac{zy}{r^2\sqrt{x^2 + y^2}} = \frac{y}{r^2 \tan\theta} \tag{D.15}$$

$$\frac{\partial \theta}{\partial x} = \frac{y}{r^2 \tan\theta} \tag{D.16}$$

$$\frac{\partial \phi}{\partial x} = \frac{1}{1 + \frac{y^2}{x^2}} \frac{-y}{x^2} = -\frac{y}{x^2 + y^2} \tag{D.17}$$

$$\frac{\partial \phi}{\partial y} = \frac{1}{x} \frac{x}{x^2 + y^2} \tag{D.18}$$

Substituting Eqs. (D.13)–(D.18) into Eq. (D.12) we finally obtain

$$\hat{l}_z = -i\hbar \left[0 \cdot \frac{\partial}{\partial r} + 0 \cdot \frac{\partial}{\partial \theta} + \left(x \frac{x}{x^2 + y^2} + y \frac{y}{x^2 + y^2} \right) \frac{\partial}{\partial \phi} \right], \tag{D.19}$$

and then

$$\boxed{\hat{l}_z = -i\hbar \frac{\partial}{\partial \phi}.} \tag{D.20}$$

By proceeding analogously, one obtains

$$\boxed{\hat{l}_x = i\hbar \left(\sin\phi \frac{\partial}{\partial \theta} + \cot\theta \cos\phi \frac{\partial}{\partial \phi} \right)} \tag{D.21}$$

and

$$\boxed{\hat{l}_y = -i\hbar \left(\cos\phi \frac{\partial}{\partial \theta} - \cot\theta \sin\phi \frac{\partial}{\partial \phi} \right).} \tag{D.22}$$

Appendix E

Hydrogen atom - solution of the radial equation

We give here all details of the solution of the radial equation for the electron wavefunction in the hydrogen atom [Eq. (7.54)], which we write again here:

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + \frac{2\mu}{\hbar^2}\left[E - V(r)\right] - \frac{l(l+1)}{r^2} \right] R(r) = 0 \qquad \text{(E.1)}$$

nota:

$$\frac{2\mu}{\hbar^2}\left[E - \left(V(r) + \frac{\hbar^2}{2\mu r^2}\, l(l+1)\right)\right] \qquad \text{(64)}$$

pot. centrifugo

potenziale effettivo

Scriviamo r in unità di raggi di Bohr r_0 ed E in unità dell'energia del livello $n=1$ dell'atomo di idrogeno di Bohr:

$$r = \rho\, r_0 \qquad\qquad r_0 = \frac{\hbar^2}{\mu e^2 Z} \qquad \text{(65)}$$

$$E = \epsilon\, E_0 \qquad\qquad E_0 = -\frac{\mu e^4 Z^2}{2\hbar^2} \qquad \text{(66)}$$

Sostituendo nella (18) e moltiplicando per r_0 otteniamo:

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$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} - \epsilon + \frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2} \right] R = 0 \qquad (67)$$

Questa equazione non è risolubile in forma chiusa.
Per cercare una soluzione approssimata, studieremo
i comportamenti nell' origine e a grande distanza
del centro.

a) per $\rho \to \infty$, l'equazione (67) diviene

$$\left(\frac{d^2}{d\rho^2} - \epsilon \right) R(\rho) = 0 \qquad \to \quad R \sim \begin{cases} e^{+\rho\sqrt{\epsilon}} & \text{diverge per } \rho \to \infty \\ e^{-\rho\sqrt{\epsilon}} \end{cases}$$

$$(68)$$

b) per $\rho \to 0$

$$\left(\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} - \frac{\ell(\ell+1)}{\rho^2} \right) R(\rho) = 0 \qquad (69)$$

Cerchiamo una soluzione di andamento $R \sim \rho^b$

Sostituendo nella Eq. (69) si ha

$$b(b-1) + 2b = \ell(\ell+1),$$

quindi

$$b(b+1) = \ell(\ell+1) \quad \to \quad b = \begin{cases} \ell \\ -\ell-1 \end{cases}$$

$$R \sim \begin{array}{l} \rho^\ell \\ \rho^{-\ell-1} \quad \text{diverge nell' origine} \end{array} \qquad (70)$$

Cerchiamo allora una soluzione, valida per $\forall \rho$, che abbia nell'origine e per $\rho \to \infty$ gli andamenti (70) e (68), rispettivamente. La scriviamo nella forma

$$R(\rho) = e^{-\rho\sqrt{\epsilon}}\, \rho^\ell\, f(\rho). \qquad\qquad (71)$$

Dobbiamo quindi trovare la funzione $f(\rho)$.
Sostituiamo l'Eq (71) nella (67), utilizzando le seguenti espressioni delle derivate prima e seconda di $R(\rho)$:

$$\frac{dR}{d\rho} = R\left(-\sqrt{\epsilon} + \frac{\ell}{\rho} + \frac{1}{f}\frac{df}{d\rho}\right);$$

$$\frac{d^2R}{d\rho^2} = \frac{d}{d\rho}\left(\frac{dR}{d\rho}\right) = \frac{dR}{d\rho}\left(-\sqrt{\epsilon} + \frac{\ell}{\rho} + \frac{1}{f}\frac{df}{d\rho}\right) + R\left(-\frac{\ell}{\rho^2} - \frac{1}{f^2}\left(\frac{df}{d\rho}\right)^2 + \frac{1}{f}\frac{d^2f}{d\rho^2}\right)$$

$$= R\left(-\sqrt{\epsilon} + \frac{\ell}{\rho} + \frac{1}{f}\frac{df}{d\rho}\right)^2 + R\left(-\frac{\ell}{\rho^2} - \frac{1}{f^2}\left(\frac{df}{d\rho}\right)^2 + \frac{1}{f}\frac{d^2f}{d\rho^2}\right)$$

$$= R\left[\epsilon + \frac{\ell^2}{\rho^2} + \frac{1}{f^2}\left(\frac{df}{d\rho}\right)^2 - 2\sqrt{\epsilon}\,\frac{\ell}{\rho} - \frac{2\sqrt{\epsilon}}{f}\frac{df}{d\rho} + \frac{2\ell}{\rho f}\frac{df}{d\rho}\right.$$

$$\left. - \frac{\ell}{\rho^2} - \frac{1}{f^2}\left(\frac{df}{d\rho}\right)^2 + \frac{1}{f}\frac{d^2f}{d\rho^2}\right];$$

otteniamo

$$\cancel{\epsilon} + \frac{\ell^2 - \cancel{\ell}}{\rho^2} - 2\sqrt{\epsilon}\,\frac{\ell}{\rho} + \left(-2\sqrt{\epsilon} + \frac{2\ell}{\rho}\right)\frac{df}{f\,d\rho} + \frac{1}{f}\frac{d^2f}{d\rho^2} +$$

$$- \frac{\ell}{\sqrt{\rho}}\sqrt{\epsilon} + \frac{2\ell}{\rho^2} + \frac{2}{\rho f}\frac{df}{d\rho} - \cancel{\epsilon} + \frac{2}{\rho} - \frac{\ell(\cancel{\ell+1})}{\rho^2} = 0.$$

Moltiplicando per f e riordinando:

$$\frac{d^2 f}{d\rho^2} + \left[\frac{2(\ell+1)}{\rho} - 2\sqrt{\epsilon} \right] \frac{df}{d\rho} + \frac{2}{\rho}\left(1 - \sqrt{\epsilon}\,(\ell+1) \right) f = 0 \qquad (72)$$

Cerchiamo e la soluzione $f(\rho)$ come serie di potenze di ρ ρ, meglio, di $(2\sqrt{\epsilon}\,\rho)$, scrivendo quindi

$$f(\rho) = \sum_{0}^{\infty} a_\nu \underbrace{\left(2\sqrt{\epsilon}\,\rho \right)^\nu}_{x}, \qquad \nu = 0,1,2,\dots \qquad (73)$$

le cui derivate sono

$$\frac{df}{d\rho} = \sum_{1}^{\infty} a_\nu \nu \left(2\sqrt{\epsilon}\,\rho \right)^{\nu-1} 2\sqrt{\epsilon} \qquad (73a)$$

$$\frac{d^2 f}{d\rho^2} = \sum_{2}^{\infty} a_\nu \nu (\nu-1) \left(2\sqrt{\epsilon}\,\rho \right)^{\nu-2} 4\epsilon \qquad (73b)$$

Sostituendo le eq. (73), (73a) e (73b) nella (72) otteniamo

$$\sum a_\nu \nu (\nu-1) 4\epsilon \, x^{\nu-2} + \left[\frac{2(\ell+1)}{x} 2\sqrt{\epsilon} - 2\sqrt{\epsilon} \right] \sum a_\nu \nu x^{\nu-1} 2\sqrt{\epsilon} +$$

$$+ \frac{2}{x} 2\sqrt{\epsilon} \left[1 - \sqrt{\epsilon}\,(\ell+1) \right] a_\nu x^\nu = 0$$

e ancora,

$$\sum 4\epsilon a_\nu \nu (\nu-1+2\ell+2) \, x^{\nu-2} - \sum 4\epsilon a_\nu \left(\nu + \ell+1 - \frac{1}{\sqrt{\epsilon}} \right) x^{\nu-1} = 0$$

$$\underbrace{\qquad}_{\nu+2\ell+1}$$

$$(74)$$

Affinché l'eq. (74) sia soddisfatta, debbono essere identicamente nulli tutti i termini di ciascun grado in ν, quindi

$$a_{\nu+1}(\nu+1)(\nu+2\ell+1) = a_\nu\left(\nu+\ell+1 - \frac{1}{\sqrt{\epsilon}}\right). \qquad (75)$$

Da questa formula, per ricorrenza si trovano tutti i coefficienti a_ν (noto il primo).

Si osserva però che la serie diverge per $x \to \infty$.
Quindi la soluzione $f(\rho)$ non può essere una serie, ma deve essere un polinomio di grado σ finito. Affinché ciò si verifichi

$$\sigma + \ell + 1 - \frac{1}{\sqrt{\epsilon}} = 0 \quad ,$$

con σ $\underbrace{\text{intero}}_{\text{positivo}}$ o nullo.

Di conseguenza $1/\sqrt{\epsilon}$ è un intero positivo:

$$\frac{1}{\sqrt{\epsilon}} = n \quad , \qquad \text{con} \quad n = \sigma + \ell + 1 = 1, 2, \ldots$$

Troviamo quindi (vedi Eq. (66)) gli autovalori dell'energia

$$\boxed{E_n = \frac{E_0}{n^2} \quad , \qquad n = 1, 2, \ldots} \qquad (76)$$

Per l'idrogeno $E_0 = -13.59 \ eV$

Appendix F

Potential Barrier and Tunnel Effect

Procedendo come nel caso della buca' di poten=
ziale finita, scriviamo la soluzione nelle tre
regioni, considerando il solo caso $E < U_0$ (*)

(1) $e^{ikx} + R e^{-ikx}$; $k = \sqrt{\frac{2mE}{\hbar^2}}$

↑incidente ↑riflessa

↑qui poniamo arbitrariamente il coefficiente pari
ad 1 perché non siamo interessati ai valori
assoluti ma solo ai rapporti di ampiezza
fra i vari termini.

(2) $A e^{\chi x} + B e^{-\chi x}$; $\chi = \sqrt{\frac{2m}{\hbar^2}(U_0 - E)}$

(3) $S e^{ikx}$

(*) per $E > 0$ vedi, per es. Merriah, Quantum Mechanics, Dover (1999)

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Raccordo ψ in $x=0$ e $x=L$:

$$\psi_{①}(0) = \psi_{②}(0) \quad\rightarrow\quad 1+R = A+B \qquad (45')$$

$$\psi'_{①}(0) = \psi'_{②}(0) \quad\rightarrow\quad ik-ikR = A\chi - B\chi \qquad (46')$$

$$\psi_{②}(L) = \psi_{③}(L) \quad\rightarrow\quad Ae^{\chi L}+Be^{-\chi L} = Se^{ikL} \qquad (47')$$

$$\psi'_{②}(L) = \psi'_{③}(L) \quad\rightarrow\quad A\chi e^{\chi L}-B\chi e^{-\chi L} = ikSe^{ikL} \qquad (48')$$

Dividiamo la (46) per (ik) e sommiamo l'Eq. così ottenuta all' Eq. (45):

$$2 = A\left(1 - i\frac{\chi}{k}\right) + B\left(1 + i\frac{\chi}{k}\right) \qquad (49')$$

Dividiamo la (48') per (ik) e uguagliamo il primo membro della equazione così ottenuta al primo membro della (47'):

$$A e^{\chi L}\left(1 + \frac{B}{A}e^{-2\chi L}\right) = -\frac{i\chi}{k} A e^{\chi L}\left(1 - \frac{B}{A}e^{-2\chi L}\right),$$

da cui otteniamo

$$\frac{B}{A}e^{-2\chi L} = -\frac{1 + i\frac{\chi}{k}}{1 - i\frac{\chi}{k}}, \qquad (50')$$

Introduciamo la (50') nella (47'):

$$A e^{\chi L}\left(1 - \frac{1 + i\frac{\chi}{k}}{1 - i\frac{\chi}{k}}\right) = S e^{ikL} \qquad ; da\ cui\ si\ ?$$

$$S = e^{-ikL} A e^{\chi L}\frac{-2i\,\chi/k}{1 - i\frac{\chi}{k}} \qquad (51')$$

Usiamo ora l'Eq. (50') per esprimere B in funzione di A

$$B = \frac{1 + \frac{i\chi}{k}}{1 - i\frac{\chi}{k}} A e^{2\chi L}$$

e sostituiamo quest'ultima espressione nella (49'):

$$2 = A\left(1 - i\frac{\chi}{k}\right) - \frac{1 + i\frac{\chi}{k}}{1 - i\frac{\chi}{k}} A e^{2\chi L}\left(1 + i\frac{\chi}{k}\right);$$

$$2 = A \frac{\left(1 - i\frac{\chi}{k}\right)^2 - \left(1 + i\frac{\chi}{k}\right)^2 e^{2\chi L}}{1 - i\frac{\chi}{k}};$$

$$A = \frac{2\left(1 - i\chi/k\right)}{\left(1 - i\frac{\chi}{k}\right)^2 - \left(1 + i\frac{\chi}{k}\right)^2 e^{2\chi L}}.$$

Inserendo quest'ultima equazione nella (51') otteniamo finalmente S.

$$S = e^{-ikL} \frac{2\left(1 - i\frac{\chi}{k}\right)}{\left(1 - i\frac{\chi}{k}\right)^2 - \left(1 + i\frac{\chi}{k}\right)^2 e^{2\chi L}} e^{\chi L} \frac{-2i\frac{\chi}{k}}{\left(1 - i\frac{\chi}{k}\right)} =$$

$$= \frac{-4i\frac{\chi}{k} e^{-ikL}}{\left(1 - i\frac{\chi}{k}\right)^2 e^{-\chi L} - \left(1 + i\frac{\chi}{k}\right)^2 e^{\chi L}} = \frac{2 e^{-ikL}}{-i\frac{k}{2\chi}\left(1 - \frac{\chi^2}{k^2}\right) \cdot 2 \sinh \chi L + 2 \cosh \chi L} =$$

$$S = e^{-ikL}\left[\cosh(\chi L) + \frac{i}{2}\left(\frac{\chi}{k} - \frac{k}{\chi}\right) \sinh(\chi L)\right]^{-1} \qquad (52')$$

Possiamo ora calcolare la probabilità che una particella proveniente da $x < 0$, con energia E inferiore all'energia della barriera ($E < U_0$) attraversi la barriera stessa:

$$T = \text{"tunneling probability"} = \frac{|\psi_{\text{③}}|^2}{|\psi_{\text{① incid}}|^2} = \frac{|SS^*|}{1} = SS^* \tag{53'}$$

$\uparrow$ o "trasparenza"

Usando l'Eq. (52'), otteniamo $(*)$

$$T = \left[\cosh^2 \chi L + \frac{1}{4}\left(\frac{\chi}{k} - \frac{k}{\chi}\right)^2 \sinh^2 \chi L \right]^{-1} =$$

$$= \left\{ 1 + \left[1 + \frac{1}{4}\left(\frac{\chi}{k} - \frac{k}{\chi}\right)^2 \right] \sinh^2 \chi L \right\}^{-1} = \tag{53 ℓ'}$$

$$= \left\{ 1 + \frac{1}{4}\frac{(\chi^2 + k^2)^2}{k^2 \chi^2} \sinh^2 \chi L \right\}^{-1} = \quad \longleftarrow \quad \text{usando } k^2 = \frac{2mE}{\hbar^2}$$

$$\chi^2 = \frac{2m}{\hbar^2}(U_0 - E)$$

$$= \left\{ 1 + \frac{1}{4}\frac{U_0^2}{E(U_0 - E)} \sinh^2 \left[\frac{2mL^2}{\hbar^2}(U_0 - E)\right]^{1/2} \right\}^{-1} =$$

$$\boxed{T = \left\{ 1 + \frac{1}{4}\frac{\sinh^2\left[\alpha^2(1-y)\right]^{1/2}}{y(1-y)} \right\}^{-1}, \tag{54'}}$$

$$\boxed{\text{dove} \quad y = \frac{E}{U_0} \leqslant 1 \quad e \quad \alpha^2 = \frac{2mL^2}{\hbar^2}U_0 \tag{55'}}$$

$(*)$ Se $f = \frac{a}{b + ic}$, $ff^* = \frac{a^2}{b^2 + c^2}$

Procedendo in modo analogo a quanto svolto finora si trova l'espressione della trasparenza anche per il caso $E > U_0$ (energia della particella maggiore dell'energia della barriera. Si trova che, per E prossime ad U_0 si ha un certo grado di riflessione e quindi $T < 1$.

L'espressione generale della T risulta essere:

$$T = \begin{cases} \left\{ 1 + \dfrac{\sinh^2 \left[\alpha^2 (1-y)\right]^{1/2}}{4\,y\,(1-y)} \right\}^{-1/2} & y \leq 1 \quad (54') \\[4mm] \left\{ 1 + \dfrac{\sin^2 \left[\alpha^2 (y-1)\right]^{1/2}}{4\,y\,(y-1)} \right\}^{-1/2} & y \geq 1 \quad (56) \end{cases}$$

con α e y date dalle Equazioni $(55')$.

L'andamento di $T(y)$ per $\alpha = 5$ è mostrato nella figura seguente:
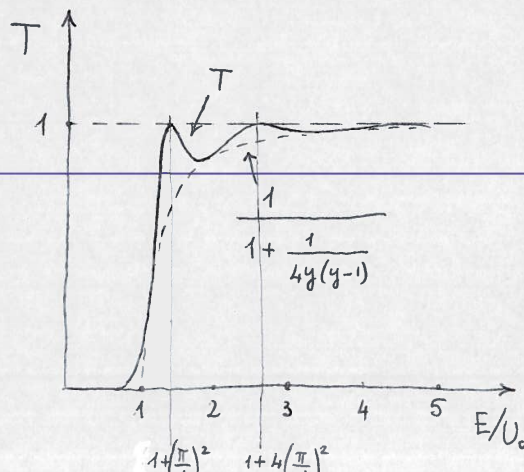
Osservazioni:

○ per $E < U_0$ e $\chi L \gg 1$ si trova

~~per $\chi L \gg 1$ si trova~~   (vedi 53 ℓ')

$$T \simeq 16 \, \frac{E}{U_0} \left(1 - \frac{E}{U_0}\right) e^{-2\chi L}$$

$\longrightarrow$ vedi Sezione 6.4

◎ per $E = U_0$:

$$T = \left[1 + \frac{1}{2} \, \frac{mL^2}{\hbar^2} U_0\right]^{-1} = \left[1 + \frac{1}{4} \, \alpha^2\right]^{-1}$$

◎ per $E > U_0$ (vedi Eq. (56))

$$T = 1, \quad \text{per} \quad \left[\alpha^2(y-1)\right]^{1/2} = n\pi \qquad n = 1, 2, \ldots$$

$$\longrightarrow y = 1 + n^2 \left(\frac{\pi}{\alpha}\right)^2$$

$\uparrow$
E/U_0

◎ per $E \gg U_0$ $T \to 1$ (limite classico)

Alcune applicazioni:

- diodo tunnel
- reazioni nucleari di fusione
- decadimento α
- microscopia a scansione a effetto tunnel.

Appendix G

Metodo dei moltiplicatori di Lagrange

Il metodo dei moltiplicatori di Lagrange consente di trovare i massimi di una funzione

$$y = f(x_1, x_2, \ldots, x_n,)$$

soggetta alle m condizioni

$$g_k(x_1, x_2, \ldots, x_n) = 0, \qquad k = 1, 2, \ldots, m.$$

Si dimostra che i massimi condizionati di f si trovano fra quelli non condizionati di

$$F = f + \alpha_1 g_1 + \alpha_2 g_2 + \alpha_3 g_3 + \ldots + \alpha_m g_m.$$

Soddisfano quindi le condizioni

$$\partial F/\partial x_i = \partial F/\partial \alpha_k = 0, \quad i = 1, 2, \ldots, n; \quad k = 1, 2, \ldots, m.$$

Le x_i estremanti si trovano allora risolvendo le i equazioni

$$\frac{\partial F}{\partial x_i} = 0.$$

I *moltiplicatori di Lagrange* α_k si trovano poi imponendo che i vincoli $g_k = 0$ siano soddisfatti.

Appendix H

Kinetic theory of the ideal gas

This Appendix contains sketchy notes, summarizing the main results of elementary kinetic theory. The students who are not familiar with these topics should refer to General Physics textbooks for undergraduates.[1]

H.1 From the macroscopic to the microscopic - Thermodynamics vs kinetic models

Thermodynamics concerns macroscopic systems (pieces of matter containing a very large number of atoms/molecules) at equilibrium [2], defined by *state variables*, such as volume V, mass m or number of moles n, pressure p, temperature T (as well as internal energy U, entropy S, enthalpy H, etc.)

In fact, pressure, temperature, internal energy, entropy are related to the microscopic behaviour of atoms/molecules (e.g. the molecules of a gas).

Kinetic theory looks for a microscopic interpretation of such properties. In a sense, kinetic theory is a link between the macroscopic world and the atomic/molecular world.

Even in a very small macroscopic quantity of matter there are very large number of atoms/molecules. E.g. in 1 mm^3 of air there are about 2.5×10^{16} molecules. [Check this number as an exercise]. Of course, we cannot study the motion of each molecule. We can only take a statistical approach, and consider *distribution functions* and appropriately averaged quantities.

In the following, we consider a very simple kinetic model of an ideal gas, leading to a few very important and general results. Before doing this, let us

---

[1]E.g. Halliday, Resnick and Krane, *Physics* (2 volumes), Wiley (2001); for the Italian speaking students, any of the textbook covering the programmes of the traditional courses of Fisica I and Fisica II.)

[2]Thermodynamic equilibrium: mechanical equilibrium and thermal equilibrium and chemical equilibrium

summarize well know ideal gas properties.

H.2 Ideal gas - Experimental facts and results from thermodynamics

An ideal gas is a gas obeying the law

$$pV = nRT, \tag{H.1}$$

where p is the pressure, V the volume occupied by the gas, n the number of moles, T the absolute temperature, and R is the so-called gas constant. Using SI units (i.e. pressure in pascal, volume in m^3, temperature in K), $R = 8.31$ J/(mol K).

At normal conditions, i.e. atmospheric pressure and temperature of 288.15 K,[3] real gases can be treated like ideal gases within reasonable tolerances. Actually, a gas behaves more like an ideal gas at higher temperature and lower pressure. In practice (e.g. for engineering applications) gases at temperatures well above boiling point and at pressures about or smaller than atmospheric pressure can be considered as ideal gases.

Summary of results from experiments and thermodynamics:

- internal energy
$$U = nC_\mathrm{v}T + \text{constant}, \tag{H.2}$$

- molar heat at constant volume

$$C_\mathrm{v} = \begin{cases} \frac{3}{2}R, & \text{monoatomic gas} \\[2mm] \frac{5}{2}R, & \text{diatomic gas} \\[2mm] 3R & \text{polyatomic gas} \end{cases} \tag{H.3}$$

- molar heat at constant pressure

$$C_\mathrm{p} = C_\mathrm{v} + R \tag{H.4}$$

- entropy

$$\begin{aligned} S &= nR\ln\left(VT^{C_\mathrm{v}/R}\right) + \text{constant} & \text{(H.5)} \\ &= n\left(C_\mathrm{v}\ln T + R\ln V\right) + \text{constant.} & \text{(H.6)} \end{aligned}$$

---

[3]More precisely, these are the International Standard Metric Conditions. Other standards refer to temperatures of 273.15 K, or 293.15 K, or 298.15 K.

H.3   Microscopic model

Basic assumptions:

- the gas consists of identical molecules, of mass m, which behave as rigid spheres, and collide elastically with each other;

- the total volume occupied by the molecules is negligible with respect to the volume V of the container;

- the molecules do not interact with each other, but when they collide, nor are subjected to any external force; therefore their path between two subsequent collisions is a straight path;

- the walls of the container have mass much larger than that of a molecule; the collisions between molecules and wall are elastic; there is no friction during the collision, so that no tangential force arises;

- the gas is homogeneous and isotropic, i.e. the average density of the molecules is everywhere the same, and molecule motion is (statistically) independent of the direction.

Exercise: justify the above assumptions, using knowledge available at the time (2nd half of the nineteenth century) the kinetic model of the ideal gas was developed.

H.4   Pressure

We know from hydrostatics that pressure in a point of a fluid is independent of the orientation of the surface we take to measure the pressure. We also know that the difference of pressure between two points of a homogeneous fluid is given by $\Delta p = \rho g h$, with ρ the fluid mass density, g gravitational acceleration, and h difference of height. Given the low density, in many cases we can neglect this difference when considering gases.

To compute the pressure of a gas consisting of N molecules in a rigid container of volume V we can then consider what happens at the walls of the container. Consider, for simplicity, a wall element of area S orthogonal to the x-axis of a Cartesian system. When a molecule hits this surface, the surface receives a small impulse. The pressure just results from the impulses delivered to the wall by the very large number of collisions occurring at the wall. (We will be more quantitative later.)

Let us start by considering a single collision of a molecule with velocity $\mathbf{v} = (v_x, v_y, v_z)$ with the wall element. Since the collision is elastic, there is no friction and the mass of wall is extremely larger than the mass of the molecule, the molecule will not change its speed: its x-component will simply change sign, while the other two components will not change; the velocity immediately after
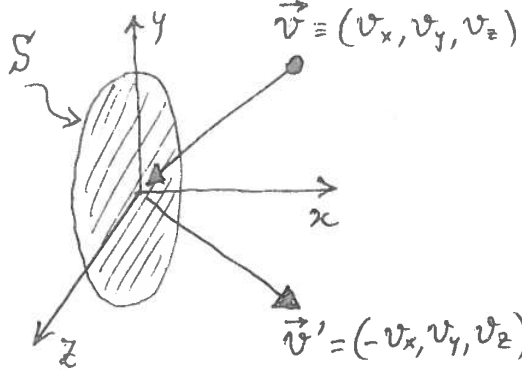
Figure H.1: Collision of a molecule with a wall element.

the collision will be $\mathbf{v}' = (-v_x, v_y, v_z)$. Momentum of the molecule will therefore change by

$$
\begin{aligned}
\Delta p_x &= -2mv_x & \text{(H.7)} \\
\Delta p_y &= 0 & \text{(H.8)} \\
\Delta p_z &= 0 & \text{(H.9)}
\end{aligned}
$$

For the impulse-momentum theorem, the particle will suffer an impulse $I_x = -2mv_x$. The wall will suffer an opposite impulse,

$$
I_x = \int_{t_0}^{t_1} f \, dt = 2mv_x, \tag{H.10}
$$

with f a force directed toward the normal to the surface, and t_0 and $t_1 = t_0 + \Delta t$ are times just before and just after the collision. The average force during the collision can than be estimated as

$$
\overline{f} = \frac{2mv_x}{\Delta t} \tag{H.11}
$$

In the same time interval the element of area S will be hit by many other molecules. Assume for the moment that all molecules have velocities with the same $x-$component v_x. The number of collisions in the interval Δt is equal to the number of molecules within a prism of basis S and height $v_x \Delta t$, i.e. $(1/2)(N/V)Sv_x\Delta t$. (The factor $1/2$ is there because in our simplified picture half of the molecules move in one direction, half in the opposite one.) The total force normal to the surface is then

$$
F = \frac{2mv_x}{\Delta t} \frac{N}{2V} Sv_x \Delta t = \frac{N}{V} Smv_x^2 \tag{H.12}
$$

To account that, in fact, molecules move with different velocities we have to replace v_x^2 with the corresponding quantity averaged over all particles, i.e. the mean square velocity $\overline{v_x^2}$. In addition, the assumption of isotropy allows us to write

$$\overline{v^2} = \overline{v_x^2 + v_y^2 + v_z^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}, \tag{H.13}$$

hence $\overline{v_x^2} = \overline{v^2}/3$. In conclusion, the pressure, i.e. the normal force acting on a unit surface is

$$p = \frac{F}{S} = \frac{1}{3}\frac{N}{V}m\overline{v^2} \tag{H.14}$$

or

$$\boxed{p = \frac{1}{3}\rho\overline{v^2}}, \tag{H.15}$$

where ρ is the mass density.

H.5   Temperature

Compare Eq. (H.14) with the ideal gas Equation-of-state (H.1):

$$\frac{1}{3}\frac{N}{V}m\overline{v^2} = \frac{nRT}{V}. \tag{H.16}$$

Writing $N = nN_{\mathrm{Av}}$, where $N_{\mathrm{Av}} = 6.022 \times 10^{23}$ is the Avogradro number. we immediately find that the average kinetic energy of a molecule is proportional to the temperature:

$$\boxed{\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_{\mathrm{B}}T}, \tag{H.17}$$

where

$$\boxed{k_{\mathrm{B}} = \frac{R}{N_{\mathrm{Av}}} = 1.3806 \times 10^{-23}\ \ \mathrm{J/K}} \tag{H.18}$$

is the Boltzmann constant.

H.6   Internal energy and equipartition of energy

The assumption of non-interacting molecules implies the absence of forces between molecules (except when they collide), and hence the absence of any potential energy. The only form of energy is kinetic energy of the molecules, and then

$$U = N\frac{1}{2}m\overline{v^2} = N\frac{3}{2}k_{\mathrm{B}}T = n\left(\frac{3}{2}R\right)T. \tag{H.19}$$

We have then recovered the classical expression of the energy of an ideal monoatomic gas; see Eqs. (H.2) and (H.3). This confirms that the energy of the gas is just the kinetic energy of the molecules.

Equation (H.17) also shows that the average kinetic energy of a point-like molecule, with three degrees of freedom is three times $(1/2)k_BT$. This result suggests that the average kinetic energy of a molecule is $(1/2)k_BT$ for each degree of freedom. Indeed this would explain the molar heats at constant volume of ideal mono-atomic gases (molecules with three degrees of freedom), diatomic gases (five degrees of freedom) and polyatomic gases (six degrees of freedom).

This observation led to a more general statement, known as **principle of equipartition of energy**: in a system with a large number of particles, the average energy per particle and per degree of freedom is equal to $\frac{1}{2}k_BT$.
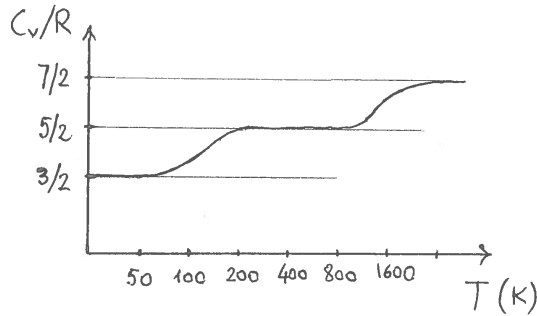

Figure H.2: Molar heat of Hydrogen vs temperature. In the temperature interval 200–600 K $C_v \simeq (5/2R)$, at higher temperatures, when molecular vibrations occur (with two additional degrees of freedom), C_v approaches $(7/2)R$.

The equipartition principle explains, e.g., the behaviour of specific heats of gases at moderate-to-high temperatures and of not-too-cold solids.[4]. However, we shall see that it is not universal: e.g. it does not apply at very low temperatures, and for photons of energy much larger than k_BT.

H.7   Entropy

To be written

H.8   Maxwell velocity distribution

Temperature is related to the average square velocity, but of course individual molecules have different velocities. Here we determine how velocity are distributed, i.e how many particles have velocity close to a certain value, or within

---

[4]The Dulong-Petit law, according to which the molar heat of solids is $3R$, is recovered since atoms in a crystalline solids can be considered as oscillators in a 3D space, and each oscillator has three degrees of freedom associated to kinetic energy and three associated to potential energy.

a certain interval, or laying in a certain volume in velocity space. In particular,

$$dN(\mathbf{v}) = NP(\mathbf{v})d\mathbf{v} = NP(\mathbf{v}) \, dv_x \, dv_y \, dv_z \qquad \text{(H.20)}$$

tells us how many particles have velocities in a phase space element of volume $dv_x \, dv_y \, dv_z$ centred about the velocity $\mathbf{v} = (v_x, v_y, v_z)$.

For the isotropy of the gas (i.e equivalence of all directions):

- P must be a function of the magnitude of the velocity only, hence $P = P(v)$ or $P = P(v^2)$ or $P = P(E)$;

- $dv_x \, dv_y \, dv_z = 4\pi v^2 dv$

The number of molecules with velocity between v and $v + dv$ is then

$$dN(v) = NP(E)4\pi v^2 dv \qquad \text{(H.21)}$$

An expression for $P(E)$ is obtained by analyzing the collisions between particles, taking into account that collisions are elastic and the gas is in equilibrium. This means that energy is conserved in each collision and that the energy (or velocity) distribution of particles cannot be changed by collisions. Let us consider a collision between two particles A and B, with energy E_a and E_b, respectively, before the collision and energy E'_a and E'_b, respectively, after the collision. The probability of such a collision is proportional to the product of the densities of the two species, i.e.

$$R_{ab \to a'b'} = C_{ab \to a'b'}P(E_a)P(E_b), \qquad \text{(H.22)}$$

where $C_{ab \to a'b'}$ is a constant. Let us also consider the probability of the opposite process, i.e. the collision between particles with energies E'_a and E'_b prior to the collision and E_a and E_b after the collision:

$$R_{a'b' \to ab} = C_{a'b' \to ab}P(E'_a)P(E'_b). \qquad \text{(H.23)}$$

The two rates must be equal, otherwise the system would not be in equilibrium; furthermore, for micro-reversibility (i.e. reversibility at the microscopic level), $C_{a'b' \to ab} = C_{ab \to a'b'}$. In addition, for energy conservation $E'_a + E'_b = E_a + E_b$, which allow us to write

$$E'_a = E_a + \Delta E; \qquad E'_b = E_b - \Delta E. \qquad \text{(H.24)}$$

Equating the rates (H.22) and (H.23) we then obtain

$$P(E_a)P(E_b) = P(E_a + \Delta E)P(E_b - \Delta E) \qquad \text{(H.25)}$$

It is easily checked that the only allowable form of the function $P(E)$ is

$$P(E) = Ae^{-\beta E} = Ae^{-\beta \frac{1}{2}mv^2}, \qquad \text{(H.26)}$$

where both A and β are positive constants. They are determined by requiring particle and energy conservation, i.e.,

$$N = \int dN(v) = \int_0^\infty NAe^{-\beta\frac{1}{2}mv^2}4\pi v^2 dv, \tag{H.27}$$

$$\frac{3}{2}Nk_BT = \int \frac{1}{2}mv^2 dN(v) = \int_0^\infty N\frac{1}{2}mv^2 Ae^{-\beta\frac{1}{2}mv^2}4\pi v^2 dv. \tag{H.28}$$

With some algebra (do it as an excercise [5]) one obtains

$$\beta = \frac{1}{k_BT}, \tag{H.29}$$

$$A = N\left(\frac{m}{2\pi k_BT}\right)^{3/2}, \tag{H.30}$$

so that the final expression of the velocity distribution function, first obtained by Maxwell, is

$$\boxed{dN(v) = N\left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\frac{mv^2}{k_BT}}4\pi v^2 dv} \tag{H.31}$$

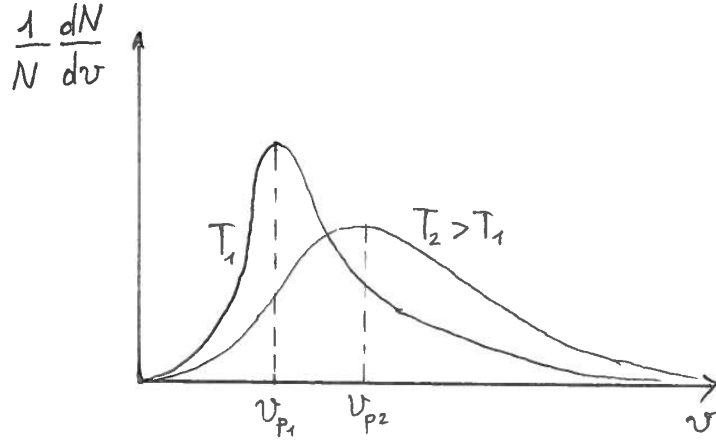

Figure H.3: Maxwell distribution function

The Maxwell velocity distribution function is plotted in Fig. H.3. We see that $F(v) \propto v^2$ as $v \to 0$, while $F(v) \propto e^{-mv^2/2k_BT}$ at large velocities. The **most probable velocity** (i.e. the velocity at the maximum of the distribution is)

$$\boxed{v_p = \sqrt{\frac{2k_BT}{m}}}. \tag{H.32}$$

---

[5]Use $\int_0^\infty x^2 e^{-ax^2}dx = (1/4a)\sqrt{\pi/a}$, and $\int_0^\infty x^4 e^{-ax^2}dx = (3/8a^2)\sqrt{\pi/a}$,

[Excercise: proof this last result]

The figure also shows that as the temperature increases,

- v_p increases;

- the peak of the distribution lowers;

- the peak broadens.

The area below the distribution, instead, remains constant, because the total number of particles is constant.

Maxwell distribution of velocities finds application in a number of areas of physics and chemistry. It explains Arrhenius law of chemical kinetics, the temperature dependence of certain types of electrical polarization, of certain magnetic properties, the temperature dependence of the rate of thermonuclear fusion reactions, etc.

H.9 Boltzmann factor

According to Eqs. (H.26) and (H.29) the probability $P(E)$ is proportional to $\exp(-E/k_BT)$, where E is the molecule kinetic energy. (Quantum) statistical mechanics indeed shows that this is a particular case of a more general result, applying to any form of energy (kinetic, gravitational, electrical, chemical, etc.): the ratio of the probabilities of two states of energy E_1 and E_2, respectively, is

$$\frac{P(E_1)}{P(E_2)} = \frac{e^{-\frac{E_1}{k_BT}}}{e^{-\frac{E_2}{k_BT}}},$$ (H.33)

with

$$\boxed{e^{-\frac{E}{k_BT}} : \quad \textbf{Boltzmann factor}}$$ (H.34)

H.10 Examples and exercises

1. Compute the average square velocity of nitrogen molecules in air at standard conditions. This velocity turns out to be about 30% larger than sound speed. Is there any connection between the two velocities?

2. Compute the molecular density of air at standard conditions.

3. Consider a container with air at standard conditions. Estimate the number of molecular collisions in one second onto a piece of wall with surface of 1 mm^2.

4. What is the average interparticle $\overline{d}$ distance in air?

5. **Cross-section and mean-free-path**

   Molecules move randomly and collide with each other. Their path consists in straight segments of different length and direction. We call **mean-free-path** the average path between two collisions, i.e. the average length of the above segments.
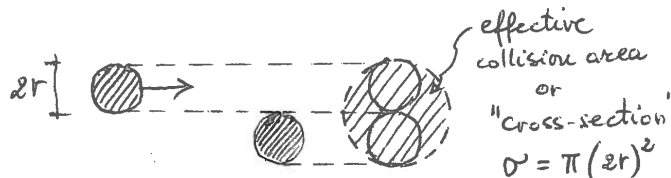

Figure H.4: Cross-section for the collision between two identical molecules.

A useful related concept is that of cross-section. Two identical spherical molecules collide if their centers come to a distance smaller than their diameter $2r$. The **cross-section** for such hard-sphere collisions[6] is then $\sigma = \pi(2r)^2$. For computing the mean-free-path, we can either think of identical molecules of radius r or of projectile molecules of radius $2R$ and target point-like molecules with vanishing radius. Using this last picture, the mean-free-path is equal to the length l of a cylinder of cross-sectional area $A = \sigma$ containing, on average, 1 molecule. Since 1 molecule occupies, on average a volume $V_1 = V/N = 1/n$ (here n is the molecule density[7]), then $V_1 = Al = \sigma l$, and

$$\boxed{l = \frac{1}{n\sigma}} = \frac{1}{n\pi(2r)^2}. \tag{H.35}$$

Use this last result to estimate the mean free path of a molecule in air. (Assume $r = 1.5 \times 10^{-10}$ m)

6. Next, show that, in air, $2r \ll \bar{d} \ll l$.

7. Finally, compute the average number of collisions suffered by a molecule of nitrogen in air at standard conditions.

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[6]A more general definition of cross-section will be discussed later in this course.

[7]Note that in other sections we have used the same symbol n to denote the number of moles.