Lecture notes on Quantum Mechanics

for the Course *Principles of Atomic and Nuclear Physics*

M.S. in Energy Engineering, Nuclear 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. 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.

Principles of Atomic and Nuclear Physics 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. Indeed, many, excellent textbooks on quantum mechanics are not adequate, because meant for one- or even two-semester courses and often using too abstract formalism.

This manuscript (as well as my lectures\(^1\)) deal with basics of special relativity and of quantum mechanics using wave mechanics formalism. It includes simple applications of quantum mechanics to a few standard model problems, which aim at providing the students examples concerning energy and momentum quantization, bound and free states, tunneling and measurement uncertainty.

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 Loren-\(^1\)Actually the lectures also include elements of kinetic theory of gases, black body spectrum, photoelectric effect, Compton effect and Bohr’s atomic model. They are not presented here because they are treated by most General Physics textbooks at the level required by the present Course.
tian 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

Preface iii

1 Classical physics: success and crisis 1

2 Special relativity 3
   2.1 The postulates 3
   2.2 Time and simultaneity 4
   2.3 Consequences of the constancy of the speed of light 4
      2.3.1 Time dilatation 5
      2.3.2 Length contraction 7
   2.4 Lorentz transformations 8
      2.4.1 Recovering time dilatation and length contraction 9
      2.4.2 Transformation of velocities 10
      2.4.3 Lorentz matrix 11
      2.4.4 Four-vectors 12
   2.5 Momentum, mass, energy 13
      2.5.1 Momentum-energy 4-vector 13
      2.5.2 Momentum 13
      2.5.3 Energy 14
      2.5.4 Kinetic energy 15

3 Old Quantum Theory 17

4 Material waves 19
   4.1 de Broglie associated wave 19
      4.1.1 Justification of de Broglie’s hypothesis 19
      4.1.2 Experimental confirmation 20
      4.1.3 Discussion 20
   4.2 Heisenberg’s uncertainty principle 22
      4.2.1 Position and momentum 22
      4.2.2 Energy and time 24
## CONTENTS

5 Quantum Mechanics: Schrödinger equation 25
  5.1 Wavefunction ........................................... 25
  5.2 Wave equation for a free particle ..................... 26
  5.3 Time-dependent Schrödinger equation .................. 27
  5.4 Time-independent Schrödinger equation ............... 28
  5.5 Interpretation of the wavefunction .................... 28
  5.6 Wavefunction normalization ............................ 29
  5.7 Eigenvalues and eigenfunctions ....................... 29
  5.8 Operators and commutators ............................ 30

6 Quantum Mechanics: 1D problems 33
  6.1 Infinite potential well ............................... 34
  6.2 Finite potential well .................................. 37
  6.3 Potential step ........................................ 43
    6.3.1 $E > V_0$ ........................................ 44
    6.3.2 $E < V_0$ ........................................ 46
  6.4 Potential barrier and tunnel effect ................... 47

7 Elementary atomic physics 49
  7.1 Operators in spherical coordinates .................... 49
  7.2 Angular momentum, z-component ....................... 50
  7.3 Total angular momentum ................................ 51
  7.4 Angular momentum and parity ........................ 54
  7.5 Schrödinger equation for the hydrogen atom .......... 54
  7.6 Spin and Pauli exclusion principle ................... 60
  7.7 Electrons in the atom ................................ 62
  7.8 Indistinguishability ................................... 63

8 Quantum statistics 65
  8.1 Descrizione del sistema ............................... 66
  8.2 Statistica di Bose-Einstein ............................ 66
    8.2.1 Statistica di Bose-Einstein per i fotoni ........... 66
    8.2.2 Statistica di Bose-Einstein per un sistema di $N$ particelle 71
  8.3 Statistica di Fermi-Dirac ............................ 72
  8.4 Limite classico: statistica di Boltzmann ............... 73

9 s-wave scattering 75
  9.1 Partial wave expansion ................................ 75
  9.2 General expression of the cross-sections ............. 76
  9.3 Scattering from a hard sphere ......................... 79
  9.4 Potential scattering and Breit-Wigner cross-section .. 80
  9.5 Absorption cross-section ................................ 84

Appendices 85

A Wave packets and group velocity 87
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 microscopic 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.

• Newton’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, magnetical, 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, 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).
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.\(^2\) 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 \(^3\):

1. The special principle of relativity

   Physical laws should be the same in every inertial frame of reference.

---

\(^1\)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)

\(^2\)A trivial example: the electrodynamic force \(q(E + \vec{v} \times \vec{B})\) depends on velocity, so a different force acts on a particle, depending on the observer’s frame. In fact, special relativity tells us how electric and magnetic fields transform from one system to another, and the resulting force does not change.

\(^3\)In fact, one also postulates that space is homogeneous and isotropic.
2. Constancy of the speed of light

Light is always propagated in empty space with a definite velocity \( c \) which is independent of the state of motion of the emitting body.\(^4\)

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 and the source move 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.

\(^4\)English translation of the original statement in A. Einstein, *Annalen der Physik* 17, 891 (1905).
2.3. CONSEQUENCES OF THE CONSTANCY OF THE SPEED OF LIGHT

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

\[
\Delta t_0 = \frac{2l}{c}. \quad (2.1)
\]

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 (see Fig. 2.3)

\[
\Delta t = \frac{2\sqrt{l^2 + (V \Delta t/2)^2}}{c} = 2\sqrt{\left(\frac{\Delta t_0}{2}\right)^2 + \left(\frac{V \Delta t}{2}\right)^2}, \quad (2.2)
\]
from which we obtain
\[ \Delta t = \frac{\Delta t_0}{\sqrt{1 - \frac{V^2}{c^2}}} : \]
(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
\[ \Delta t = \Delta t_0 \gamma, \]
(2.4)
with the function \( \gamma \) (known as the relativistic \( \gamma \) factor) defined by
\[ \gamma = \frac{1}{\sqrt{1 - \frac{V^2}{c^2}}} \geq 1. \]
(2.5)

An important experimental evidence (one of many): the elementary particle \( \mu \) is unstable, with measured (proper) mean lifetime of 2.2 \( \mu s \). A \( \mu \) moving
2.3. CONSEQUENCES OF THE CONSTANCY OF THE SPEED OF LIGHT

with velocity approaching that of light has an average path of 660 m. A large number of \( \mu \)’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 dilatated 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 \( M_1 \).

![Figure 2.4: Experiment to evidence length contraction. The ruler with the mirrors move 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.](image)

For an observer sitting on the ruler

\[
\Delta t_0 = 2L_0/c, \tag{2.6}
\]

with \( \Delta t_0 \) a proper time.

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

\[
\Delta t = \Delta t_1 + \Delta t_2 = \frac{L}{c-V} + \frac{L}{c+V} = \frac{2L}{c} \left( \frac{1}{c-V} + \frac{1}{c+V} \right). \tag{2.7}
\]

Time intervals \( \Delta t \) and \( \Delta t_0 \), in turn, are related by Eq. (2.3), and then

\[
\Delta t = \frac{\Delta t_0}{\sqrt{1 - \frac{V^2}{c^2}}} = \frac{2L_0/c}{\sqrt{1 - \frac{V^2}{c^2}}}. \tag{2.8}
\]
We find the relation between the lengths by equating the right hand sides of Eq. (2.7) and Eq. (2.8), which gives

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

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 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

$$x = \frac{x' + Vt'}{\sqrt{1 - \frac{V^2}{c^2}}} \quad (2.10)$$
$$y = y' \quad (2.11)$$
$$z = z' \quad (2.12)$$
$$t = \frac{t' + Vx'}{\sqrt{1 - \frac{V^2}{c^2}}} \quad (2.13)$$

Figure 2.5: Reference frames $S = (xyz)$ and $S' = (x'y'z')$
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 \(x = x' + Vt; t = t'\) 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 sistem \(S'\), 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 \(\Delta t\) given by Eq. (2.13) with \(x' = 0\), i.e.

\[
\Delta t = \frac{\Delta t'}{\sqrt{1 - \frac{V^2}{c^2}}} \tag{2.18}
\]

which is just Eq. (2.3).

#### Length contraction

We assume that an observer in frame \(S\) measures a given length \(\Delta x\) 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

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

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

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

(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

\[ v_x = \frac{dx}{dt}, \quad (2.23) \]
\[ v_y = \frac{dy}{dt}, \quad (2.24) \]
\[ v_z = \frac{dz}{dt}, \quad (2.25) \]

and

\[ v'_x = \frac{dx'}{dt'}, \quad (2.26) \]
\[ v'_y = \frac{dy'}{dt'}, \quad (2.27) \]
\[ v'_z = \frac{dz'}{dt'}. \quad (2.28) \]

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

\[ dx = \gamma(dx' + V dt'), \quad (2.29) \]
\[ dy = dy', \quad (2.30) \]
\[ dz = dz', \quad (2.31) \]
\[ dt = \gamma(dt' + \frac{V}{c^2} dx'). \quad (2.32) \]
and then we can write the velocity components in the $S$ frame as

$$v_x = \frac{\gamma(dx' + V dt')}{\gamma(dt' + \frac{V}{c^2} dx')}$$  \hspace{1cm} (2.33)$$

$$v_y = \frac{dy'}{\gamma(dt' + \frac{V}{c^2} dx')}$$  \hspace{1cm} (2.34)$$

$$v_z = \frac{dz'}{\gamma(dt' + \frac{V}{c^2} dx')}$$  \hspace{1cm} (2.35)$$

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

$$v_x = \frac{v_x' + V}{1 + \frac{V}{c^2} v_x'}$$ \hspace{1cm} (2.37)$$

$$v_y = \frac{v_y'}{\gamma(1 + \frac{V}{c^2} v_x')}$$ \hspace{1cm} (2.38)$$

$$v_z = \frac{v_z'}{\gamma(1 + \frac{V}{c^2} v_x')}$$ \hspace{1cm} (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

$$v_x = \frac{v_x' + c}{1 + \frac{c^2}{c^2} v_x'} = \frac{v_x' + c}{c + v_x'} = c.$$ \hspace{1cm} (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

$$\vec{x} = (x_1, x_2, x_3, x_4) = (x, y, z, ct) = (\vec{x}, ct)$$ \hspace{1cm} (2.41)$$

and analogously

$$\vec{x}' = (x_1', x_2', x_3', x_4') = (x', y', z', ct') = (\vec{x}', ct'),$$ \hspace{1cm} (2.42)$$
we can write the Lorentz transformations as

\[\begin{align*}
x_1' &= \gamma x_1 - \beta \gamma x_4, \\
x_2' &= x_2, \\
x_3' &= x_3, \\
x_4' &= -\beta \gamma x_1 + \gamma x_4,
\end{align*}\]

(2.43) (2.44) (2.45) (2.46)

where \(\beta = V/c\). In compact vector form

\[x' = Ax^T,\]

(2.47)

where \(x^T\) is the transpose of \(x\) and

\[A = \begin{pmatrix} \gamma & 0 & 0 & -\beta \gamma \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -\beta \gamma & 0 & 0 & \gamma \end{pmatrix}\]

(2.48)

is the Lorentz matrix. Analogously,

\[x = A^{-1}x'^T,\]

(2.49)

where

\[A^{-1} = \begin{pmatrix} \gamma & 0 & 0 & \beta \gamma \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ \beta \gamma & 0 & 0 & \gamma \end{pmatrix}\]

(2.50)

is the inverse of matrix \(A\).

### 2.4.4 Four-vectors

The four-component vectors \(x\) and \(x'\) 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 \(a\) is a four-component vector

\[a = (a_1, a_2, a_3, a_4)\]

(2.51)

that transforms according to Lorentz transformations, \(a' = Aa\), where \(A\) is Lorentz matrix.

The inner product of two \(4\)-vectors \(a\) and \(b\) is defined by

\[a \cdot b = a_1 b_1 + a_2 b_2 + a_3 b_3 - a_4 b_4.\]

(2.52)

(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,

\[\langle x, ct \rangle^2 = \langle x', ct' \rangle^2,\]

(2.53)

or

\[x^2 + y^2 + z^2 - c^2t^2 = x'^2 + y'^2 + z'^2 - ct'^2.\]

(2.54)
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 \( \sum m_i \vec{v}_i \) 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 \( \vec{x} = (x, y, z, ct) \) we define the 4-vector

\[
\vec{p} = (m_0 \frac{dx}{dt_0}, m_0 \frac{dy}{dt_0}, m_0 \frac{dz}{dt_0}, m_0 \frac{dc}{dt_0})
\]

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 \( \vec{p} \) can also be written as

\[
\vec{p} = (m_0 \gamma v_x, m_0 \gamma v_y, m_0 \gamma v_z, m_0 \gamma c)
\]

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

\[
\vec{p} = (m_0 \gamma v_x, m_0 \gamma v_y, m_0 \gamma v_z, m_0 \gamma c),
\]

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

\[
\vec{p} = (mv_x, mv_y, mv_z, mc) = (m\vec{v}, mc) = (\vec{p}, mc).
\]

2.5.2 Momentum

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

\[
\vec{p} = m\vec{v},
\]

but with the mass \( m \) depending on velocity:

\[
m = m_0 \gamma = \frac{m_0}{\sqrt{1 - v^2 / c^2}}
\]

The mass tends to infinity as the velocity approaches the speed of light \( c \).
CHAPTER 2. SPECIAL RELATIVITY

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

$$\vec{p} = m_0 c \gamma \vec{\beta}.$$  \hfill (2.62)

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

\[
|\vec{p}|^2 = |m\vec{v}|^2 - m^2 c^2 = (m_0 \gamma v)^2 - (m_0 \gamma c)^2 = m_0^2 \gamma^2 (-v^2 + c^2) \\
= -m_0^2 \gamma^2 \frac{1 - v^2}{c^2} = -m_0^2 c^2,
\]

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 $d|\vec{p}|^2 = d(|\vec{p}|^2 - m^2 c^2) = 0$, or

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

from which

$$\vec{v} \cdot d\vec{p} = c^2 dm.$$ \hfill (2.65)

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. (2.65) as

$$\vec{F} \cdot \vec{v} dt = c^2 dm.$$ \hfill (2.66)

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

$$dE = c^2 dm,$$ \hfill (2.67)

or

\[
E = mc^2 = \frac{m_0 c^2}{\sqrt{1 - \frac{v^2}{c^2}}} = m_0 c^2 \gamma.
\]  \hfill (2.68)

Equation (2.68) 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

$$E = \Delta m c^2.$$ \hfill (2.69)

Hence mass conservation is replaced by mass-energy conservation.
Note that using Eq. (2.68) the 4-vector $p$ can be written as

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

hence the name of momentum-energy 4-vector.

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

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

and using Eq. (2.63) we obtain an important relation between energy, momentum and rest mass, namely

$$E^2 = (pc)^2 + (m_0c^2)^2. $$

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. (2.66), $\vec{F} \cdot d\vec{v} = e^2 dm$, and integrate assuming a body at rest at time $t = 0$, thus obtaining

$$L = E - E_0 = mc^2 - m_0c^2, $$

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

$$T = mc^2 - m_0c^2 = m_0c^2(\gamma - 1).$$

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

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

and

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

We see that the classical limit $T = (1/2)m_0 V^2$ is recovered when the velocity $Vv \ll c$. As $v \rightarrow c$, $T$ grows indefinitely: see Fig. 2.6.
Figure 2.6: Kinetic energy $T$ vs $v^2$. 
Chapter 3

Particles, photons and Old Quantum Theory

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 \( E(\nu) = n\hbar\nu \) and giving up the principle of equipartition of energy in favour of level occupation according to the Boltzmann factor \( \exp(-E/k_B T) \).

- 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 \( l = nh = n\hbar/2\pi \), 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 \( E_n \),

\[
\begin{align*}
  r_n &= r_0 n^2, \\
  E_n &= E_0/n^2,
\end{align*}
\]

with \( r_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2} = 5.292 \times 10^{-11} \) m; Bohr’s radius.

17
and

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

with \( \varepsilon_0 \) 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 \( \nu_{mn} = (E_m - E_n)/\hbar \).

Treatments of
- Maxwell-Boltzmann distribution
- energy equipartition principle
- black body
- photoelectric effect
- Compton effect
- Bohr’s atom

at the level of detail required in this Course can be found in many General Physics textbooks. The reader is urged to refer to them.
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

$$\lambda = \frac{\hbar}{p}. \quad (4.1)$$

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

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

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

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

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

$$v_g = \frac{\lambda^2}{\hbar} \frac{dE}{d\lambda}. \quad (4.4)$$
By imposing $v = v_g$ we obtain
\[ \frac{dE}{dp} = -\frac{\lambda^2}{h} \frac{dE}{d\lambda}, \]
(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)
\[ 2\pi r = n\lambda = \frac{n \hbar}{mv}, \]
(4.6)
or
\[ l = mvr = \frac{n \hbar}{2\pi} = nh, \]
(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\(^1\)Free on-line edition: http://www.feynmanlectures.caltech.edu/
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 ∆\( f \) the uncertainty in the measurement of quantity \( f \), defined as root mean square deviation of a sequence of measurements,

\[
\Delta f = \sqrt{\langle f^2 \rangle - \langle f \rangle^2},
\]

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,

\[
\Delta x \Delta p_x \geq \frac{\hbar}{2},
\]

and analogously

\[
\Delta y \Delta p_y \geq \frac{\hbar}{2},
\]

\[
\Delta z \Delta p_z \geq \frac{\hbar}{2},
\]

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 \( \Delta x \Delta p_x \approx \hbar \) or \( \Delta x \Delta p_x \approx \hbar \), qualitatively in agreement with Heisenberg’s principle.

\(^2\)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

![Diagram showing uncertainties in a conceptual experiment for the measurement of position and momentum.]

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

$$\sim e^{i(kx-\omega t)},$$  \hspace{1cm} (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

$$\Psi(x, t) = \int_{-\infty}^{\infty} g(k) e^{i(kx-\omega t)} dk,$$  \hspace{1cm} (4.13)
with the $k$-spectrum $g(k)$ given by the Fourier transform of $\Psi(x,t)$ (actually, we take the transform at $t = 0$)

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

$$\Delta x \Delta p_x \geq \hbar.$$  \hspace{1cm} (4.15)

### 4.2.2 Energy and time

An uncertainty relation also applies to energy and time:

$$\Delta E \Delta t \geq \hbar.$$  \hspace{1cm} (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 $\tau$. The energy of the excited level, and then the energy of the emitted particle or photon is affected by an uncertainty

$$\Delta E = \frac{\hbar}{\tau}.$$  \hspace{1cm} (4.17)

This is the natural width of the emission line.
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, $\Psi$ is a complex quantity.
• The equation describing the time-evolution of \( \Psi \) 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

\[
\hat{E} = \frac{\vec{p}^2}{2m},
\]

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.

\[
\Psi(x, t) = e^{i(kx - \omega t)},
\]

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

\[
\Psi(x, t) = e^{i(px - Et)/\hbar}.
\]

Differentiating this expression with respect to \( x \) we obtain

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

We can rewrite this last equation as

\[
-\imath \hbar \frac{\partial \Psi(x, t)}{\partial x} = p \Psi(x, t),
\]

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

\[
\hat{p}_x \equiv -\imath \hbar \frac{\partial}{\partial x}.
\]
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 $x$:

$$\frac{\partial^2 \Psi(x, t)}{\partial x^2} = -\frac{p_x^2}{\hbar^2} e^{i(p_x - E)t}/\hbar = -\frac{p_x^2}{\hbar^2} \Psi(x, t) = -\frac{2mE}{\hbar^2} \Psi(x, t). \quad (5.7)$$

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

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

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

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

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

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

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

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

### 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

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + V(\hat{x}) = \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x). \quad (5.12)$$

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

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

or, more compactly,

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

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

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

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

and then

$$\left[ \hat{H} \psi = E \psi \right]. \quad (5.17)$$

or, writing the operator and the dependent variable explicitly,

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

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

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

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

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

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

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
\[ |\Psi(x, y, z, t)^*\Psi(x, y, z, t)| \] (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
\[ |\psi(x, y, z)^*\psi(x, y, z)|, \] (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
\[ \int\int\int_{\text{whole space}} |\psi(x, y, z)^*\psi(x, y, z)|dxdydz = 1. \] (5.25)

When the wavefunction is normalized the probability density \( p(P) \) at point \( P(x,y,z) \) is
\[ p(x, y, z, t) = |\Psi(x, y, z, t)^*\Psi(x, y, z, t)| \] (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)\(^1\)
\[ |A| = \sqrt{\frac{mJ}{\hbar k}}, \] (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

\(^1\)In general, the quantum mechanics probability current is
\[ \vec{J} = -\frac{i\hbar}{2m}(\psi^*\nabla\psi - \psi\nabla^*\psi) \] (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

$$\hat{A}\psi(\vec{r}) = a\psi(\vec{r}).$$  \hfill (5.29)

If a system is in an eigenstate $\psi_n$, 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

$$\langle A \rangle = \frac{\iiint \Psi^* \hat{A} \Psi \, dx \, dy \, dz}{\iiint \Psi^* \Psi \, dx \, dy \, dz}. \hfill (5.30)$$

If the wavefunction is normalized, then

$$\langle A \rangle = \iiint \Psi^* \hat{A} \Psi \, dx \, dy \, dz. \hfill (5.31)$$

### 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.

$$\hat{y} = y \hfill (5.32)$$

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

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:

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

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,
\[ [\hat{x}, \hat{p}_x] = i\hbar. \quad (5.35) \]

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

One can easily verify that
\[ [\hat{l}_x, \hat{l}_y] = \hbar \hat{l}_z; \quad [\hat{l}_y, \hat{l}_z] = \hbar \hat{l}_x; \quad [\hat{l}_z, \hat{l}_x] = \hbar \hat{l}_y. \quad (5.37) \]
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

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar} (E - V) \psi(x) = 0.$$  \hspace{1cm} (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

$$\psi(x) = \begin{cases} A \sin kx + B \cos kx, & E > V, \\ A' e^{kx} + B' e^{-kx}, & E < V, \end{cases}$$  \hspace{1cm} (6.2)

with

$$k = \sqrt{\frac{2m}{\hbar^2} |E - V|}.$$  \hspace{1cm} (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 $\psi''$, 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

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

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

(6.4)

to be solved with the boundary conditions

$$\psi(0) = \psi(L) = 0.$$

(6.5)

The general solution of Eq. (6.4) is

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

(6.6)

with

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

(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

$$A \sin kL = 0,$$

(6.8)

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

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

(6.9)
6.1. INFINITE POTENTIAL WELL

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

\[
E_n = \frac{\hbar^2 k^2}{2m} = n^2 \frac{\pi^2 \hbar^2}{2mL^2},
\]

and the corresponding wavefunctions (eigenfunctions) are

\[
\psi_n(x) = A_n \sin \frac{n\pi x}{L}.
\]

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, \( m = m_p = 1836m_e \) and \( L \) of the order of the nuclear radius \( r_n \approx 3 \times 10^{-5}r_0 \). We then have nucleon energies of the order of MeV and

\[
\frac{E_{\text{nucleon}}}{E_{\text{electron}}} \approx \frac{m_e r_0^2}{m_p r_n^2} \approx 6 \times 10^5.
\]

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

\[
1 = \int_0^\infty |\psi^*(x)\psi(x)|dx = \int_0^L A_n^2 \sin^2(k_n x)dx = A_n^2 \left( \frac{L}{n\pi} \right) \int_0^{n\pi} \sin^2 ydy.
\]

Using

\[
\int_0^{n\pi} \sin^2 ydy = \frac{n}{2} \int_0^{2\pi} \sin^2 ydy = \frac{n\pi}{2},
\]

we obtain

\[
A_n = \sqrt{\frac{2}{L}},
\]

independent on \( n \). The shapes of the wavefunctions for \( n = 1\text{--}4 \) 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 \( \Delta x \) 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,

\[
U(x) = \begin{cases} 
U_1 & x \leq 0 \quad \text{region 1} \\
0 & 0 < x < L \quad \text{region 2} \\
U_1 & x \geq 0 \quad \text{region 3}
\end{cases}
\]  \hspace{1cm} (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

\[
\frac{\partial^2 \psi(x)}{\partial x^2} - \chi^2 \psi(x) = 0,
\]  \hspace{1cm} (6.17)

with

\[
\chi = \sqrt{\frac{2m(U_1 - E)}{\hbar^2}},
\]  \hspace{1cm} (6.18)

and has solutions of the form

\[
\psi(x) \sim e^{\pm \chi x}.
\]  \hspace{1cm} (6.19)

Analogously, in region 2, the relevant equation becomes

\[
\frac{\partial^2 \psi(x)}{\partial x^2} + k^2 \psi(x) = 0,
\]  \hspace{1cm} (6.20)

with

\[
k = \sqrt{\frac{2mE}{\hbar^2}},
\]  \hspace{1cm} (6.21)

and has solutions of the form

\[
\psi(x) \sim \sin(kx + \delta).
\]  \hspace{1cm} (6.22)
By imposing that \( \psi(x) \) be finite for any value of \( x \) we can write the general solution as

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

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

\[
\begin{align*}
\psi_1(0) &= \psi_2(0) & A_1 &= A_2 \sin \delta, \\
\psi_1'(0) &= \psi_2'(0) & A_1 \chi &= A_2 k \cos \delta, \\
\psi_2(L) &= \psi_3(L) & A_2 \sin(kL + \delta) &= A_3 e^{-\chi L}, \\
\psi_2'(L) &= \psi_3'(L) & A_2 k \cos(kL + \delta) &= -A_3 \chi e^{-\chi L}.
\end{align*}
\] (6.24)

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

\[
\delta = \arctan \frac{k}{\chi} + m_1 \pi,
\] (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

\[
\delta = -kL - \arctan \frac{k}{\chi} + m_2 \pi,
\] (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

\[
n\pi - kL = 2 \arctan \frac{k}{\chi},
\] (6.27)

with \( n \) an integer number. It is now convenient to express \( k \) and \( \chi \) as functions of two new quantities, \( K \) and \( \xi \)

\[
K = \sqrt{\frac{2mU_1}{\hbar^2}},
\] (6.28)

\[
\xi = \sqrt{\frac{E}{U_1}},
\] (6.29)

so that

\[
k = K \xi, \quad (6.30)
\]

\[
\chi = K \sqrt{1 - \xi^2},
\] (6.31)

with \( 0 < \xi < 1 \). We then have

\[
\frac{k}{\chi} = \frac{\xi}{\sqrt{1 - \xi^2}}.
\] (6.32)
and Eq. (6.27) becomes

\[ n\pi - K\xi L = 2\arctan \frac{\xi}{\sqrt{1 - \xi^2}} = 2\arcsin \xi. \] (6.33)

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

\[ n = 0, 1, \ldots, n_{\text{max}} = \left\lfloor \frac{KL}{\pi} + 1 \right\rfloor, \] (6.34)

with corresponding energy eigenvalues

\[ E_n = \xi_n^2 U_1; \quad n = 0, 1, \ldots, n_{\text{max}} \] (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 \(K = 8.13 \times 10^{10} \text{ m}^{-1}\), \(KL = 8.13\) and \(n_{\text{max}} = \left\lfloor \frac{KL}{\pi} + 1 \right\rfloor = 3\). The three values of \(\xi\) 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 eigenfunctions \(\psi_n(x)\), \((n = 1, 2, 3)\), obtained as follows. First, the unnormalized eigenfunction corresponding to the eigenvalue \(n\) (and then to \(\xi_n\)) is obtained by
using the continuity conditions (6.24). We have

\[ \delta_n = \arcsin \xi_n \] (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)

and then

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

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

\[ \int_{-\infty}^{\infty} |\psi_n^*(x)\psi_n(x)| \, dx. \] (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

\[ p_{\text{out},n} = 2 \int_{-\infty}^{0} |\psi_n^*(x)\psi_n(x)| \, dx. \] (6.41)

With lengthy but simple algebra, one finds

\[ p_{\text{out},n} = \frac{\xi_n^3}{\xi_n^3 + (1 - \xi_n^2)^{1/2} [KL \xi_n + \frac{1}{2} \sin (KL \xi_n)].} \] (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.
6.2. FINITE POTENTIAL WELL

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

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 \( F = -\frac{dU}{dx} \) directed toward the left only near \( x = 0 \). We assume that particles approach the step coming from the left. Classically particles with energy \( E = \frac{1}{2}mv^2 > V_0 \) will proceed to the right hand side of the step, with lower velocity \( v_1 \), since, for energy conservation \( \frac{1}{2}mv_1^2 = E - V_0 \). Particles with the 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

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

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

- incident wave: \( \psi(x) \propto e^{ikx} \); \quad (6.44)
- reflected wave: \( \psi(x) \propto e^{-ikx} \). \quad (6.45)

We now consider separately the cases \( E > V_0 \) and \( E < V_0 \).
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

$$\psi(x) = \psi_a(x) = Ae^{ika_x} + Be^{-ika_x}, \quad x < 0 \quad (6.46)$$

$$\psi(x) = \psi_b(x) = Ce^{ikb_x} + De^{-ikb_x}, \quad x > 0 \quad (6.47)$$

with

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

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

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 $x = 0$:

$$\psi_a(0) = \psi_b(0) \quad \rightarrow \quad A + B = C, \quad (6.50)$$

$$\psi'_a(0) = \psi'_b(0) \quad \rightarrow \quad (A - B)k_a = Ck_b, \quad (6.51)$$

and then

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

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

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 6.8: Potential step; case $E > V_0$. 

**CHAPTER 6. QUANTUM MECHANICS: 1D PROBLEMS**
6.3. POTENTIAL STEP

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

$$J_a = A^2 \hbar k_a / m, \quad (6.53)$$

$$J_c = C^2 \hbar k_b / m, \quad (6.54)$$

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

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

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

$$B \rightarrow -1 \quad (6.56)$$

$$C \rightarrow 0 \quad (6.57)$$

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 6.9: Potential step; case $E > V_0$. Incoming and transmitted wavefunctions.
CHAPTER 6. QUANTUM MECHANICS: 1D PROBLEMS

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

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

with

$$k_a = \sqrt{\frac{2mE}{\hbar^2}} \quad (6.60)$$
$$\chi = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} \quad (6.61)$$

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

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

$$\psi_a(0) = \psi_b(0) \quad \rightarrow \quad A + B = C,$$
$$\psi'_a(0) = \psi'_b(0) \quad \rightarrow \quad i(A - B)k_a = -C\chi. \quad (6.62)$$
from which we obtain
\[
\frac{B}{A} = \frac{1 - i\chi/k_a}{1 + i\chi/k_a},
\]
\[\frac{C}{A} = 1 + \frac{B}{A} = \frac{2}{1 + i\chi/k_a}.\] (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
\[
\frac{P(x > 0)}{P(x = 0)} = \frac{|\psi^* (x)\psi(x)|}{|\psi^* (0)\psi(0)|} = \frac{|Ce^{-\chi x}|^2}{|A + B|^2} = e^{-2\chi x}.\] (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

\(^1\)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.
\( \chi \) defined by Eq. (6.61), an 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,

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

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

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

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

where \( x_1 \) and \( x_2 \) are lower and upper bound of the region to be tunnelled.

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.

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\[ \text{This is the so-called WKB approximation, discussed in many books on mathematical physics or on quantum mechanics. A nice presentation, with both historical and pedagogical references, can be found in Wikipedia: http://en.wikipedia.org/wiki/WKB_approximation} \]
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 $(r, \theta, \phi)$ is also convenient to deal with angular momentum. We recall (see Fig. 7.1) that spherical coordinates $(r, \theta, \phi)$ are related to Cartesian coordinates.
(x, y, z) by
\[ r = \sqrt{x^2 + y^2 + z^2}, \quad (7.1) \]
\[ \theta = \arctan \frac{\sqrt{x^2 + y^2}}{z}, \quad (7.2) \]
\[ \phi = \arctan \frac{y}{x}, \quad (7.3) \]

and
\[ x = r \sin \theta \cos \phi, \quad (7.4) \]
\[ y = r \sin \theta \sin \phi, \quad (7.5) \]
\[ z = r \cos \theta. \quad (7.6) \]

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
\[ \frac{\partial}{\partial z} = \frac{\partial r}{\partial z} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z} \frac{\partial}{\partial \phi}. \quad (7.7) \]

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
\[ \hat{l}_z = (\hat{\mathbf{r}} \times \hat{\mathbf{p}})_z = \hat{x} \times \hat{p}_y = -i\hbar (x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}). \quad (7.8) \]

Its expression in spherical coordinates is
\[ \hat{l}_z = -i\hbar \frac{\partial}{\partial \phi}, \quad (7.9) \]

as shown in Appendix D.

The possible values of the z-component of the angular momentum are obtained by solving the operator equation
\[ \hat{l}_z \psi(r, \theta, \phi) = l_z \psi(r, \theta, \phi), \quad (7.10) \]
or
\[ -i\hbar \frac{\partial \psi(\phi)}{\partial \phi} = l_z \psi(\phi), \quad (7.11) \]

which has solutions
\[ \psi(\phi) = \text{const} \ e^{i(l_z/\hbar)\phi}. \quad (7.12) \]
Imposing the boundary condition
\[ \psi(\phi) = \psi(\phi + n\pi), \] (7.13)
we find that \( l_z/\hbar \) must be an integer. Therefore the \textbf{z-component of the angular momentum is quantized}. It can take the values
\[ l_z = \hbar m, \quad m = 0, \pm 1, \pm 2, \ldots \] (7.14)
For historical reasons, this quantum number \( m \) is called \textit{magnetic quantum number}. The corresponding eigenfunctions are
\[ \psi(\phi) = \text{const} \ e^{im\phi}. \] (7.15)

### 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
\[ \hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2, \] (7.16)
or, in spherical coordinates,
\[ \hat{l}^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \] (7.17)
We then have to solve the eigenvalue equation
\[ \hat{l}^2 Y(\theta, \phi) = l^2 Y(\theta, \phi), \] (7.18)
with eigenvalues \( l^2 \) and eigenfunctions \( Y \). We solve Eq. (7.18) by separation of variables, i.e. we factorize the wavefunction as the product of a function of \( \theta \) and a function of \( \phi \)
\[ Y(\theta, \phi) = \Theta(\theta)\Phi(\phi). \] (7.19)
We substitute this last expression into Eq. (7.18) and multiply by \(-\sin^2 \theta/(\Theta(\theta)\Phi(\phi))\). We also set
\[ l^2 = \hbar^2 \beta, \] (7.20)
where \( \beta \) is a dimensionless quantity, and obtain
\[ \frac{\sin \theta}{\Theta(\theta)} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \beta \sin^2 \theta = -\frac{1}{\Phi(\phi)} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2}. \] (7.21)
We observe that the left hand side of this equation depends only on \( \theta \), while the right hand side only on \( \phi \). Since the equality holds for any value of \( \theta \) and \( \phi \), 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

\[-\frac{1}{\Phi(\phi)} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} = (m^*)^2, \quad (7.22)\]

\[\sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \beta \sin^2 \theta = (m^*)^2. \quad (7.23)\]

We first consider Eq. (7.22), which has solution

\[\Phi(\phi) = \text{const} \ e^{im^*\phi}. \quad (7.24)\]

This is just the same solution found in the previous section for the wavefunction of the \(z\)-component of the angular momentum [Eq. (7.15)]. We recognize that \(m^* = m\), with \(m\) the magnetic quantum number, and then

\[\Phi(\phi) = \text{const} \ e^{im\phi}. \quad (7.25)\]

We now consider the equation for \(\Theta\). Multiplying Eq. (7.23) by \(\Theta(\theta)/\sin^2 \theta\) we have

\[
\frac{1}{\sin \theta} \frac{d}{d \theta} \left( \sin \theta \frac{d \Theta(\theta)}{d \theta} \right) + \beta \Theta(\theta) - \frac{m^2 \Theta(\theta)}{\sin^2 \theta} = 0. \quad (7.26)
\]

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

\[
\frac{d}{dw} \left[ (1 - w^2) \frac{dP(w)}{dw} \right] + \left( \beta - \frac{m^2}{1 - w^2} \right) P(w) = 0. \quad (7.27)
\]

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.\(^1\). It is found that the solution \(P(w)\) is everywhere finite only for

\[\beta = l(l + 1), \quad l = 0, 1, 2, \ldots \quad \text{and} \quad l \geq |m|. \quad (7.28)\]

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

\[|\hat{\mathbf{l}}| = \hbar \sqrt{l(l + 1)} \quad (7.29)\]

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 \(P^{|m|}_l(w)\) defined by

\[P^{|m|}_l(w) = (1 - w^2)^{|m|/2} \left( \frac{d}{dw} \right)^{|m|} P_l(w), \quad (7.30)\]

\(^1\)The solution procedure is analogous to that for the radial equation of the Hydrogen atom, which we will describe in detail later.
where $P_l$ is the Legendre Polynomial of order $l$,

$$P_l(w) = \frac{1}{2l!} \left( \frac{d}{dw} \right)^l (w^2 - 1)^l.$$  (7.31)

The normalized angular momentum wavefunctions turn out to be

$$Y(\theta, \phi) = Y_l^m(\theta, \phi) = \Theta_l(\theta) \Phi(\phi) = A_{l,m} P_l^{|m|}(\cos \theta) e^{im\phi},$$ (7.32)

with normalization constants

$$A_{l,m} = i^l \left[ \frac{2l + 1}{4\pi} \frac{(l - |m|)!}{(l + |m|)!} \right]^{1/2} \times \left\{ \begin{array}{ll} (-1)^m & m > 0 \\ 1 & m \leq 0 \end{array} \right\}$$ (7.33)

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

$$P_0 = 1$$ (7.34)

$$P_1 = \cos \theta$$ (7.35)

$$P_2 = \frac{1}{2} (3 \cos^2 \theta - 1)$$ (7.36)

$$P_3 = \frac{1}{2} (5 \cos^3 \theta - 3 \cos \theta)$$ (7.37)

The $l = 0$ eigenfunction is therefore spherically symmetric.
7.4 Angular momentum and parity

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

$$x \rightarrow x' = -x; \quad y \rightarrow y' = -y; \quad z \rightarrow z' = -z.$$  (7.38)

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-decay.)

It is useful to consider the parity of angular momentum wavefunctions, because it enters in the determination of the so-called selection rules, ruling possible (and forbidden) atomic transitions. When the coordinates are reflected according to Eq. (7.38), the polar coordinates change as

$$r \rightarrow r' = r; \quad \theta \rightarrow \theta' = \pi - \theta; \quad \phi \rightarrow \phi' = \phi + \pi.$$  (7.39)

Then, aside from normalization constants,

$$Y(\theta', \phi') = Y_l^m(\theta', \phi') = P_l^{|m|}(\cos \theta')e^{im\phi'} = -P_l^{|m|}(\cos \theta)e^{im\phi}(-1)^{|m|}.$$  (7.40)

We also observe that the associate Legendre polynomials $P_l^{|m|}(x)$ appearing in the angular momentum eigenfunctions $Y_l^m$ (see Eq. [7.32]) 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 anti-symmetric in $x$) if $l - |m|$ is odd. It follows that

$$Y_l^m(\theta', \phi') = (-1)^l Y_l^m(\theta, \phi).$$  (7.41)

The parity of angular momentum eigenfunctions is then only determined by the angular quantum number $l$ and is simply

$$\Pi_l = (-1)^l.$$  (7.42)

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

$$\nabla^2 \psi(r, \theta, \phi) + \frac{2\mu}{\hbar^2} [E - V(r)] \psi(r, \theta, \phi) = 0,$$  (7.43)
7.5. SCHRÖDINGER EQUATION FOR THE HYDROGEN ATOM

where

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$  \hspace{1cm} (7.44)$$

and

$$V(r) = -\frac{e^2}{4\pi \varepsilon_0 r}.$$  \hspace{1cm} (7.45)$$

Here \( r \) is the distance of the electron from the nucleus, \( \mu \) 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. (7.44) is just equal to \(-\hat{l}^2 / \hbar^2 \) [see Eq. (7.17)], we can write Eq. (7.43) as

$$2 \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{\hat{l}^2}{\hbar^2} + \frac{2 \mu \hbar^2}{\hbar^2} [E - V(r)] \right\} \psi(r, \theta, \phi) = 0.$$  \hspace{1cm} (7.46)$$

Furthermore, in the previous section we have found that

$$\hat{l}^2 Y(\theta, \phi) = \hbar^2 l(l + 1) Y(\theta, \phi).$$  \hspace{1cm} (7.47)$$

We also notice that while the angular momentum term depends on \( \theta \) and \( \phi \), the other terms only depend on the radial variable \( r \). This suggests to factorize

$$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi),$$  \hspace{1cm} (7.48)$$

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. (7.48) and Eq. (7.47) in Eq. (7.46), and multiplying by \( r^2 / Y \) we have

$$\frac{\partial}{\partial r} \left( r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{2 \mu \hbar^2}{\hbar^2} [E - V(r)] R(r) - l(l + 1) R(r) = 0.$$  \hspace{1cm} (7.49)$$

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

$$\frac{d}{dr} \left( r^2 \frac{d}{dr} \right) = r^2 \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right).$$  \hspace{1cm} (7.50)$$

We substitute this expression into Eq. (7.49) and divide by \( r^2 \), to obtain

$$\left\{ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} + \frac{2 \mu \hbar^2}{\hbar^2} [E - V(r)] - \frac{l(l + 1)}{r^2} \right\} R(r) = 0.$$  \hspace{1cm} (7.51)$$

\(^2\text{Note that } \nabla^2 \text{ can be written in a slightly different form, using the identity}\)

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) = \frac{1}{r} \frac{\partial^2 (r \psi)}{\partial r^2}.$$
Note that this last equation can also be written as
\[ \left\{ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} + \frac{2\mu}{\hbar^2} [E - V_{\text{eff}}(r)] \right\} R(r) = 0 \] (7.52)
with an effective potential equal to the sum of the potential of the central force and a centrifugal potential due to the angular momentum.\(^3\)

\[ V_{\text{eff}}(r) = V(r) + \frac{l(l+1)\hbar^2}{2\mu r^2} \] (7.55)

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.
\[ r = \rho r_0, \quad r_0 = \frac{4\pi\varepsilon_0 \hbar^2}{\mu e^2} \] (7.56)
\[ E = \varepsilon E_0, \quad E_0 = -\frac{1}{2} \left( \frac{\mu e^4}{(4\pi\varepsilon_0)^2 \hbar^2} \right) \] (7.57)
and use Eq. (7.45) for the potential energy. Equation (7.51) becomes
\[ \left\{ \frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} - \varepsilon + \frac{2}{\rho} \frac{l(l+1)}{\rho^2} \right\} R(r) = 0, \] (7.58)
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. (7.58) reduces to
\[ \left( \frac{d^2}{d\rho^2} - \varepsilon \right) R(r) = 0, \] (7.59)
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 \( \rho \). We are then left with
\[ R(\rho) \sim e^{-\rho \sqrt{\varepsilon}} = R(\infty)(\rho), \] (7.60)

In the limit \( \rho \to 0 \), we instead have
\[ \left\{ \frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} - \frac{l(l+1)}{\rho^2} \right\} R(r) = 0. \] (7.61)

\(^3\)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
\[ \frac{\partial^2}{\partial r^2}(r R) + \frac{2\mu E}{\hbar^2} r R, \] (7.53)
with solutions
\[ R(r) \sim e^{\pm i k r}, \quad k = \left( \frac{2\mu E}{\hbar} \right)^{1/2} \] (7.54)
i.e. a combination of in-going and out-going spherical waves.
We look for a solution of the form \( R \sim \rho^b \). By substituting this last expression into Eq. (7.61) we have
\[
b(b + 1) = l(l + 1),
\]
which has solutions \( b = l \) and \( b = -l - 1 \). Discarding the solution \( \rho^{-l-1} \), that diverges in the origin, we are left with
\[
R(\rho) \sim \rho^l = R(0)(\rho).
\]  

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
\[
R(\rho) = R(0)(\rho)R(\infty)(\rho)f(\rho) = \rho^l e^{-\rho\sqrt{\varepsilon}} f(\rho),
\]  

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

We substitute Eq. (7.63) for \( R \) in Eq. (7.58). Lengthy, but elementary algebra (detailed in Appendix E) leads to the equation
\[
\frac{d^2 f}{d\rho^2} + \left[ \frac{2(l + 1)}{\rho} - 2\sqrt{\varepsilon} \right] \frac{df}{d\rho} + \frac{2}{\rho} \left[ 1 - \sqrt{\varepsilon}(l + 1) \right] f = 0
\]  

We assume \( f(\rho) \) can be written as a series of powers of \( \rho \) or, better, of \( x = 2\sqrt{\varepsilon} \rho \),
\[
f(\rho) = \sum_{i=0}^{\infty} a_i x^i,
\]  

and then substitute
\[
R(\rho) = e^{-x/2} R(x/2\sqrt{\varepsilon}) \sum_{i=0}^{\infty} a_i x^i,
\]
into Eq. (7.58). Again with lengthy algebra (see Appendix E), we find that the coefficients \( a_i \) satisfy the recurrence relation
\[
a_{i+1} = a_i \frac{i + l + 1 - (1/\sqrt{\varepsilon})}{(i + 1)(i + 2l + 1)}.
\]  

The series so obtained diverges, because \( a_{i+1} \rightarrow a_i / i \), 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 \( \sigma \), which occurs if \( a_{\sigma+1} = 0 \). From Eq. (7.67) we see that this requires
\[
\sigma + l + 1 - \frac{1}{\sqrt{\varepsilon}} = 0,
\]  

with \( \sigma \) 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
\[
E(n) = E_n = \frac{E_0}{n^2}, \quad n = 1, 2, \ldots
\]  

(7.69)
in agreement with Bohr’s model. Notice that the energy levels only depend on \( n \).

From Eq. (7.68), which can now be written as \( \sigma + l + 1 - n = 0 \), we also see that \( l = n + \sigma - 1 \), and then

\[
l = 0, 1, 2, \ldots, n - 1. \tag{7.70}
\]

The radial eigenfunction then is

\[
R_{nl}(\rho) = \rho^l e^{-\rho/\sqrt{n}} \sum_{i=0}^{\sigma} a_i \left( \frac{2}{n} \right)^i \rho^i, \tag{7.71}
\]

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

\[
\Psi(r, \theta, \phi) = \Psi_{nlm} = A_{nlm} R_{nl}(\rho) P_{l}^{(m)}(\cos \theta) e^{im\phi}. \tag{7.72}
\]

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

\[
\psi(r, \theta, \phi) = \psi(r) = A_{n00} e^{-r} = \text{const} e^{-r/\sqrt{\alpha}}. \tag{7.73}
\]

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

The spatial distribution of the probability density of the electron in the hydrogen atom are shown in Fig. 7.3.

---

\( ^4 \)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
Le particelle elementari sono dotate, oltre che di massa (a riposo) e carica elettrica, di un'ultra proprietà intrinseca: il momento angolare intrinseco, o spin, rappresentato dal vettore $\mathbf{S}$, di modulo

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

dove $s$, spesso detto semplicemente "spin", è un numero non negativo, intero o semintero. La componente $S_z$ di $\mathbf{S}$ lungo un asse $z$, determinato per es. tramite l'applicazione di un campo magnetico, può assumere i valori

$$S_z = m_s \hbar,$$

dove $m_s$ è il numero quantico di spin, i cui $(2s+1)$ valori variano da $-s$ a $s$ per intervalli unitari.

$\begin{array}{c|c}
s &= 0 \\
0 & m_s = 0 \\
1/2 & m_s = -1/2, 1/2 \\
1 & m_s = -1, 0, 1 \\
3/2 & m_s = -3/2, -1/2, 1/2, 3/2 \\
\end{array}$

Chiamiamo:

- **fermioni** le particelle con $s$ semintero
- **bosoni** le particelle con $s$ intero

Sono **fermioni**:
- elettrone, protone, neutrone, neutrino $s = 1/2$
- ...
- sistemi con numero dispari di fermioni (per es., l'atomo di deuterio, costituito da nucleo con un protone e un neutrone, e un elettrone)

Sono **bosoni**:
- fotone $s = 1$
- mesoni, ...
- sistemi con numero pari di fermioni (per es., l'atomo di idrogeno, costituito da nucleo con un protone, e un elettrone)

$^1$ da E. Fermi, che per primo ne studiò la statistica (statistica di Fermi-Dirac)
$^2$ da S. N. Bose, che per primo ne studiò la statistica (statistica di Bose-Einstein)
Per i fermioni vale il

**PRINCIPIO DI ESCLUSIONE** (Pauli, 1925)³

"Non possono esistere in un sistema due fermioni con gli stessi valori dei numeri quantici"

oppure

"Uno stato quantico può essere occupato al più da un fermione"

Per gli elettroni spesso il principio di Pauli si enuncia in un modo leggermente diverso, che tiene conto del fatto che il numero quantico di spin dell’elettrone può assumere due valori ($m_s = \pm 1/2$, o come spesso si dice "spin su" e "spin giù"). Se per "stato" si intende quello descritto dalle sole coordinate di posizione, il principio diviene:

"Uno stato quantico può essere occupato al più da due elettroni di (numero quantico di) spin opposto"

**Nessuna limitazione esiste invece per i bosoni.**
7.7 Electrons in the atom

... quattro numeri quantici (n, \ell, m, m_s)

principio di esclusione

n = 0, 1, 2, ...

n° quantico principale

\ell = 0, 1, ... (n - 1)

n° quantico angolare
(o secondario)

m = 0, \pm 1, ..., \pm \ell

n° quantico azimuthale
(o retaggio)

m_s = \pm \frac{1}{2}

n° quantico di spin

⇒ disposizione degli elettroni negli atomi o

"aufbau" dell’atomo (x)

⇒ sistema periodico degli elementi

Notazione di uso frequente

n = 1, 2, 3, 4

K L M N

\ell = 0, 1, 2, 3

s p d f

(x) Vedi, per es., P. Silvestrini, "Fondamenti di Chimica", oppure le dispense di Fisica atomica e nucleare di F. Fratelli.
7.8 Indistinguishability

Un altro postulato della meccanica quantistica, di cui si deve tener conto nell’elaborazione della statistica quantistica, riguarda l’indistinguibilità delle particelle: non esiste alcun modo per distinguere particelle identiche, quindi

“Due sistemi che si ottengono l’uno dall’altro tramite scambio di particelle sono indistinguibili ( = sono lo stesso sistema)”

Questo principio, va applicato, per esempio, nel calcolo della probabilità termodinamica, e quindi dell’entropia, di sistemi quantistici, oppure nello studio di collisioni fra particelle identiche.
Chapter 8

Quantum statistics

In this chapter we describe the procedure to obtain the equilibrium distribution functions for particles that obey the laws of quantum mechanics. We will obtain the expressions for the Bose-Einstein distribution function, which applies to bosons, i.e., to particles with integer spin (such as photons, helium atoms, and electron pairs in superconductors), and for the Fermi-Dirac distribution function, which applies to fermions, i.e., to particles with half-integer spin (such as electrons). We will also see in what limit the classical Boltzmann distribution approximates the quantum distributions.

The configurations of a quasistatic system in macroscopic equilibrium actually vary in time, fluctuating in proximity of the most probable configuration. However, it is verified that, because the systems considered are composed of a vast number of particles, the fluctuations (relative to the most probable configuration) are extremely small. The physical properties of a macroscopic system can therefore be described, with excellent precision, through the properties of the most probable configuration. This justifies the procedure we will follow, in which instead of determining the average distribution, we will determine the most probable one.

Concerning this last point, we have seen (cfr. Mencuccini-Silvestrini, Vol. I, § XVII.4 and XVII.5; Sette-Alipr, vol. I, § 17.12), that a thermodynamically isolated system tends to reach the state that corresponds to the maximum value of the thermodynamic probability \( W \), defined as the number of distinguishable microstates that can be realized for a given macroscopic state. In equilibrium thermodynamic conditions, the thermodynamic probability is linked to the entropy through the relation

\[
S = k_B \ln W, \quad (8.1)
\]

due \( k_B = 1.3807 \times 10^{-23} \text{J/K} \) 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 $\varepsilon_s$ 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

$$ N = \sum_s n_s, $$

$$ E = \sum_s n_s \varepsilon_s, $$

(8.2)

(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

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

(8.4)

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

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

$$ \varepsilon = h \nu, $$

$$ p = \frac{h \nu}{c}, $$

(8.5)

(8.6)
8.2. STATISTICA DI BOSE-EINSTEIN

L'energia di un fotone è data da:

\[ \varepsilon = \hbar \nu \]

dove \( \hbar \) 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 \( \nu \) 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)

\[ dN(\nu) = N(\nu)d\nu = \frac{4\pi V^2}{c^3} \nu^2 d\nu. \]  

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

\[ g_s = 2N(\nu)d\nu = \frac{8\pi V^2}{c^3} \nu^2 d\nu \]

**Probabilità termodinamica**

Calcoliamo ora la probabilità termodinamica \( W \). 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

\[ z_1, z_2, z_3, \ldots, z_{g_s} \]

e le particelle con
\[ a_1, a_2, a_3, \ldots, a_{n_s}. \]  
(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
\[ z_1 a_1 a_2 z_2 a_3 z_3 a_4 a_5 a_6 z_4 z_5 a_7 \ldots z_{g_s-1} z_{g_s} a_{n_s-1} a_{n_s} \]  
(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 \( a_{n_s-1} e a_{n_s} \). Osserviamo che tutte le possibili stringhe 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
\[ W_s = \frac{g_s(g_s + n_s - 1)!}{g_s!n_s!} = \frac{(g_s + n_s - 1)!}{(g_s - 1)!n_s!} \]  
(8.12)

Inoltre, essendo per ipotesi \( n_s \gg 1 \) e \( g_s \gg 1 \), possiamo scrivere
\[ W_s \simeq \frac{(g_s + n_s)!}{g_s!n_s!}. \]  
(8.13)

Il numero di configurazioni possibili dell’intero sistema è pari al prodotto del numero di configurazioni di tutte le shell, ovvero
\[ W = \prod_s W_s \simeq \prod_s \frac{(g_s + n_s)!}{g_s!n_s!}, \]  
(8.14)
e quindi si ha
\[ \ln W \simeq \sum_s [\ln(g_s + n_s)! - \ln g_s! - \ln n_s!]. \]  
(8.15)
8.2. STATISTICA DI BOSE-EINSTEIN

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

\[
\ln W \simeq \sum \left[ (g_s + n_s) \ln(g_s + n_s) - g_s \ln g_s - n_s \ln n_s \right]. 
\tag{8.16}
\]

**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,

\[
\sum \ n_s \varepsilon_s = E, 
\tag{8.17}
\]

ovvero

\[
E - \sum \ n_s \varepsilon_s = 0. 
\tag{8.18}
\]

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

\[ F = \ln W + \beta (E - \sum \ n_s \varepsilon_s), \]

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

\[
F = \sum \left[ (g_s + n_s) \ln(g_s + n_s) - g_s \ln g_s - n_s \ln n_s \right] + \beta (E - \sum \ n_s \varepsilon_s) + \beta E. 
\tag{8.20}
\]

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

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

da cui si ha

\[
\ln \frac{g_s + n_s}{n_s} = \beta \varepsilon_s, 
\tag{8.22}
\]

e quindi

\[
\frac{n_s}{g_s} = \frac{1}{e^{\beta \varepsilon_s} - 1}. 
\tag{8.23}
\]

\( \beta = 1/k_B T \)

La relazione fra il moltiplicatore di Lagrange \( \beta \) 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

$$\sum_s n_s \varepsilon_s = E \quad (8.24)$$

otteniamo

$$\sum_s n_s \delta \varepsilon_s + \sum_s \delta n_s \varepsilon_s = \delta E. \quad (8.25)$$

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

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

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 $\delta Q$ scambiato dal sistema:

$$\sum_s \varepsilon_s \delta n_s = \delta Q \quad (8.27)$$

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

$$\delta \ln W = \beta \sum_s \varepsilon_s \delta n_s \quad (8.28)$$

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

$$\delta \ln W = \beta \delta Q. \quad (8.29)$$

Esprimendo la probabilità termodinamica $W$ tramite l’Eq. (8.1), $S = k_B \ln W$, e la quantità di calore scambiato nella trasformazione infinitesima tramite la definizione di entropia ($\delta S = \delta Q/T$), si ha

$$\beta = \frac{1}{k_B T}. \quad (8.30)$$

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

$$\frac{n_s}{g_s} = \frac{1}{e^{\hbar \nu/k_B T} - 1} \quad (8.31)$$

dove abbiamo scritto la frequenza $\nu$ omettendo il pedice $s$. 
8.2. STATISTICA DI BOSE-EINSTEIN

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 $\nu$ 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 $\nu$ e $\nu + d\nu$ è quindi data da

$$
\frac{u(\nu)d\nu}{V} = \frac{n_s \hbar \nu}{V} = \frac{1}{V} \frac{g_s}{e^{\hbar \nu/k_B T} - 1} = \frac{8\pi \hbar \nu^3 d\nu}{e^{\hbar \nu/k_B T} - 1}
$$

(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

$$
F = \ln W + \alpha (N - \sum s n_s) + \beta (E - \sum s n_s \varepsilon_s),
$$

(8.33)

dove $\alpha$ 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:

$$
f(\varepsilon) = \frac{n_s}{g_s} = \frac{1}{e^{\hbar \varepsilon/k_B T} - 1}.
$$

(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 $\hbar^3$. Si ha quindi

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

(8.35)

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

---


$^3$Si noti che alcuni testi definiscono $\alpha$ 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 termo-dinamica 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:

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

Utilizzando la formula di Stirling possiamo scrivere

$$\ln W_s \simeq g_s \ln g_s - n_s \ln n_s - (g_s - n_s) \ln(g_s - n_s).$$  \hfill (8.37)

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

$$F = \sum_s \left[ g_s \ln g_s - n_s \ln n_s - (g_s - n_s) \ln(g_s - n_s) \right] + \alpha(N - \sum_s n_s) + \beta(E - \sum_s n_s \varepsilon_s).$$  \hfill (8.38)

Derivando rispetto a ciascuna $n_s$ otteniamo

$$\frac{\partial F}{\partial n_s} = -\ln n_s - 1 + \ln(g_s - n_s) + \frac{g_s - n_s}{g_s - n_s} - \alpha - \beta \varepsilon_s \quad \Rightarrow \quad \ln \frac{g_s - n_s}{n_s} = \alpha + \beta \varepsilon_s.$$  \hfill (8.39)

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

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

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

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

\[
f(\varepsilon) = \frac{n_s}{g_s} = \frac{1}{e^{\alpha \varepsilon/k_B T} + 1}
\]  
(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

\[
f(\varepsilon) = \frac{n_s}{g_s} = \frac{1}{e^{\alpha \varepsilon/k_B T} \pm 1},
\]  
(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, \( \alpha \) 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 \( \varepsilon \), ottenendo

\[
N = \int_0^\infty \frac{g(\varepsilon)}{e^{\alpha \varepsilon/k_B T} \pm 1} d\varepsilon,
\]  
(8.44)

col 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

\[
\alpha = -\varepsilon_0/k_B T,
\]  
(8.45)

dove \( \varepsilon_0 \) è un’energia caratteristica, che dipende dalla densità di particelle \( N/V \) e, molto debolmente, dalla temperatura. Si ha allora

\[
f(\varepsilon) = \frac{1}{e^{(\varepsilon-\varepsilon_0)/k_B T} \pm 1},
\]  
(8.46)

Nel caso della statistica di Fermi-Dirac, \( \varepsilon_0 \) prende il nome di energia di Fermi e si indica usualmente con il simbolo \( \varepsilon_F \). La statistica di Fermi verrà discussa e utilizzata nel seguito del corso per studiare alcune proprietà di metalli e semi-conduttori (vedi Sette-Bertolotti, Vol. II, § 16.3–16.5 e Mencuccini-Silvestrini, Vol. II, § XII.9.2).

Quando il termine \( \exp[\alpha + (\varepsilon/k_B T)] \) nel denominatore dell’Eq. (8.43) è molto maggiore dell’unità, l’Eq. (8.43) stessa può essere scritta

\[
f(\varepsilon) \approx e^{-\alpha} e^{-\varepsilon/k_B T},
\]  
(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

$$W = N! \prod_s \frac{g_s^{n_s}}{n_s!}. \quad (8.48)$$

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

$$F = \ln W + \alpha(N - \sum_s n_s) + \beta(E - \sum_s n_s \varepsilon_s). \quad (8.49)$$

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 $s$,

$$\ln \frac{g_s}{n_s} - \alpha - \beta \varepsilon_s = 0 \quad (8.50)$$

e quindi l’espressione della funzione di distribuzione

$$f(\varepsilon_s) = \frac{n_s}{g_s} = e^{-\alpha} e^{-\beta \varepsilon_s} = e^{-\alpha} e^{-\varepsilon_s / k_B T}. \quad (8.51)$$
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

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 $L = pb = \hbar kb$. According to quantum mechanics angular momentum can only take values $L = h\sqrt{l(l+1)} \approx hl$, 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

\[
\psi_0 = A \sum_{l=0}^{\infty} (2l + 1) i^l j_l(kr) P_l(\cos \theta).
\]

(9.1)

Here \( P_l \) is the Legendre polynomial of order \( l \) [Eq. (7.31)] and \( j_l \) is the spherical Bessel function of order \( l \), which asymptotically, for \( kr \gg 1 \) approaches

\[
j_l(kr) \simeq \frac{\sin(kr - l\pi/2)}{kr}.
\]

(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

\[
\psi_0 = \frac{Ae^{-ikr}}{2ikr} + \frac{Ae^{ikr}}{2ikr},
\]

(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
9.2. GENERAL EXPRESSION OF THE CROSS-SECTIONS

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 an outgoing spherical wave,\(^3\) and can then be written as

\[
\psi(r) = -Ae^{-ikr} + A\eta e^{ikr} + A\eta e^{-ikr},
\]

(9.4)

where \(\eta\) is a complex quantity. While in general \(\eta\) depends on \(\theta\) and \(\phi\), in the \(l = 0\) approximation \(\eta\) is a (complex) constant. It is useful to write such a wave in a slightly different way, i.e.

\[
\psi(r) = A\frac{e^{ikr} - e^{-ikr}}{2ikr} + A(\eta - 1)\frac{e^{ikr}}{2ikr},
\]

(9.5)

which highlights the difference between incoming wave and scattered wave.

The knowledge of \(\eta\) 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 \(\sigma_{sc} = \int_0^{\Omega} d\Omega \sigma(\theta)\). However s-wave scattering is symmetric in the centre-of-mass system, and then we simply have \(\sigma_{sc} = 4\pi \sigma(\theta)\). By definition

\[
\sigma_{sc} = \frac{\text{particles scattered per unit time}}{\text{incident particles per unit time and area}} = \frac{(dN/dt)_{sc}}{J_{inc}},
\]

(9.6)

where the current of the incident beam is (see Eq. (5.28))

\[
J_{inc} = \frac{\hbar k}{m |A|^2}.
\]

(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

$$\left( \frac{dN}{dt} \right)_\text{sc} = \left| (\eta - 1)A \frac{e^{ikr}}{2ikr} \right|^2 \times 4\pi r^2 \times \frac{\hbar k}{m} = \frac{A^2 |\eta - 1|^2}{4\pi r^2 \hbar k/m} = \frac{A^2 |\eta - 1|^2}{\pi \hbar k},$$

and finally

$$\sigma_\text{sc} = \pi \lambda^2 |\eta - 1|^2,$$

where we have introduced $\lambda = \lambda/2\pi = 1/k$.

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 $\sigma_\text{reaction}$. It can be shown that

$$\sigma_\text{reaction} = \pi \lambda^2 (1 - |\eta|^2),$$

and the total cross-section is

$$\sigma_\text{tot} = \sigma_\text{sc} + \sigma_\text{reaction} = 2\pi \lambda^2 [1 - \Re(\eta)].$$
9.3 Scattering from a hard sphere of radius $R$

or "Potential scattering"  

- Scattering length $\sigma$ < superbar radius  
- $\Psi(r) \to 0$ as $r \to \infty$

- Scattering: no particles are lost $\Rightarrow |\eta| = 1$

We can then write $\eta = e^{i\delta}$ (and $\eta^{-1} = e^{i\delta}$),

we impose $\Psi(r=R)=0$, i.e.

$$\left[ \begin{array}{c} e^{-ikr} \\
-2ikr 
\end{array} \right] = 0$$

$\Rightarrow -e^{-ikr} + 2ikr = 0$

$\Rightarrow 2i\delta + kr = 0$

$\Rightarrow \delta = -kr$

and the scattering cross section $\sigma_{sc} = \pi \lambda^2 |\eta^{-1}|^2$ becomes

$$\sigma_{sc} = \pi \lambda^2 \left| \frac{2ie^{-ikR} \mu_k \mu_R}{2i(k+b)} \right|^2 = \frac{4\pi \lambda^2 \mu_k^2 \mu_R}{k+b}.$$  (**)

For $kr \ll 1$ (i.e. $R \ll \lambda$) $\mu_k^2 KR \approx k^2 R^2$;

s-wave $\sigma_{sc} \approx 4\pi R^2$ (***) Notice the final factor 4!

Exercise: when is (i.e. in which energy) is $\lambda \gg R$ for a neutron interacting with a nucleus of mass $AM_x$?
Potential scattering and Breit-Wigner cross section

Let us consider a more physical case, allowing to discuss both scattering and reactions.

"outside" wave function $\psi_{\text{out}}(r)$ $r \geq R$

"inside" wave function $\psi_{\text{in}}(r)$ $r \leq R$

At $r = R$:

- continuity of $\psi$
- continuity of $d\psi/dr$

Setting $\psi(r) = u(r)/r$ we can write the matching conditions at $r = R$ as a single condition:

\[
\left. \frac{du_{\text{out}}}{dr} \right|_{r=R} = \left. \frac{du_{\text{in}}}{dr} \right|_{r=R} \quad \Rightarrow \quad \frac{u_{\text{out}}}{u_{\text{in}}} = \frac{1}{f}
\]

We know $u_{\text{out}}(r) = r \psi(r) = \frac{1}{2i} \left[ e^{-ikr} + \eta e^{ikr} \right]$

(see eq. (9.4))

\[
\Rightarrow \quad f = \eta e^{ikR} + \eta e^{-ikR} = \frac{e^{-ikR} + \eta e^{ikR}}{e^{-ikR} + \eta e^{ikR}}
\]

Which can be solved for $\eta$:

\[
\eta = \frac{f + iKR}{f - iKR}
\]
Since \( f \) is a complex quantity, we can write

\[ f = f_r + i f_i, \]

and then

\[ \eta = \frac{f_r + i (f_i + KR)}{f_r + i (f_i - KR)} e^{-2iKR}. \]  

We can then write scattering and reaction cross sections as functions of \( f_r \) and \( f_i \).

For the scattering cross section, \( \sigma_{sc} = \pi f^2 \left| 1 - \eta \right|^2 \) we need to compute \( 1 - \eta \):

\[ 1 - \eta = e^{-2iKR} \left[ e^{iKR} - \frac{f_r + i (f_i + KR)}{f_r + i (f_i - KR)} \right] = \\
= e^{-2iKR} \left[ e^{iKR} (e^{-2iKR} + 1) \right] \]

we have subtracted and added "1"

\[ = 2i e^{-2iKR} \left[ e^{iKR} \sin KR + \frac{KR}{i(KR-f_i) - f_r} \right], \]

and then

\[ \sigma_{sc} = 4\pi f^2 \left| e^{iKR} \sin KR + \frac{KR}{i(KR-f_i) - f_r} \right|^2. \]
Analogously (algebra omitted):

$$
\sigma_{\text{res}} = \pi \lambda^2 \left( 1 - |\eta|^2 \right) = \pi \lambda^2 \frac{-4 f_i KR}{f_R^2 + (KR - f_i)^2}.
$$

We immediately see that if $f_i = 0$, $\sigma_{\text{res}} = 0$.

$$
\Rightarrow \text{pure scattering}
$$

For pure scattering, therefore, Eq. [1], previous page, becomes

$$
\sigma_{\text{sc}} = 4\pi \lambda^2 \left| e^{iKR} \sin KR + \frac{KR}{iKR - f_R} \right|^2,
$$

and we consider two limiting cases:

a) $\left| \frac{KR}{iKR - f_R} \right|^2 \ll \sin^2 KR \Rightarrow \sigma_{\text{sc}} \approx 4\pi \lambda^2 \sin^2 KR$

we have recovered Eq. (1), page 4

and then

$$
\sigma_{\text{sc}} \approx 4\pi R^2 \quad \text{for } KR \ll 1
$$

see Eq. (1x), Sec. (9.3)

b) $\left| \frac{KR}{iKR - f_R} \right|^2 \gg \sin^2 KR$

$$
\sigma_{\text{sc}} = 4\pi \lambda^2 \frac{K^2 R^2}{K^2 R^2 + f_R^2}
$$

$\sigma_{\text{sc}}$ is maximum when $f_R = 0$ $[f_R(E_0) = 0]$

# Do the algebra as an exercise.
We then expand \( f_R(E) \) in proximity of \( E = E_0 \) as
\[
f_R(E) = f_R(E_0) + f_R'(E_0)(E - E_0) + \ldots
\]
thus obtaining
\[
\sigma_{sc}^i = 4\pi \frac{k^2 R^2}{(f_R'(E_0))^2} \frac{\phi}{(E - E_0)^2 + \frac{k^2 R^2}{(f_R'(E_0))^2}}
\]
We get \( \Gamma_i = \frac{2kR}{f_R'(E_0)} \) and write the cross section in the form
\[
\sigma_{sc} = \pi \frac{\lambda^2}{(E - E_0)^2 + \frac{\Gamma_i^2}{4}}
\]

\[\uparrow\]

**BRÉIT-WIGNER CROSS SECTION FOR SCATTERING CLOSE TO A RESONANCE**

It can be shown (see e.g. Serre: Nuclei and Particles, p. 460) that under similar assumptions
\[
\sigma_{res} = \pi \frac{\lambda^2 \Gamma_i \Gamma_r}{(E - E_0)^2 + \left(\frac{\Gamma_i + \Gamma_s}{2}\right)^2}, \text{ with } \frac{\Gamma_i}{\sqrt{kL}} \propto v
\]

Hence, for absorptive reactions with nearly constant \( \Gamma_r \gg \Gamma_s \), if \( \Gamma_i \gg (E - E_0) \) or \( E \ll E_0 \), so that the denominator is approximately constant, we have
\[
\sigma_{res} \approx \pi \frac{\lambda^2 \Gamma_i \Gamma_r}{4} \propto \frac{1}{\sqrt{kL}}.
\]

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

\[ \psi_{\text{in}}(r) = \frac{e^{-iKr}}{r}, \quad \text{i.e.} \quad \mu_{\text{in}} = r \frac{\psi_{\text{in}}}{\psi_{\text{in}}} = e^{-iKR}, \]

where \( K \) is the wave number of the neutron inside the nucleus;
\( K \approx 1.6 \text{ fm}^{-1} \) if \( E_{\text{neutron}} \approx 50 \text{ keV}. \)

We can then compute \( f = R \frac{\partial u}{\partial r} \bigg|_{u(r)} \) using \( u = u_{\text{in}} : \)

\[ f = -R \frac{iKr}{e^{-iKR}} e^{iK^2} = -iK^2. \]

Inserting this last expression into Eq.\((1)\), Sec.9.4, we obtain

\[ \eta = \frac{iK^2 + iK^2}{iK^2 - iK^2} e^{-2iK^2R} = \frac{K - iK}{K + K} e^{-iK^2R} \]

and then the (absorption) reaction cross section

\[ \sigma_{\text{abs}} = \pi \lambda^2 \left[ 1 - \eta^2 \right] = \pi \lambda^2 \left( 1 - \left( \frac{K - iK}{K + K} \right)^2 \right) = \pi \lambda^2 \frac{4Kk}{(K + K)^2}, \]

where \( K \) is the wave number of the incoming neutron,
\( K = \sqrt{2} \propto \sqrt{E} \propto \nu. \)

For a "low" energy neutron \( K \ll K \), and then

\[ \sigma_{\text{abs}} \propto \frac{1}{\nu}, \]

\[ \sigma_{\text{abs}} \ll \frac{1}{\nu} \leq \text{"+\nu" law} \]
Appendices
Appendix A

Wave packets and group velocity

Consideriamo il pacchetto d'onde descritto dalla funzione

\[ u(x, t) = \int a(k) e^{i(kx - \omega t)} \, dk, \quad \omega = \omega(k) \]

Supponiamo \( a(k) \) sia concentrata attorno a \( k \) e

\[ a(k) \approx \delta(k - k_0) \]

con \( k_0 \) pari a \( K \)

\[ u(x, t) = \int a(k) e^{i(kx - \omega t)} \, dk =
\]

\[ = e^{i(k_0x - \omega_0 t)} \int a(k_0 + k') e^{i(k'x - \omega_0 t)} \, dk' =
\]

\[ A(x, t) \]

\[ \Rightarrow \] facciamo un'onda con numero d'onda \( k_0 \) pulsazioni \( \omega_0 \)

e ampiezza \( A(x, t) \) che varia da punto a punto e da estremità a estremità.
Ci chiamiamo velocità di gruppo la velocità di un punto del pacchetto come data $A$, per es. del punto di massimo. Quest'ultimo si trova in formulato

$\frac{dA(x,t)}{dt} = 0$

$\frac{\partial A(x,t)}{\partial x} \frac{dx}{dt} + \frac{\partial A(x,t)}{\partial t} = 0$

Vel. di gruppo: $U = \frac{dx}{dt} \Rightarrow U = \frac{-\partial A/\partial t}{\partial A/\partial x}$

$\partial A = i \int \omega_A (k + \xi) \frac{e^{i(kx-wxt)}}{dk} dk$; $(*)$

$\partial A = i \int k \omega_A (k + \xi) \frac{e^{i(kx-wxt)}}{dk} dk$; $(**)$

Dove, per l'ipotesi di pacchetto "stretto", possiamo scrivere

$\omega_A (k) = \omega (k) - \omega_o = \left[ \omega_o + \left( \frac{d\omega}{dk} \right) (k - k_o) + ... \right] - \omega_o$

$\simeq \frac{d\omega}{dk} \bigg|_{k=k_o} (k - k_o) = \frac{d\omega}{dk} \bigg|_{k=k_o} k_o$

Sostituendo quest'ultima espressione nelle eq. $(*)$ e $(**)$

$U = -\frac{\partial A/\partial t}{\partial A/\partial x} = \frac{d\omega}{dk}$. 
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 $F(\omega)$

$$F(\omega) = \int_{-\infty}^{\infty} f(t)e^{-i\omega t}dt$$  \hspace{1cm} (B.1)

of a function $f(t)$, which can be recovered by anti-transforming $F(\omega)$, according to

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega)e^{i\omega t}d\omega.$$  \hspace{1cm} (B.2)

Let us assume that $F(\omega)$ is given by

$$F(\omega) = e^{-\omega^2},$$  \hspace{1cm} (B.3)

i.e. it is a Gaussian $\exp\left(-\omega^2/2\sigma^2\right)$, with standard deviation $\sigma_\omega = 1/\sqrt{2}$. We now use Eq. (B.2) to obtain $f(t)$:

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-\omega^2+i\omega t}d\omega =$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-(\omega-it/2)^2-t^2/4}d\omega =$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-x^2-t^2/4}dx = e^{-t^2/4}2\pi =$$

$$= \frac{1}{2\sqrt{\pi}} e^{-t^2/4},$$  \hspace{1cm} (B.4)

which is a Gaussian in $t$, with standard deviation $\sigma_t = \sqrt{2}$, so that $\sigma_t \sigma_\omega = 1$. 

89
APPENDIX B. FOURIER TRANSFORM OF A GAUSSIAN
Appendix C

A proof of the uncertainty relations

\[ \sqrt{\int_{-\infty}^{\infty} f(x)^2 \, dx} = A \epsilon \]

*Il fattore che aspettiamo, sezione 10.*

*Per il postulato interpretativo P3 le variabili di una funzione di probabilità (coordinate x) è data da
\[ \Delta x = \sqrt{\int_{-\infty}^{\infty} \left[ x - \sqrt{\frac{\int_{-\infty}^{\infty} f(x)^2 \, dx}{\int_{-\infty}^{\infty} f(x) \, dx}} \right]^2 \, dx} \]

Si definisce \( \Delta x \sqrt{\Delta p} \), abbiamo \( \Delta x = \frac{\Delta p}{2} \).

*La trasformata di Fourier \( \phi(k) \) della \( f(x) \)
\[ \text{è data da} \quad \phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} \, dx \]

\[ \phi(k) = \left[ \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} \, dx \right] \phi(\theta) \]

\[ \frac{\Delta p}{2} = \sqrt{\frac{\int_{-\infty}^{\infty} f(x)^2 \, dx}{\int_{-\infty}^{\infty} f(x) \, dx}} \]
\[ \phi(k) = \frac{A}{2\pi} \int_{-\infty}^{\infty} e^{-\left(\frac{x^2}{a^2} + ikx\right)} dx = \]

\[ = \frac{A}{2\pi} \int_{-\infty}^{\infty} e^{\left[-\left(\frac{x}{a} + \frac{ik}{2}\right)^2 + \frac{k^2}{4}a^2\right]} dx = \]

\[ = \frac{A}{2\pi} e^{-\frac{k^2}{4}} \int_{-\infty}^{\infty} e^{-\left(\frac{x}{a} + \frac{ik}{2}\right)^2} dx = \frac{A}{2\pi} e^{-\frac{k^2}{4}} \sqrt{\pi} \]

\[ \phi(k) = \frac{Aa}{2\sqrt{\pi}} e^{-\frac{k^2}{4a^2}} \]

\[ \text{def. } b = \frac{a}{2} \]

\[ \Rightarrow \Delta k = \frac{b}{2} = \frac{1}{\alpha} = \frac{\lambda}{2\Delta x} \]

\[ \text{hence } k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} \rightarrow p = \frac{k\hbar}{2\pi} \]

\[ \text{and } \Delta p = \hbar \Delta k = \frac{\hbar}{2\Delta x} \]

\[ \Delta p \cdot \Delta k = \frac{\hbar}{2} \]
Appendix D

Angular momentum operators in spherical coordinates

Figure D.1: Spherical and Cartesian coordinates.

We introduce spherical coordinates $r, \theta, \phi$, related to the Cartesian coordinates $x, y, z$ by

\begin{align*}
r &= \sqrt{x^2 + y^2 + z^2} \quad \text{(D.1)} \\
\theta &= \arctan \sqrt{x^2 + y^2} \quad \text{(D.2)} \\
z &= \arctan \frac{y}{x} \quad \text{(D.3)}
\end{align*}
We want to obtain the expressions of the angular momentum operators

\[
\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}) \quad (D.7)
\]

\[
\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z}) \quad (D.8)
\]

\[
\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}) \quad (D.9)
\]

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

\[
\frac{\partial}{\partial z} = \frac{\partial r}{\partial z} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z} \frac{\partial}{\partial \phi}. \quad (D.10)
\]

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.

\[
- y \left( \frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi} \right) \right], \quad (D.11)
\]

and reordering the terms on the right hand side,

\[
\hat{L}_z = -i\hbar \left[ \left( \frac{x}{\frac{\partial r}{\partial y} - \frac{\partial r}{\partial x}} \right) \frac{\partial}{\partial r} 
\right.

\[
+ \left( \frac{x}{\frac{\partial \theta}{\partial y} - \frac{\partial \theta}{\partial x}} \right) \frac{\partial}{\partial \theta} 
\right.

\[
+ \left( \frac{x}{\frac{\partial \phi}{\partial y} - \frac{\partial \phi}{\partial x}} \right) \frac{\partial}{\partial \phi} \right], \quad (D.12)
\]
where, using Eqs. (D.4)–(D.6), we can write

\[
\frac{\partial r}{\partial y} = \frac{1}{2\sqrt{x^2 + y^2 + z^2}} \cdot 2y = \frac{y}{r} \quad \text{(D.13)}
\]

\[
\frac{\partial r}{\partial x} = \frac{x}{r} \quad \text{(D.14)}
\]

\[
\frac{\partial \theta}{\partial y} = \frac{1}{1 + \frac{x^2 + y^2 + z^2}{z^2}} \cdot 2\sqrt{x^2 + y^2} \cdot 2y = \frac{zy}{r^2 \sqrt{x^2 + y^2}} = \frac{y}{r^2 \tan \theta} \quad \text{(D.15)}
\]

\[
\frac{\partial \theta}{\partial x} = \frac{y}{r^2 \tan \theta} \quad \text{(D.16)}
\]

\[
\frac{\partial \phi}{\partial x} = \frac{1}{1 + \frac{y^2}{x^2}} \quad \text{(D.17)}
\]

\[
\frac{\partial \phi}{\partial y} = \frac{1}{x} = \frac{x}{x^2 + y^2} \quad \text{(D.18)}
\]

Substituting Eqs. (D.13)–(D.18) into Eq. (D.12) we finally obtain

\[
i_z = -i\hbar \left[ 0 \cdot \frac{\partial}{\partial r} + 0 \cdot \frac{\partial}{\partial \theta} + \left( \frac{x}{x^2 + y^2} \cdot \frac{\partial}{\partial \phi} + y \cdot \frac{\partial}{\partial \phi} \right) \right], \quad \text{(D.19)}
\]

and then

\[
i_z = -i\hbar \frac{\partial}{\partial \phi}. \quad \text{(D.20)}
\]

By proceeding analogously, one obtains

\[
i_x = i\hbar \left( \sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \quad \text{(D.21)}
\]

and

\[
i_y = -i\hbar \left( \cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right). \quad \text{(D.22)}
\]
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. (7.51)], which we write again here:

\[
\left[ \frac{d^2}{dr^2} + \frac{2 \mu}{r} \frac{d}{dr} + \frac{2 \mu}{\hbar^2} [E - V(r)] - \frac{l(l + 1)}{r^2} \right] R(r) = 0 \quad (E.1)
\]
APPENDIX E. HYDROGEN ATOM: RADIAL EQUATION

\[
\left\{ \frac{d^2}{dp^2} + \frac{2}{p} \frac{d}{dp} - \epsilon + \frac{2}{p} - \frac{\ell(\ell+1)}{p^2} \right\} R = 0 \quad (67)
\]

This equation may be solved in a form similar to the previous ones.

For a unique solution, the approximations in the quantum mechanics of the hydrogen atom may be simplified.

a) For \( p \to \infty \), the equation \( (67) \) becomes

\[
(\frac{d^2}{dp^2} - \epsilon) R(p) = 0 \quad \rightarrow \quad R \sim \left\{ \begin{array}{ll}
\text{diverges for } p \to \infty \\
\text{decreases for } p \to 0
\end{array} \right.
\]

\[
(68)
\]

b) For \( p \to 0 \)

\[
(\frac{d^2}{dp^2} + \frac{2}{p} \frac{d}{dp} - \frac{\ell(\ell+1)}{p^2}) R(p) = 0 \quad (69)
\]

Obtaining a solution \( \epsilon \) in agreement \( R \sim p \).

Substituting into Eq. \((69)\) with \( \ell = k \)

\[
\ell (\ell+1) + 2k = \ell (\ell+1),
\]


Hence

\[
\ell (\ell+1) = \ell (\ell+1) \quad \rightarrow \quad \ell = \ell - \ell - 1
\]

\[
R \sim \frac{p^\ell}{\ell!} \quad \text{diverges for } \ell \to \infty \quad (70)
\]
Consideriamo allora una soluzione, stabile per \( \psi \), che all'origine è per \( \rho = 0 \) e per \( \rho = \infty \) rispettivamente (70) e (62), rispettivamente. La scriveremo nella forma

\[ R(\rho) = \mathcal{E} \rho^\frac{1}{2} \rho \mathcal{F}(\rho) \]  

(\text{1})

Dobbtiamo quindi trovare la funzione \( \mathcal{F}(\rho) \).

Sostituendo l'Eq. (71) nella (62), utilizzando le seguenti espressioni delle derivate prima e seconda di \( R(\rho) \):

\[
\frac{dR}{d\rho} = R \left( -\sqrt{\mathcal{E}} + \frac{1}{\rho} + \frac{1}{f} \frac{df}{d\rho} \right)
\]

\[
\frac{d^2 R}{d\rho^2} = \frac{d}{d\rho} \left( \frac{dR}{d\rho} \right) = \frac{dR}{d\rho} \left( -\sqrt{\mathcal{E}} + \frac{1}{\rho} + \frac{1}{f} \frac{df}{d\rho} \right) + R \left( \frac{1}{\rho^2} \frac{1}{f} \frac{df}{d\rho} \right)^2 + \frac{1}{f} \frac{d^2 f}{d\rho^2}
\]

\[
= R \left( -\sqrt{\mathcal{E}} + \frac{1}{\rho} + \frac{1}{f} \frac{df}{d\rho} \right)^2 + R \left( \frac{1}{\rho^2} \frac{1}{f} \frac{df}{d\rho} \right)^2 + \frac{1}{f} \frac{d^2 f}{d\rho^2}
\]

\[
= R \left[ \mathcal{E} + \frac{1}{\rho^2} + \frac{1}{f} \frac{df}{d\rho} \right] - 2 \sqrt{\mathcal{E}} \frac{1}{\rho} - \frac{2 \mathcal{E} f}{f} \frac{df}{d\rho} + \frac{2 \mathcal{E} f}{f} \frac{df}{d\rho} - \frac{1}{\rho^2} \frac{1}{f} \frac{df}{d\rho} \frac{d^2 f}{d\rho^2}
\]

otteniamo

\[
\mathcal{E} + \frac{\mathcal{E} f}{f^2} - 2 \sqrt{\mathcal{E}} \frac{1}{\rho} + \left( -2 \sqrt{\mathcal{E}} + \frac{\mathcal{E}}{\rho} \right) \frac{df}{d\rho} + \frac{1}{f} \frac{d^2 f}{d\rho^2} +
\]

\[
\frac{2 \mathcal{E} f}{f} \frac{df}{d\rho} - \frac{1}{\rho^2} \frac{1}{f} \frac{df}{d\rho} \frac{d^2 f}{d\rho^2} = 0
\]
Multiplicando per $f$ e riordinando:

$$\frac{d^2 f}{dp^2} + \left[ \frac{2(l+1)}{p} - 2 \sqrt{\frac{\alpha}{x}} \right] \frac{df}{dp} + \frac{2}{p} \left[ 1 - \sqrt{\frac{\alpha}{x}} (l+1) \right] f = 0 \quad (72)$$

Se deriviamo la soluzione $f(p)$ come serie di potenze di $p$, si ottiene:

$$f(p) = \sum_{\nu=0}^{\infty} a_{\nu} \left( \frac{2 \sqrt{\bar{\alpha}}}{x} \right)^{\nu} \quad \nu = 0, 1, 2, \ldots \quad (73)$$

Le cui derivate sono:

$$\frac{df}{dp} = \sum_{\nu=1}^{\infty} \nu a_{\nu} \left( \frac{2 \sqrt{\bar{\alpha}}}{x} \right)^{\nu-1} \frac{2 \sqrt{\bar{\alpha}}}{x} \quad (73a)$$

$$\frac{d^2 f}{dp^2} = \sum_{\nu=2}^{\infty} \nu (\nu-1) a_{\nu} \left( \frac{2 \sqrt{\bar{\alpha}}}{x} \right)^{\nu-2} \frac{2 \sqrt{\bar{\alpha}}}{x} \quad (73b)$$

Sostituendo le eq. (73), (73a) e (73b) nella (72) otteniamo:

$$\sum_{\nu} \nu a_{\nu} (\nu-1) 4 \alpha x^{\nu-2} + \left[ \frac{2(l+1)}{x} - 2 \sqrt{\frac{\alpha}{x}} \right] \sum_{\nu} a_{\nu} x^{\nu} \sqrt{\frac{\alpha}{x}} + \frac{2 \bar{\alpha}}{x} \frac{2 \sqrt{\bar{\alpha}}}{x} \left[ 1 - \sqrt{\frac{\alpha}{x}} (l+1) \right] a_{\nu} x^{\nu} = 0$$

e dunque:

$$\sum 4 \alpha a_{\nu} (\nu-1 + 2l + 2) x^{\nu-2} - \sum 4 \alpha a_{\nu} (\nu + l + \frac{1}{2}) x^{\nu-1} = 0$$

$$\nu + 2l + 1 \quad (74)$$
Affinché l'eq. (74) sia soddisfatta, devono essere
identicamente nulli tutti i termini di ciascun grado
in \( v \), quindi

\[
a_{v+1}(v+1)(v+2l+1) = a_v(v+l+1 = \frac{1}{\sqrt{\varepsilon}}), \quad (75)
\]

Da questa formula, per ricorrere si trovaro tutti i coefficienti
a_v (not. il primo).

Si osserva però che la serie diverge per \( x \to \infty \).

Quindi la soluzione \( f(x) \), una quant'a un infinito serie,
una deve essere un polinomio di grado \( s \) fisso. Affinché
ciò si verifichi

\[
\delta + l + 1 - \frac{1}{\sqrt{\varepsilon}} = 0,
\]

con \( \delta \) intero o nullo.

Di conseguenza \( \frac{1}{\sqrt{\varepsilon}} \) è un intero positivo:

\[
\frac{1}{\sqrt{\varepsilon}} = n, \quad \text{con} \quad n = \delta + l + 1 = 1, 2, ...
\]

Troviamo quindi (vedi Eq. (66)) gli autovalori
dell'energia:

\[
E_n = \frac{E_0}{n^2}, \quad n = 1, 2, ...
\]

Per l'idrogeno \( E_0 = -13.59 \text{ eV} \).
BARRIERA DI POTENZIALE
ed EFFETTO TUNNEL

Procedendo come nel caso della buca di potenziale finita, scriviamo la soluzione nelle tre regioni, considerando il solo caso \( E < U_0 \) (*)

\[ i k x \quad + \quad R e^{-i k x} \quad ; \quad K = \sqrt{\frac{2m(E - U_0)}{\hbar^2}} \]

\[ \begin{align*}
\text{incidente} & \quad \text{riflessa} \\
A e^{i k x} + B e^{-i k x} ; & \quad \chi = \sqrt{\frac{2m}{\hbar^2}(U_0 - E)} \\
\end{align*} \]

(*) per \( E > 0 \) vedi, per es. Messiah, Quantum Mechanics, Dover (1999)
Raccordo a in \( x=0 \) e \( x=L \):

\[ \psi_0(0) = \psi_0(L) \rightarrow 1 + R = A + B \quad (45') \]

\[ \psi'_0(0) = \psi'_0(L) \rightarrow ik - iKR = AX - BX \quad (46') \]

\[ \psi_0(L) = \psi_0(L) \rightarrow A e^{XL} + Be^{-XL} = S e^{iKL} \quad (47') \]

\[ \psi'_0(L) = \psi'_0(L) \rightarrow AXe^{XL} - BXe^{-XL} = ikSe^{iKL} \quad (48') \]

Dividiamo la \((46')\) per \((ik)\) e sommiamo l'Eq. così ottenuta all'Eq. \((45')\):

\[ 2 = A \left(1 - i \frac{X}{K}\right) + B \left(1 + i \frac{X}{K}\right) \quad (49') \]

Dividiamo la \((48')\) per \((ik)\) e equagiamo il primo membro della equazione così ottenuta al primo membro della \((47')\):

\[ Ae^{\frac{XL}{A}} \left(1 + \frac{B}{A} e^{-2XL}\right) = -i \frac{X}{K} A e^{\frac{XL}{K}} \left(1 - \frac{B}{A} e^{-2XL}\right), \]

da cui otteniamo

\[ \frac{B}{A} e^{-2XL} = -\frac{1 + i \frac{X}{K}}{1 - i \frac{X}{K}}. \quad (50') \]

Introduciamo la \((50')\) nella \((47')\):

\[ Ae^{\frac{XL}{A}} \left(1 - \frac{1 + i \frac{X}{K}}{1 - i \frac{X}{K}}\right) = S e^{iKL} \]

\[ S = e^{-iKL} A e^{\frac{XL}{A}} - 2i \frac{X}{K} \]

\[ = 1 - i \frac{X}{K}. \quad (51) \]
Uniamo ora l'Eq. (50') per esprimere \( B \) in funzione di \( A \)
\[
B = \frac{1 + \frac{ix}{k}}{1 - \frac{ix}{k}} e^{2XL} A e^{2XL}
\]

e sostituendo quest'ultima espressione nella (49'):
\[
2 = A \left( 1 - \frac{ix}{k} \right) - \frac{1 + \frac{ix}{k}}{1 - \frac{ix}{k}} \frac{A e^{2XL} (1 + \frac{ix}{k})}{e^{2XL}}
\]
\[
2 = A \left( \frac{(1 - i \frac{X}{k})^2 - (1 + i \frac{X}{k})^2}{1 - i \frac{X}{k}} \right) e^{2XL}
\]
\[
A = \frac{2 \left( 1 - i \frac{X}{k} \right)}{(1 - i \frac{X}{k})^2 - (1 + i \frac{X}{k})^2 e^{2XL}}
\]

Inserendo quest'ultima equazione nella (51') otteniamo finalmente \( S \).
\[
S = e^{-iKL} \frac{2 \left( 1 - i \frac{X}{k} \right)}{(1 - i \frac{X}{k})^2 - (1 + i \frac{X}{k})^2 e^{2XL}} e^{XL} \frac{-2i \frac{X}{k}}{(1 - i \frac{X}{k})}
\]
\[
= \frac{-4i \frac{X}{k} e^{-iKL}}{(1 - i \frac{X}{k})^2 e^{XL} - (1 + i \frac{X}{k})^2 e^{XL}} = \frac{2e^{-iKL}}{-i \frac{kX}{e^{XL} \left( 1 - \frac{X}{k} \right) \sinh (X) + 2 \cosh (X)}}
\]

\[
S = e^{-iKL} \left[ \cosh (XL) + \frac{i}{2} \left( \frac{X}{k} - \frac{X}{X} \right) \sinh (XL) \right]^{-1} \quad (52)
\]
Possiamo ora calcolare la probabilità che una particella proveniente da $x < 0$, con energia $E < U_0$, attraversi la barriera stessa:

$$T = \text{"tunneling probability"} = \frac{| \Psi_0 |^2}{| \Psi_{\text{incident}} |^2} = \frac{SS^*}{1} = SS^*$$

o "trasparenza".

Usando l'Eq. (52'), otteniamo (*):

$$T = \left[ \cosh^2 XL + \frac{1}{4} \left( \frac{X}{K} - \frac{K}{X} \right)^2 \sinh^2 XL \right]^{-1}$$

$$= \left\{ 1 + \left[ 1 + \frac{1}{4} \left( \frac{X}{K} - \frac{K}{X} \right)^2 \right] \sinh^2 XL \right\}^{-1}$$

$$= \left\{ 1 + \frac{1}{4} \frac{(X^2 + K^2)^2}{K^2 X^2} \sinh^2 XL \right\}^{-1}$$

$$= \left\{ 1 + \frac{1}{4} \frac{U_0^2}{E(U_0 - E)} \sinh^2 \left[ \frac{2mL^2}{\hbar^2} (U_0 - E) \right]^{1/2} \right\}^{-1}$$

$$T = \left\{ 1 + \frac{1}{4} \frac{\sinh^2 \left[ \alpha^2 (1 - y) \right]^{1/2}}{y (1 - y)} \right\}^{-1},$$

dove $y = \frac{E}{U_0}$ e $\alpha^2 = \frac{2mL^2}{\hbar^2} U_0$.

(*): $Sc \quad f = \frac{a}{b + ic}, \quad ff^* = \frac{a^2}{b^2 + c^2}$.
Procedendo in modo analogo a quanto visto in zona 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 \( E \) prossimo ad \( U_0 \), si ha un certo grado di riflessione e quindi \( T < 1 \).

L’espressione generale della \( T \) risulta essere:

\[
T = \begin{cases} 
1 + \frac{\sinh^2 \left[ \frac{\alpha^2 (y-1)}{4y} \right]}{4y (y-1)} & y < 1 \\
1 + \frac{\sin^2 \left[ \frac{\alpha^2 (y-1)}{4y} \right]}{4y (y-1)} & y > 1 
\end{cases} \quad (54')
\]

con \( \alpha \) e \( y \) date dalle Equazioni (55).

L’andamento di \( T(y) \) per \( \alpha = 5 \) è mostrato nella figura seguente:
Osservazioni:

0 per $E < U_0$ e $X \ll 1$: si trova

$$T \approx \frac{16}{U_0} \left(1 - \frac{E}{U_0}\right) e^{-\frac{2XL}{U_0}}$$

(vedi 53 b')

0 per $E = U_0$:

$$T = \left[1 + \frac{1}{2} \frac{mL^2}{h^2} U_0\right]^{-1} = \left[1 + \frac{1}{4} \alpha^2\right]^{-1}$$

0 per $E > U_0$

$$T = 1, \quad \text{per} \quad \alpha^2 (y-1) = n\pi \quad n = 1, 2, ...$$

$$\Rightarrow y = 1 + n^2 \left(\frac{\pi}{\alpha}\right)^2$$

$$\uparrow \frac{E}{U_0}$$

0 per $E \gg U_0$ \quad $T \to 1$ (limite classico)

Alcune applicazioni:

- diodo tunnel
- reazioni nucleari di fusione
- decadimento $\alpha$
- microscopia e 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

\[ g_k(x_1, x_2, \ldots, x_n) = 0, \quad k = 1, 2, \ldots, m. \]

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

\[ \frac{\partial F}{\partial x_i} = \frac{\partial F}{\partial \alpha_k} = 0, \quad i = 1, 2, \ldots, n; \quad k = 1, 2, \ldots, m. \]

Le \( x_i \) estremanti si trovano allora risolvendo le \( i \) equazioni

\[ \frac{\partial F}{\partial x_i} = 0. \]

I moltiplicatori di Lagrange \( \alpha_k \) si trovano poi imponendo che i vincoli \( g_k = 0 \) siano soddisfatti.