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Quantum Optics

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Dedicated to
University students
C.S.

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ABBREVIATIONS

Abbreviation	Name
1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
1LS	single-level system
2LS	two-level system
3LS	three-level system
MLS	multi-level system
AF	atom - field
EM	electromagnetic
S.I.	Système International
FWHM	Full Width at Half Maximum
HOMO	Highest Occupied Molecular Orbital
IR	infrared
LASER	Light Amplification by Stimulated Emission of Radiation
LED	Light-Emitting Diode
LUMO	Lowest Unoccupied Molecular Orbital
RWA	Rotating Wave Approximation
TB	Tight Binding
TE	Transverse Electric
TEM	Transverse ElectroMagnetic
TM	Transverse Magnetic
UV	ultraviolet
$AB = -BA$	anticommutation
$\{A, B\} = AB + BA$	anticommutator
$AB = BA$	commutation
$[A, B] = AB - BA$	commutator
ΔE_C	conduction band offset
δ	delta function
Γ	Gamma function
ΔE_V	valence band offset

SYMBOLOTHEQUE

Table 1: Mathematical Symbols.

Symbol	**Meaning**
$:=$	defined as equal
$\overset{\mathrm{def}}{=}$	equal by definition
$\equiv$	equivalent
$\mathscr{N}$	the set of natural numbers
$\mathscr{Z}$	the set of integers
$\Re$	the set of real numbers
$\mathscr{C}$	the set of complex numbers
$\exists$	exists, exist
$\nexists$	does not exist, do not exist
$\nearrow$	denotes increase
$\searrow$	denotes decrease

Table 2: Physical constants (data from NIST:CODATA [1]).

Symbol	Name	Value
e	elementary charge	$1.602176565(35) \times 10^{-19}$ C
h	Planck constant	$6.62606957(29) \times 10^{-34}$ J s $4.135667516(91) \times 10^{-15}$ eV s
$\hbar$	reduced Planck constant	$1.054571726(47) \times 10^{-34}$ J s
k_B	Boltzmann constant	$1.3806488(13) \times 10^{-23}$ J/K $8.6173324(78) \times 10^{-5}$ eV/K
c	speed of light in vacuum	2.99792458×10^{8} m/s
m_p	proton mass	$1.672621777(74) \times 10^{-27}$ kg
m_n	neutron mass	$1.674927351(74) \times 10^{-27}$ kg
m_e	electron mass	$9.10938291(40) \times 10^{-31}$ kg
ε_0	electrical permittivity of vacuum	$8.854187817... \times 10^{-12}$ F/m
μ_0	magnetic permeability of vacuum	$4\pi \times 10^{-7}$ N/A^2

The units of a physical magnitude M will be denoted as $[M]$.

Bibliography

[1] *CODATA Internationally recommended values of the Fundamental Physical Constants. National Institute of Standards and Technology (NIST), USA.* 2021.

CHAPTER 1

OVERVIEW

In this Chapter:

A panoramic overview of the book contents is presented. I explain concepts that are developed further below.

Prerequisite knowledge: Some knowledge of Quantum Mechanics, Electromagnetism and Statistical Physics is necessary, although we will explain what we need.

This book is an evolution of the book [1] and of newer university lectures [2]. Other sources that the readers could consult are the following textbooks and university lectures [3, 4, 5, 6].

Let us start with a panoramic overview of the contents. Let us explain the basic notions, which will be further expanded below, and sketch the structure of this book. The book also includes tables with abbreviations, a glossary, that is, a dictionary of terminology, as well as a symbolotheque, which includes physical constants and symbols. Before starting, the author would like to formulate an axiom: "There is always an error." Hence, generally, in all human activities, errors exist. During the process of finding these errors we learn more and understand deeper. It is not a sin to make an error, but to think that you never make errors. Let us hope that this formulation will motivate readers to think, find and communicate to me errors and omissions in order to make the book, hopefully in a later edition, better. To the Chinese philosopher Confucius, 551 - 479 BCE, who died in the year of the Battle of Plataea, is attributed, among other things, the saying "I hear and forget, I see and I remember, I do and I understand"; a saying that should accompany the learning process in general. In particular, attending a university course, one should use lectures, notes, an organized e-class, an e-book, solved old exam problems, exercises, video lectures and experiment, if possible. Above all, a lively interaction between teacher and students should exist. The joy of interaction cannot be replaced by anything. Let us keep in mind that the purpose is not evaluation, but evolution. Finally, in a playful mood, instead of bullets, the following initial comment for commutation and anticommutation and comments on chapters are marked in Linear B.

𐀕𐀲𐀳𐀯-𐀀𐀴𐀕𐀲𐀳𐀯 At first, for the notation: To simplify the notation A (operation) B, we will write AB. Here the "operation" can be in the simpler cases addition or multiplication of numbers or of

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matrices, but it can also be any other exotic operation. Although we will discuss this issue in detail below, let us say a few words about commutation and anticommutation. The following objects are defined, the commutator

$$[A, B] := AB - BA,$$

and the anticommutator

$$\{A, B\} := AB + BA.$$

If the commutator vanishes, i.e., $[A, B] = 0$, then $AB = BA$, that is, objects A and B commute, in other words, AB does not differ from BA. This is called commutative property. If the anticommutator vanishes, i.e., $\{A, B\} = 0$, then $AB = -BA$, that is, objects A and B anticommute, in other words, AB is opposite to BA. This is called anticommutative property (from Greek *anti* which signifies opposition). The representation with operators, annihilation or lowering and creation or raising, that is, with ladder operators, is called second quantization in physics. Hence, bosons (like photons) commute, i.e., the operators which describe annihilation (lowering) an creation (raising) of bosons follow commutation relations, with objects $[,]$, while, fermions (like electrons) anticommute, i.e., the operators, which describe annihilation (lowering) an creation (raising) of fermions follow anticommutation relations with objects $\{,\}$.

In Chapter 2 we proceed to an introduction to the quantum nature of light. We present the idealization called the "black body" and relevant notions. In short, a black body is an object which absorbs all EM (electromagnetic) waves that fall onto it, regardless of frequency and angle of incidence, that is, something "pitch-black", if we can express ourselves in this vulgar way. We define one of the most central physical quantities in this book, namely, the energy density of EM radiation in an infinitesimal frequency range, initially, of a black body, in thermodynamic equilibrium, $\rho(\nu, T)$. The units of measurement in S.I. are $[\rho(\nu, T)] = \frac{\mathrm{J}}{\mathrm{m^3 Hz}}$, hence, the units of measurement of $[\rho(\nu, T)d\nu] = \frac{\mathrm{J}}{\mathrm{m^3}}$, that is, $\rho(\nu, T)d\nu$ is energy density. We present the important laws for black body radiation in thermodynamic equilibrium, that is, for the quantity $\rho(\nu, T)$: Rayleigh-Jeans (classical, theoretical, in absolute discrepancy with the experiment), Wien (empirical, fitting with experiment at high frequencies), Planck (quantum mechanical, theoretical, in agreement with the experiment for all frequencies) laws. We also state the Stefan-Boltzmann law (again, for the black body) in two forms: the first formulation refers to energy density, $\varrho(T)$, with units $[\varrho(T)] = \frac{\mathrm{J}}{\mathrm{m^3}}$, and the second formulation refers to radiation intensity, I, with units $[I] = \frac{\mathrm{J}}{\mathrm{sm^2}} = \frac{\mathrm{W}}{\mathrm{m^2}}$.

We remind the readers of the Maxwell equations in differential and in integral form, of the boundary conditions at an interface between two media, as well as of EM fields in cavities. Then, we define another important quantity, $g(\nu) = \frac{dN}{d\nu}$, that is, the infinitesimal number of EM field normal modes in an infinitesimal frequency range. Normal modes means frequencies and forms (shapes). The quantity $g(\nu)$ and classical physics, that is, the equipartition of energy theorem, lead to the Rayleigh-Jeans law, which is in absolute discrepancy with the experiment. Whereas, the quantity $g(\nu)$ and some (paleo)quantum hypotheses lead to the Planck's law, which agrees with the experiment for all frequencies. However, the Planck's law, "proven" via this route, reminds us of a student who, not knowing how to solve the exam problem, tries strange tricks, to find the correct result without remorse of wrong intermediate paths. A robust proof of Planck's law was given by Einstein; we will discuss it in Chapter 3. Next, we present the Wien's displacement law in the form $\lambda_0 T = \text{constant}$ (which gives the wavelength λ_0 where we have maximum EM radiation of a black body at temperature T) and in the form $\nu_0/T = \text{constant}'$ (which gives the frequency ν_0 where we have maximum EM radiation of a black body at temperature T). Finally, we describe the photoelectric effect, which, together with black body radiation, convinced us of the quantum nature of light. All these happened at the end of 19th century - beginning of 20th century, already far in the past.

Chapter 3 is devoted to the interaction mechanisms (or processes) between the EM radiation and the 2LS. Necessary abbreviations here are: 1LS = single-level system, 2LS = two-level system, 3LS = three-level system, MLS = multi-level system. Exampli gratia, a 2LS might be the two consecutive levels of an atom, molecule, quantum dot or alternatively nanoparticle. This is schematically shown in Figure 1.1. We will see how we construct a 2LS from two 1LSs, approaching each other, later, in Chapter

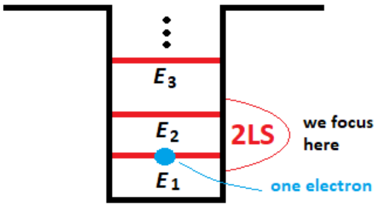


Figure 1.1: Schematically, a two-level system (2LS).

4. Anyway, schematically, the explanation is given in Figure 1.2. Let as assume, for the sake of simplicity, that each isolated 1LS has an energy level ε. Then, the unified system, that is, the 2LS, has, within a simple Tight-Binding approach, energy levels E_1 and E_2, which have an energetic separation $2|t|$, where t is the transfer integral, $t = \langle \phi_\mathrm{L} | \hat{H} | \phi_\mathrm{R} \rangle$, which shows how strongly the two 1LSs interact to build the 2LS. [If the isolated 1LSs are not identical, their levels will not have the same energy, but the result is qualitatively similar.]

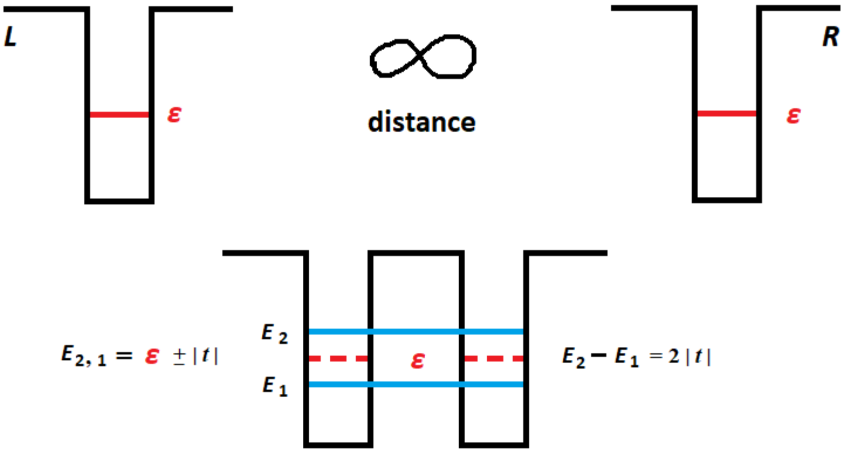


Figure 1.2: Schematically, how, approaching two single-level systems (1LSs), which are separated by infinite distance, one left (L) and one right (R), we construct a two-level system (2LS). The energetic separation of the two levels is determined by the transfer integral $t = \langle \phi_\mathrm{L} | \hat{H} | \phi_\mathrm{R} \rangle$, that is, from how strongly the once (upper panel) separated 1LSs interact to build the unified system, i.e., the 2LS (lower panel). For the sake of simplicity, we assume that each isolated 1LS has an energy level ε, while, the unified system, that is, the 2LS, has energy levels E_1 and E_2, which, within a simple Tight-Binding approach, are energetically separated by $2|t|$.

In summary, the mechanisms or processes of EM radiation - 2LS interaction are: (Stimulated) Absorption, Spontaneous Emission, Stimulated Emission. A process is characterized as *stimulated* when it exists due to the existence of energy density of EM radiation, ρ, whereas it is characterized as *spontaneous* when it is not due to the existence of ρ. The reason why we put parentheses in "(Stimulated) Absorption" is exactly that there is no other way: absorption will necessarily be forced, that is, it will owe its existence to ρ. Of these three processes, Stimulated Emission, which was introduced by Einstein, is fundamental to the operation of LASERs. Actually, the acronym means exactly this: Light Amplification by Stimulated Emission of Radiation. Let us notice that within this book, we mainly focus on one electron in a 2LS or 3LS or MLS and on its electric dipole interaction, due to its electric charge, with the EM field. However, similarly, we could, if we had space and time, extend to phenomena which require magnetic dipole moment and interaction due to electron spin. This will maybe be done in a next edition. The probability of (Stimulated) Absorption is

$$dW^{\mathrm{st}}_{\mathrm{abs}} = B_{12}\rho(\nu, T)dt,$$

that is, proportional to time dt and to $\rho(\nu, T)$, with proportionality factor B_{12}. The index 12 means that with the photon absorption, the electron will be transferred from level 1 to level 2. The probability of Spontaneous Emission is

$$dW^{\mathrm{sp}}_{\mathrm{em}} = A_{21}dt,$$

that is, proportional to time dt, with proportionality factor A_{21}. The index 21 means that with the photon emission, the electron will be transferred from level 2 to level 1. Since this process is spontaneous, $dW^{\mathrm{sp}}_{\mathrm{em}}$ does not depend on $\rho(\nu, T)$. The probability of Stimulated Emission is

$$dW^{\mathrm{st}}_{\mathrm{em}} = B_{21}\rho(\nu, T)dt,$$

that is, proportional to time dt and to $\rho(\nu, T)$, with proportionality constant B_{21}. The index 21 means that with the photon emission, the electron will be transferred from level 2 to level 1. These are shown schematically in Figure 1.3. In (Stimulated) Absorption, a photon is absorbed, leading to an electron being transferred from the lower level to the upper level. In Spontaneous Emission, an electron, which was in the upper level, falls spontaneously at the lower level, which happens to be empty, and as a result, a photon is emitted, which however, has random direction, phase, polarization. In Stimulated Emission, a stimulating or *driving* photon (i.e., this is a stimulated or driven oscillation), let us call it *stimulating photon*, with energy $E_\phi = h\nu$, momentum $p_\phi = E_\phi/c$, obliges the electron, which initially was at the upper level, to fall at the empty lower level, leading to another photon being emitted. This second photon is identical to the stimulating photon, i.e, they have same energy, momentum (direction), phase, polarization. The properties of LASER are due to this process: same energy ⇒ monochromaticity, same momentum ⇒ directionality, same phase ⇒ coherence, same polarization ⇒ polarized light. It is implied that we must have conservation of energy and momentum; we will discuss all these thoroughly in Chapter 3.

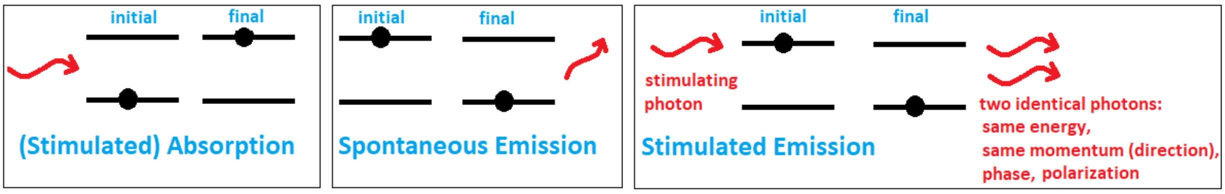


Figure 1.3: Schematically, (Stimulated) Absorption, Spontaneous Emission and Stimulated Emission.

Chapter 4 is devoted to the continuous and the discrete spectrum. The discrete energy spectrum is a feature of atoms and molecules as well as of artificial atoms and molecules, i.e., quantum dots or nanoparticles, which are mainly human-made, either via physical or via chemical paths, as well as of color centers, which usually appear as defects in crystals. Some other human-made objects or artifacts have discrete-continuous energy spectrum, meaning that they have discrete spectrum in one or two dimensions and continuous spectrum in the rest dimensions. Such systems are quantum wires, with discrete spectrum in two dimensions and continuous in one dimension, and quantum wells, with discrete spectrum in one dimension and continuous in two dimensions. The continuous spectrum is a feature of solids, either crystalline or amorphous (with important differences). We also devote space to color centers and quantum dots, which have discrete spectrum. Moreover, in Chapter 4 we study the transition from two 1LSs to one coupled system, the 2LS, which is done with three variants of the Tight-Binding method, with graded simplicity. For quantum wells, wires and dots, we mainly describe their electronic states and their corresponding density of states.

In Chapter 5 we deal with the so-called semiclassical approximation of the EM field - 2LS, 3LS, MLS interaction. Semiclasical means that, while we treat the EM field classically, we treat 2LS, 3LS, MLS quantum mechanically, that is, as a system of eigenstates. Here, we introduce the reader to the dipole approximation. The electric dipole moment between two charges, one positive (plus, P), $q > 0$, and one negative (minus, M), $-q < 0$, is defined as $\vec{\mathscr{P}} := q\vec{d}$, where we define $\vec{d} = \overrightarrow{\mathrm{MP}}$ (Figure 1.4). Usually, when studying an atom, we consider the position vector of the electron (E) relative to the nucleus (N), $\overrightarrow{\mathrm{NE}} = \vec{r} = -\vec{d}$. Then, $\vec{\mathscr{P}} := q\vec{d} = -e\vec{r}$, if we refer to e.g. the hydrogen atom.

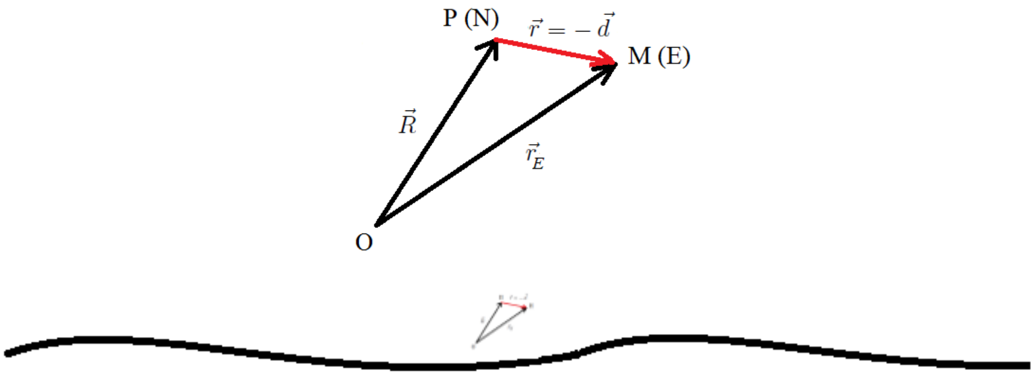


Figure 1.4: (Upper panel) The axes origin O, the positive charge P (plus), which can be represented by the nucleus N in an atom, the negative charge M (minus), which can be represented by one electron E moving around the nucleus. We define $\vec{d} := \overrightarrow{\mathrm{MP}}$. Usually, when studying an atom, we consider the position vector of the electron relative to the nucleus $\overrightarrow{\mathrm{NE}} = \vec{r} = -\vec{d}$. The electric dipole moment is defined as $\vec{\mathscr{P}} := q\vec{d}$ something that we can therefore write $\vec{\mathscr{P}} = -e\vec{r}$, if we refer to e.g. the hydrogen atom. For the latter case, we notice the vectors $\overrightarrow{OP} := \vec{R}$ and $\overrightarrow{OE} := \vec{r}_E$. (Lower panel) Very schematically: Under these conditions, the wave length is much larger than the spatial extent of the system, something like $\lambda >> \alpha$; thus, the electric field is practically homogeneous. For example, for optical wavelengths, $\lambda \sim 500$ nm, and for the hydrogen atom $\alpha \sim \alpha_0$ (Bohr radius), hence, $\lambda/a_0 \sim 10^4$. The triangle OPM (ONE), which is shown in the upper panel, is shown in the lower panel smaller than the wavelength, but in fact it is much ($\sim 10^4$ times) smaller.

We will use time-dependent perturbation theory. Here, by the term *unperturbed* system we mean the eigenstate system without EM field, while, by the term *perturbed* system we mean that the potential energy of interaction with the EM field, which is time-dependent, has been added. Let us call the Hamiltonian of the unperturbed system $\hat{H}_0$, the potential energy of the perturbation $U_{\mathscr{E}}(\vec{r}, t)$ and the Hamiltonian of the perturbed system $\hat{H}$. Then,

$$\hat{H} = \hat{H}_0 + U_{\mathscr{E}}(\vec{r}, t).$$

The potential energy of the perturbation, that is, of the interaction with the electric field $\vec{\mathscr{E}}$, has the form

$$U_{\mathscr{E}} = -\vec{\mathscr{P}} \cdot \vec{\mathscr{E}}.$$

Almost everywhere in this book we neglect the electron spin and hence the potential energy of interaction with the magnetic field, which has a similar form, that is,

$$U_{\mathscr{B}} = -\vec{\mu} \cdot \vec{\mathscr{B}},$$

where $\vec{\mu}$ is the magnetic dipole moment and $\vec{\mathscr{B}}$ is the magnetic induction. Nice analogies exist between electric dipole moment inside an electric field and magnetic dipole moment inside magnetic field. We remind these analogies to the reader below, as we list the electric dipole moment, magnetic dipole moment, potential energy of electric dipole, potential energy of magnetic dipole and the respective torques. $\vec{L}$ is the orbital momentum, $\vec{S}$ is the spin, g a dimensionless factor, and q, m are the particle charge and mass, respectively.

Analogies Reminder

$\vec{\mathscr{E}}$ (Electric Field) $\vec{B}$ (Magnetic Field)

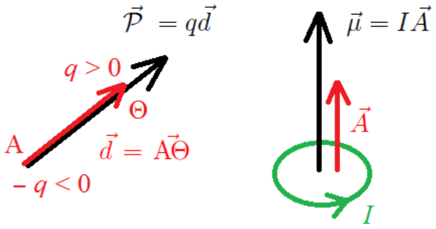


Figure 1.5: Electric and magnetic dipole.

$\vec{\mathscr{P}} = q\vec{d}$ electric dipole moment

$U_{\mathscr{E}} = -\vec{\mathscr{P}} \cdot \vec{\mathscr{E}}$ potential energy

$\vec{\tau} = \vec{\mathscr{P}} \times \vec{\mathscr{E}}$ torque

$[\vec{\mathscr{P}}] = \mathrm{Cm}$

$[U_{\mathscr{E}}] = \mathrm{Cm}\dfrac{\mathrm{N}}{\mathrm{C}} = \mathrm{Nm} = \mathrm{J}$

$[\vec{\tau}] = \mathrm{Cm}\dfrac{\mathrm{N}}{\mathrm{C}} = \mathrm{Nm}$

$\vec{\mu} = I\vec{A}$ magnetic dipole moment

or $\vec{\mu} = (q/2m)(\vec{L} + g\vec{S})$

$U_B = -\vec{\mu} \cdot \vec{B}$ potential energy

$\vec{\tau} = \vec{\mu} \times \vec{B}$ torque

$[\vec{\mu}] = \mathrm{Am}^2$

$[U_B] = \mathrm{Am}^2\dfrac{\mathrm{N}}{\mathrm{Am}} = \mathrm{Nm} = \mathrm{J}$

$[\vec{\tau}] = \mathrm{Am}^2\dfrac{\mathrm{N}}{\mathrm{Am}} = \mathrm{Nm}$

The essence of the approach we use is shown in Figure 1.4. The wavelength is much larger than the spatial dimensions of the system under study, i.e.,

$$\lambda >> \alpha.$$

If, for example, we study the hydrogen atom, $\alpha = \alpha_0$ is, let's say, the Bohr radius. If we examine optical wavelengths, i.e., $\lambda \sim 500\,\mathrm{nm}$, since $\alpha_0 \approx 0.529\,\text{Å} \sim 0.5{\times}10^{-1}\,\mathrm{nm}$, then $\lambda/\alpha_0 \sim 10^4$, i.e., the approximation holds for optical transitions and atomic physics. If indeed this happens, i.e., if the wavelength is much larger than the system's spatial extent, then, in a good approximation, the electric field has only temporal dependence but it is spatially homogeneous. In physics, *homogeneous* means the same everywhere, i.e., in every point of space, while, *isotropic* means the same towards all directions.

Under these conditions, in Chapter 5 we study and analytically solve the temporal evolution of 2LS and 3LS, with one electron somehow placed initially (e.g. at the lower level) and finally we obtain the so-called Rabi oscillations, i.e., how do the probabilities to find the electron at each level oscillate as functions of time. For this purpose, we make the so-called Rotating Wave Approximation (RWA). Practically, this means that if we denote by ω the cyclic frequency of the EM field and by $\hbar\Omega$ the energetic separation between e.g. the two levels of a 2LS and solve the problem, then we obtain fast terms containing $\pm(\omega + \Omega)$ and slow terms containing $\pm(\omega - \Omega)$, but we only keep the slow terms. These oscillations the electron performs between the two levels are called Rabi oscillations and we meet them here for the first time, within the semiclassical approximation. Such an example of oscillations of the probability to find an

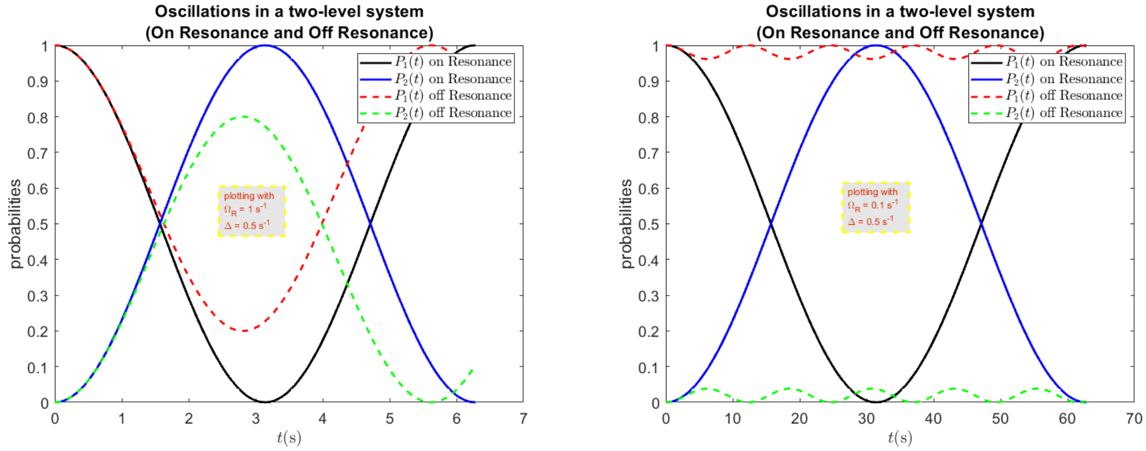


Figure 1.6: We present the oscillations of the probability to find the electron at the two levels of a two-level system (2LS) at resonance ($\Delta = 0$, continuous lines) and out of resonance ($\Delta \neq 0$, dashed lines). The period of the oscillations is $T_\mathrm{R} = {}^{2\pi}\!/\!\sqrt{\Omega_\mathrm{R}^2 + \Delta^2}$, while, the maximum transfer percentage is $\mathscr{A} = {}^{\Omega_\mathrm{R}^2}\!/\!(\Omega_\mathrm{R}^2 + \Delta^2)$. To make a graphical representation, we have assigned some values to Ω_R and Δ. $\Delta = \omega - \Omega$ is the so-called detuning and Ω_R is the Rabi frequency, which shows how much the two levels are tangled by the electric field.

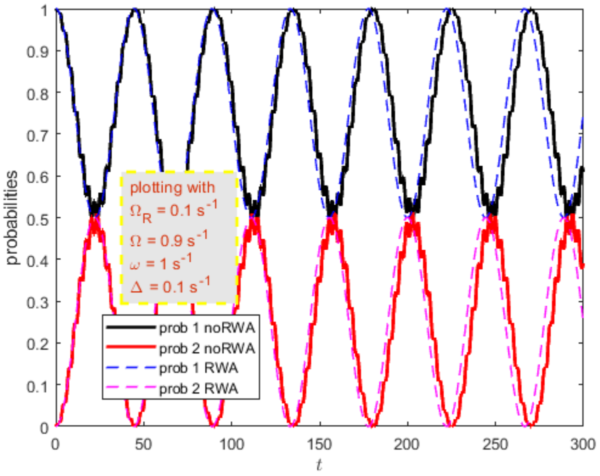


Figure 1.7: A comparison between the Rotating Wave Approximation (RWA) and the full numerical solution (noRWA), for some arbitrary values of Ω_R, Ω, ω, Δ. We present the probabilities to find the electron at the two levels as functions of time, for initial placement at level 1. The RWA curves are smoother, since they lack the high-frequency terms $\pm(\Omega + \omega)$ and only low-frequency terms $\pm(\Omega - \omega)$ have been kept. Also, we observe a slight dephasing, i.e., the RWA curves are little by little left behind the full numerical solution curves.

electron at the two levels of a 2LS, within RWA, is shown in Figure 1.6. A comparison of RWA with the full numerical solution, i.e., without ignoring the fast terms, is shown in Figure 1.7. Finally, in Chapter 5 we examine the MLS within RWA, under the assumption that levels are equidistant.

Chapter 6 is also devoted to the semiclassical approximation. Here, we focus on full numerical solutions, but we also compare with approximate methods, such as the popular RWA and the first and second order averaging method [7]. Hence, also in Chapter 6, we study again Rabi oscillations in a 2LS and MLS, at the semiclassical approximation. The solution of the –perturbed by the electric component of the EM field– 2LS is approached in three ways: (a) via the rotating wave approximation (RWA),

(b) via the averaging method, (AM), and (c) numerically, by solving the original differential equations without approximation (noRWA). Ways (a) and (b) give approximate solutions. Indicatively, we test the following initial conditions:

1. $C_1(0) = 1, C_2(0) = 0$ (initial placement of the electron at the lower level),
2. $C_1(0) = 0, C_2(0) = 1$ (initial placement of the electron at the upper level),
3. $C_1(0) = \frac{1}{\sqrt{2}}e^{i\theta}, C_2(0) = \frac{1}{\sqrt{2}}e^{i\phi}$ (initial equiprobable placement of the electron at the two levels, but generally with different initial phase).

We compare the results of the approximate methods (a) and (b) with the results of the numerical solution of the relevant differential equations (c) [with matlab, via the trapezoid, Runge-Kutta (2,3) and Runge-Kutta (4,5) methods]. This study includes resonance ($\Delta = 0$), as well as out-of-resonance ($\Delta \neq 0$) cases.

Chapter 7 is devoted to the so-called allowed and forbidden optical transitions, mainly within the dipole approximation, and to the so-called selection rules, which, in brief, tell us "what is allowed and what is forbidden". A model system which is often used to explain these concepts is the hydrogen atom. We will use it here, too. Given the chance, we also analyze the atomic orbitals of the hydrogen atom, i.e., their parity (whether they are even or odd) and nodal surfaces (surfaces where the wave function vanishes). We explain the so-called allowed and forbidden transitions within the dipole approximation as well as the relevant selection rules. Within the dipole approximation, everything is finally reduced to the integral

$$\vec{r}_{k'k} = \int d^3r \quad \Phi^*_{k'}(\vec{r}) \quad \vec{r} \quad \Phi_k(\vec{r}),$$

which expresses the matrix element of the position of the negative charge with respect to the positive charge e.g. the position of the electron relative to the nucleus. k and k' are the states between which we ask whether an optical transition can take place. If this integral is zero, then the optical transition is "forbidden", while, if it is not zero, the optical transition is "allowed"; the larger this integral is the stronger the optical transition. The reason is that the matrix element of the potential energy of the perturbation, which tries to tangle states k and k' via the electric field, $\vec{\mathscr{E}}$, is

$$U_{\mathscr{E}k'k}(t) = e\vec{\mathscr{E}} \cdot \vec{r}_{k'k}.$$

We observe that, everything reduces to the symmetry of the eigenfunctions of the unperturbed system, since whether the matrix element $\vec{r}_{k'k}$ is zero or not is determined by which of them are even or odd, given that the function $\vec{r}$ is obviously odd. Moreover, in Chapter 7 we discuss hybrid sp, sp^2, and sp^3 orbitals.

In chapter 8 we advance to the full quantum mechanical treatment of photon - 2LS, 3LS, MLS interaction and to the EM field quantization inside a cavity, which is performed with a somehow heuristic manner. We mainly focus here on Rabi oscillations of the number of photons within a cavity and of the probability to find the electron at the levels of a 2LS (or 3LS, MLS) as the electron interacts with the photons inside the cavity. Hence, here many photons and a single electron are tangled, an electron which descends and ascends between the two levels. Many-fermion phenomena are out of the subject of this book. A photon is a boson, i.e., it is benign, in the sense that many bosons can occupy the same quantum state. But an electron is a fermion, i.e., it is snob, in the sense that two fermions cannot occupy the same quantum state. This way, while we can condense bosons, we cannot condense (pure) fermions (although for example, Cooper pairs can be condensed). The Hamiltonian of the m mode of the EM field, $\hat{H}_{\mathrm{EM},m}$, is expressed via photon (boson) annihilation and creation operators. The EM field Hamiltonian is the sum of all the $\hat{H}_{\mathrm{EM},m}$ terms. The 2LS Hamiltonian, $\hat{H}_{\mathrm{2LS}}$, (or 3LS, MLS), which is described via spinors, is expressed via electron (fermion) annihilation and creation operators. We also need a Hamiltonian, to express the interaction of the m mode of the EM field with the 2LS (or 3LS, MLS), let us call it $\hat{H}_{\mathrm{EM},m\text{-}\mathrm{2LS}}$.

This has alternative notations as $U_{\mathscr{E},m}$, $\hat{H}_{\text{AF},m}$; AF has its roots in good old atomic physics, it means atom-field. U reminds us that it is the perturbing potential energy, which emanates from the electric field $\mathscr{E}$. Hence, finally, we have to add all these individual Hamiltonians.

A popular full Hamiltonian of this kind is the Rabi Hamiltonian. It describes an EM field mode, m, a 2LS, and the interaction between them. After some initial simplifications, it can be written in the form

$$\hat{H}_{\text{R},m} = \hbar\omega_m \hat{a}_m^\dagger \hat{a}_m + \hbar\Omega \hat{S}_+ \hat{S}_- + \hbar g_m (\hat{S}_+ + \hat{S}_-)(\hat{a}_m^\dagger + \hat{a}_m).$$

The first term expresses the mode m of the EM field, the second term expresses the 2LS and the third term expresses their interaction. ω_m is the (cyclic) frequency of mode m of the EM field and $\hat{a}_m^\dagger$ ($\hat{a}_m$) is the photon creation (annihilation) operator of such a photon. $\hbar\Omega$ is the energy separation of the two levels and $\hat{S}_+$ ($\hat{S}_-$) is the electron raising (lowering) operator between the upper and the lower level. Finally, g_m expresses the strength and permissibility of the interaction of mode m of the EM field with the 2LS. The third term of the Rabi Hamiltonian can be expanded into four addends. From these, the first addend expresses raising of the electron and creation of a photon ($\hat{S}_+\hat{a}_m^\dagger$), the second addend raising of the electron and annihilation of a photon ($\hat{S}_+\hat{a}_m$), the third addend lowering of the electron and creation of a photon ($\hat{S}_-\hat{a}_m^\dagger$), and the fourth addend lowering of the electron and annihilation of a photon ($\hat{S}_-\hat{a}_m$). If there is only one type of photons in the cavity, that is, only one mode m, then the first and the fourth addends seem energetically unreasonable. If we dismiss them, we arrive at the Jaynes-Cummings Hamiltonian [8], a form of which is

$$\hat{H}_{\text{JC},m} = \hbar\omega_m \hat{a}_m^\dagger \hat{a}_m + \hbar\Omega \hat{S}_+ \hat{S}_- + \hbar g_m (\hat{S}_+ \hat{a}_m + \hat{S}_- \hat{a}_m^\dagger).$$

Using the Jaynes-Cummings Hamiltonian, we study photon absorption and emission and the relevant Rabi oscillations of the probability to find the electron at each level (at the lower level $\langle \hat{S}_- \hat{S}_+ \rangle$, at the upper level $\langle \hat{S}_+ \hat{S}_- \rangle$) and of the number of photons of mode m in the cavity ($\langle \hat{a}_m^\dagger \hat{a}_m \rangle$). Two examples are shown in Figure 1.8. We calculate, among other things, the average (expected) values $\langle \hat{a}_m^\dagger \hat{a}_m \rangle$, $\langle \hat{S}_+ \hat{S}_- \rangle$, $\langle \hat{S}_+ \hat{a}_m \rangle$, $\langle \hat{S}_- \hat{a}_m^\dagger \rangle$, for $\hat{H}_{\text{JC},m}$. Finally, we notice that the eigenstates of the electron in the 2LS and the EM mode m, without the interaction between them, are usually expressed as $|\uparrow, n_m\rangle$, $|\downarrow, n_m\rangle$, where n_m is the

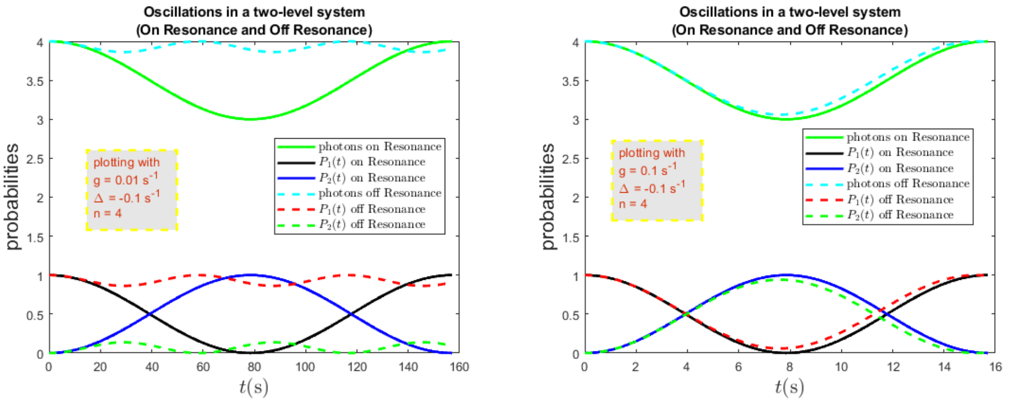
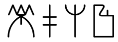


Figure 1.8: Two examples of Rabi oscillations during a photon absorption, i.e., the initial condition is 4 photons in the cavity and 1 electron at the lower level. We use some arbitrary values of the parameters to make an indicative figure. On the right, the two levels are tangled more strongly (the parameter g is larger). We present, the temporal evolution of the expected value of the number of photons in the cavity, $\langle \hat{a}_m^\dagger \hat{a}_m \rangle = n - \frac{ng^2}{\Omega_n^2} \sin^2(\Omega_n t)$ (dashed cyan line), both on resonance ($\Delta = 0$) and out of resonance ($\Delta \neq 0$), as well as of the expected value of the number of electrons at the upper level, $\langle \hat{S}_+ \hat{S}_- \rangle = \frac{ng^2}{\Omega_n^2} \sin^2(\Omega_n t)$ and at the lower level, $\langle \hat{S}_- \hat{S}_+ \rangle$. $\Omega_n = \sqrt{(\Delta/2)^2 + ng^2}$.

number of photons of EM mode m and $|\uparrow\rangle$ ($|\downarrow\rangle$) means that the electron resides at the upper (lower) level.

 Chapter 9 is also devoted to the full quantum mechanical approach. We discuss bosons, fermions, commutations, anticommutations, ladder operators and second quantization. We are interested in:

- the commutator, $[A, B] = AB - BA$, and
- the anticommutator, $\{A, B\} = AB + BA$.

* If the commutator vanishes, $AB = BA$, we have the commutative property.

* If the anticommutator vanishes, $AB = -BA$, we have the anticommutative property.

Boson (e.g. photon) commutation relations: Let us call $\hat{a}_m$ the boson annihilation operator and $\hat{a}_m^\dagger$ the boson creation operator at the state or mode m, where $\hbar\omega_m$ is the energy of the created or annihilated boson, then, for bosons, the following commutation relations hold:

$$
\begin{aligned}
[\hat{a}_m, \hat{a}_\ell^\dagger] &= \delta_{ml} \\
[\hat{a}_m, \hat{a}_\ell] &= 0 \\
[\hat{a}_m^\dagger, \hat{a}_\ell^\dagger] &= 0
\end{aligned}
$$

When $[A, B] = 0 \Rightarrow AB - BA = 0 \Rightarrow AB = BA$, i.e., the quantities A and B commute, which shows the name origin. Simultaneously, $\hat{a}_m^\dagger$ can be called raising operator because it raises the energy by $\hbar\omega_m$, $\hat{a}_m$ can be called lowering operator because it lowers the energy by $\hbar\omega_m$ and therefore, since this is a ladder of raisings and lowerings, the operators $\hat{a}_m$, $\hat{a}_m^\dagger$ are called ladder operators.

Fermion (e.g. electron) anticommutation relations: Let us call $\hat{\mathrm{a}}_i$ the fermion annihilation operator and $\hat{\mathrm{a}}_i^\dagger$ the fermion creation operator at state i, where $\hbar\Omega_i$ is the energy of the created or annihilated fermion, then, for fermions, the following anticommutation relations hold:

$$
\begin{aligned}
\{\hat{\mathrm{a}}_i, \hat{\mathrm{a}}_j^\dagger\} &= \delta_{ij} \\
\{\hat{\mathrm{a}}_i, \hat{\mathrm{a}}_j\} &= 0 \\
\{\hat{\mathrm{a}}_i^\dagger, \hat{\mathrm{a}}_j^\dagger\} &= 0
\end{aligned}
$$

When $\{A, B\} = 0 \Rightarrow AB + BA = 0 \Rightarrow AB = -BA$, i.e., the quantities A, B anticommute, which shows the name origin. Simultaneously, $\hat{\mathrm{a}}_i^\dagger$ can be called raising operator because it raises the energy by $\hbar\Omega_i$, $\hat{\mathrm{a}}_i$ can be called lowering operator because it lowers the energy by $\hbar\Omega_i$ and therefore, since this is a ladder or raisings and lowerings, operators $\hat{\mathrm{a}}_i$, $\hat{\mathrm{a}}_i^\dagger$ are called ladder operators, too. Alternatively, we use the notation: $\hat{S}_+$ for the raising operator at the upper 2LS level from the lower 2LS level and $\hat{S}_-$ for the lowering operator to the lower 2LS level from the upper 2LS level. Simultaneously, $\hat{S}_+$ could be called electron creation operator at the upper level and destruction operator at the lower level, while $\hat{S}_-$ could be called electron destruction operator at the upper level and creation at the lower level. If we apply the relation $\{\hat{\mathrm{a}}_i^\dagger, \hat{\mathrm{a}}_j^\dagger\} = 0$ for the same state, e.g. putting $i = j = r$, we obtain $\{\hat{\mathrm{a}}_r^\dagger, \hat{\mathrm{a}}_r^\dagger\} = 0 \Rightarrow \hat{\mathrm{a}}_r^\dagger \hat{\mathrm{a}}_r^\dagger = 0$, which means that we cannot put two fermions at the same state, which is the Pauli exclusion principle.

In linear algebra as well as in its applications in quantum mechanics, we define the raising operator, which increases the eigenvalue of another operator, and the lowering operator, which decreases the eigenvalue of another operator. These are collectively called ladder operators. In quantum mechanics, the raising operator is frequently called creation operator, and the lowering operator is frequently called annihilation operator. Well-known applications of ladder operators are in the simple harmonic oscillator and in angular momentum. In quite a few areas of physics and chemistry, the use of these operators instead of wavefunctions is known as second quantization.

ᛯ‡ᛘ🗋 In Chapter 10 we discuss the density operator and matrix. We clarify what a pure state is (the system is described by a wave function), what a mixed state is (the system cannot be described by a well-defined wave function, e.g., because it is coupled to a reservoir with which it can exchange heat, particles etc.). We also discuss the relation of the density operator and matrix with the temporal evolution of the system and the von Neumann equation. The density operator for a pure state can be written as

$$\hat{\rho} = |\Psi\rangle\langle\Psi|, \qquad |\Psi\rangle = \begin{bmatrix} c_1(t) \\ c_2(t) \\ \vdots \\ c_N(t) \end{bmatrix}.$$

That is, $|\Psi\rangle = \sum_k c_k(t)\,|\Phi_k\rangle$, where $|\Phi_k\rangle$ is our basis. Hence, $\langle\Psi| = \begin{bmatrix} c_1^*(t) & c_2^*(t) & \cdots & c_N^*(t) \end{bmatrix}$, hence, the representation of the density operator in matrix form is

$$|\Psi\rangle\langle\Psi| = \begin{bmatrix} c_1(t) \\ c_2(t) \\ \vdots \end{bmatrix} \begin{bmatrix} c_1^*(t) & c_2^*(t) \cdots & \end{bmatrix} = \begin{bmatrix} c_1(t)c_1^*(t) & c_1(t)c_2^*(t) & \cdots \\ c_2(t)c_1^*(t) & c_2(t)c_2^*(t) & \cdots \\ \vdots & \vdots & \end{bmatrix}.$$

The temporal evolution of the density operator is given by the Liouville - von Neumann equation

$$i\hbar\frac{\partial\hat{\rho}(t)}{\partial t} = [\hat{H}, \hat{\rho}(t)],$$

where $\hat{H} = \hat{H}_0 + U_{\mathscr{E}}(\vec{r}, t)$ is the system Hamiltonian. If we include energy level relaxations due to spontaneous emission or de-excitations, collisions with gas atoms etc, then

$$i\hbar\frac{\partial\hat{\rho}(t)}{\partial t} = [\hat{H}, \hat{\rho}(t)] - \frac{i\hbar}{2}\{\hat{\Gamma}, \hat{\rho}(t)\},$$

where $\hat{\Gamma}\Phi_k(\vec{r}) = \gamma_k\Phi_k(\vec{r})$, $\gamma_k \in \Re$ and the Hamiltonian is written $\hat{H} = \hat{H}_0 + U_{\mathscr{E}}(\vec{r}, t) - \frac{i\hbar}{2}\hat{\Gamma}$.

ᛯ‡ᛘ🗋 Chapter 11 is devoted to LASERs; specifically, to the operation principles, rate equations for the level populations and for the energy density of the EM waves in the cavity, longitudinal and transverse modes, and types of LASERs. As a prototype system, we examine the He - Ne LASER, while we also mention other LASER types, such as the p-n junction LASER, the quantum dot LASER etc. We focus on the rate equations for the level populations N_1 and N_2, for the levels which participate in the emission of coherent EM waves and for the energy density of EM waves in the cavity ρ, that is, on $^{dN_1}/_{dt}$, $^{dN_2}/_{dt}$, $^{d\rho}/_{dt}$. We explain what the longitudinal and transverse modes are. We discuss the optical transition line widths. Apart from the temporal evolution of N_1, N_2, ρ, generally, we also focus on the values of N_1, N_2, ρ, at the steady state, i.e., when a dynamical equilibrium between the statistical set of 2LSs (we have a large number of 2LSs in the cavity) and the energy density of EM waves in the cavity has been established. We explain what pumping, critical pumping and population inversion is. The differential equations, which tangle N_1, N_2, ρ, generally, cannot be solved analytically, but numerically. Here we solve them by matlab; an example is shown in Figure 1.9. We notice, finally, that even though the emission of coherent EM waves (aka lasing) is usually between two tangled levels (2LS), other levels are also involved in the whole process with auxiliary role.

The LASER rate differential equations in dimensionless form have the form

$$\frac{d\nu_1}{d\tau} = \nu_2 + \varrho(\nu_2 - \nu_1) - \frac{\nu_1}{\tau_1},$$

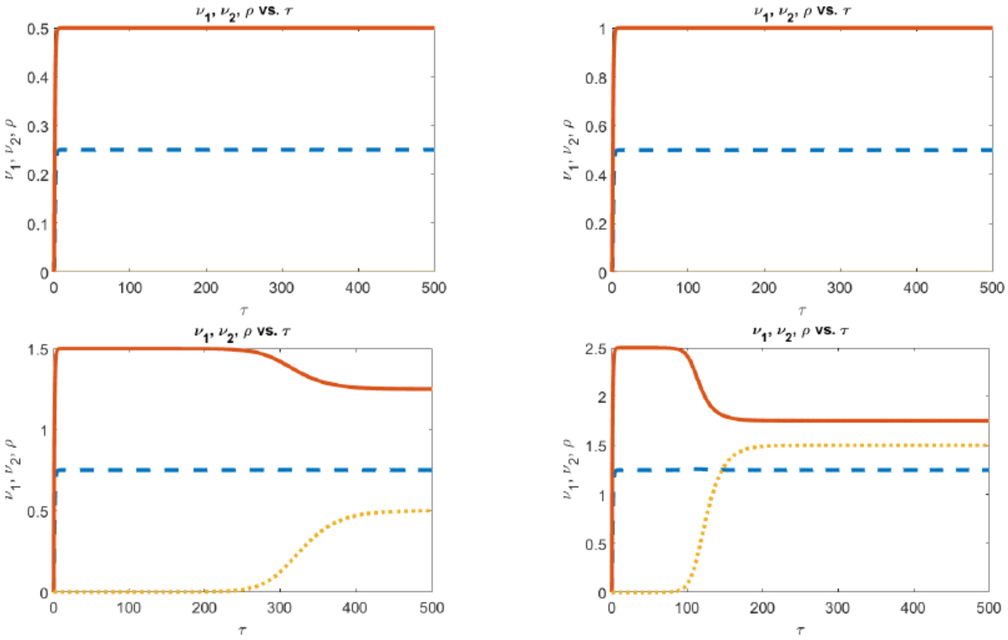


Figure 1.9: We modify only one parameter (from the set r_N, τ_1, τ_0, A'/A) and we observe the temporal evolution of the dimensionless level populations (ν_1, ν_2) as well as of the dimensionless energy density of EM waves inside the cavity (ϱ) as functions of the dimensionless time (τ).

$$\frac{d\nu_2}{d\tau} = r_N + \varrho(\nu_1 - \nu_2) - \nu_2,$$

$$\frac{d\varrho}{d\tau} = -\frac{\varrho}{\tau_0} + \left\{ \frac{A'}{A}\nu_2 + \varrho(\nu_2 - \nu_1) \right\} \frac{1}{\tau_0(1-\tau_1)}.$$

Here $\nu_1, \nu_2, \varrho, \tau$ are dimensionless N_1, N_2, ρ, t (time), while, r_N, τ_1, τ_0, A'/A dimensionless parameters, whose meaning is explained in Chapter 11. At the steady state, ignoring $A'/A \ll 1$, the following equations hold

$$\nu_1 = \tau_1 r_N, \quad \forall\ r_N$$

$$\nu_2 = \begin{cases} r_N, & \forall\ r_N \leq 1 \\ \tau_1 r_N + (1 - \tau_1), & \forall\ r_N \geq 1 \end{cases}$$

$$\varrho = \begin{cases} 0, & \forall\ r_N \leq 1 \\ r_N - 1, & \forall\ r_N \geq 1 \end{cases}$$

An example of numerical solution of the rate equations is shown in Figure 1.9, where we modify only one of the parameters r_N, τ_1, τ_0, A'/A; Details in Chapter 11. Finally, in Chapter 11 we touch upon the isolation of the fundamental mode TEM_{00} as well as of higher order modes $\mathrm{TEM}_{p'q'}$ (here TEM means transverse electromagnetic).

In Chapter 12 we lay down various other useful elements. Among these, we examine the Fresnel equations, which concern the incidence of an EM wave at an interface between two media, 1 and 2 (Figure 1.10). The plane of incidence q is the plane defined by the incident wave vector $\vec{k}_i$ and the normal to the interface, at the point of incidence, unit vector $\hat{n}$, that is, in Figure 1.10, the xy-plane. The reader can see the angles of incidence, reflection, refraction or transmission, θ_i, θ_r, θ_t, respectively, as well as the components of the electric field $\vec{E}$, the so-denoted s from the German senkrecht or TE (transverse electric) with $\vec{E}_s \perp q$ and the so-denoted p from parallel or TM (transverse magnetic) with

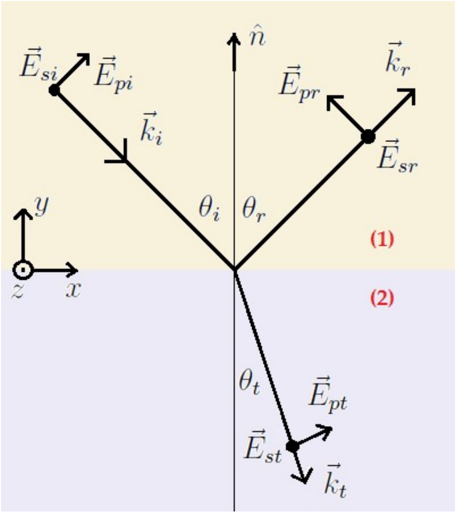


Figure 1.10: Incidence of EM wave at an interface between two media 1 and 2. Plane of incidence q is the plane defined by the incident wave vector $\vec{k}_i$ and the normal to the interface, at the point of incidence, unit vector $\hat{n}$, that is here plane xy. We observe the angles of incidence, reflection, refraction or transmission, $\theta_i, \theta_r, \theta_t$, respectively, as well as the s (perpendicular to q) and p (belonging to q) components of the incident, reflected, refracted or transmitted electric field $\vec{E}_{si}, \vec{E}_{pi}, \vec{E}_{sr}, \vec{E}_{pr}, \vec{E}_{st}, \vec{E}_{pt}$, respectively.

$\vec{E}_p \in q$, that is, the components of the incident (i), reflected (r), refracted or transmitted (t) electric field $\vec{E}_{si}, \vec{E}_{pi}, \vec{E}_{sr}, \vec{E}_{pr}, \vec{E}_{st}, \vec{E}_{pt}$, respectively. The angle of incidence for which there is no reflected p polarization, is called the Brewster angle. We will also define reflectance, $R := |\vec{E}_r|^2/|\vec{E}_i|^2$, and transmittance, $T := (|\vec{E}_t|^2/|\vec{E}_i|^2)\sqrt{\varepsilon_2\mu_1/\varepsilon_1\mu_2}\,(\cos\theta_t/\cos\theta_i)$, which are connected via $R + T = 1$, the Poynting vector, $\vec{S} := \vec{E} \times \vec{H}$ which has units of power per unit area, as well as other relevant quantities and properties.

After this overview, it is time to take things from the start ...

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CHAPTER 2

THE QUANTUM NATURE OF LIGHT

In this Chapter:
We discuss the quantum nature of light. The chapter is devoted to phenomena and concepts that historically led to our perception of the quantum nature of light. Specifically: Initially, we refer to the concept *black body* and relevant concepts. Then, we describe the energy density of EM radiation in an infinitesimal frequency interval, of a black body in thermodynamic equilibrium. We refer to Planck's law and compare it with Rayleigh-Jeans and Wien approximations. Later, we delineate two formulations of the Stefan-Boltzmann law, the first with energy density and the second with intensity of radiation. We continue by discussing the Maxwell equations in total charge and current formulation as well as the boundary conditions at an interface. Also, we discuss the existence of EM waves in the absence of current and charge density, fields inside an ideal conductor, fields at the boundary of an ideal conductor, fields inside cavities. Then, we discuss the normal EM modes inside a rectangular parallelepiped cavity, and we calculate the infinitesimal number of EM field normal modes per infinitesimal frequency interval. At this point we are in the position to prove the classical Rayleigh-Jeans law, using the equipartition of energy theorem and the infinitesimal number of EM field normal modes per infinitesimal frequency interval. This law is a colossal failure of classical physics. Next, we present the proof of Planck's law as Planck proved it. Then, we prove the Wien displacement law in several variations. Finally, we describe the photoelectric effect.
Prerequisite knowledge: Basic knowledge of Physics and Mathematics plus a little bit of Electromagnetism and Statistical Physics.

2.1 Black body and related concepts.

Let us start by some definitions. Let us assume that electromagnetic (EM) waves or, in other words, electromagnetic radiation impinges on a body, as schematically depicted in Figure 2.1. Then, we define the following physical quantities:

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Kallipos, Open Academic Editions. https://dx.doi.org/10.57713/kallipos-186

- **absorption coefficient**, α, is the fraction of EM radiation the body absorbs.
- **transmission coefficient**, τ, is the fraction of EM radiation that passes through the body.
- **reflection coefficient**, ρ, is the fraction of EM radiation the body reflects.

These three quantities are connected through the relation

$$\alpha + \tau + \rho = 1. \tag{2.1}$$

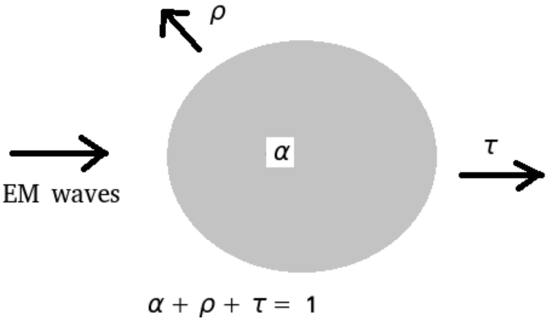

Figure 2.1: Electromagnetic waves impinge on a body. We show schematically the absorption (α), transmission (τ), and reflection (ρ) coefficients, obeying the relation $\alpha + \tau + \rho = 1$.

But what does the term “black” exactly mean? The scientific definition is rather strict... A **black body** is an idealized physical body that absorbs all incident electromagnetic radiation, **regardless of frequency** and **regardless of angle of incidence**. A black body lets all incident radiation pass inside it, reflecting no incident radiation ($\rho = 0$), absorbing all incident radiation ($\alpha = 1$) and letting no radiation pass through it ($\tau = 0$); all these hold **for all frequencies** and **for all angles of incidence**. Thus, a black body is a perfect absorber of incident EM radiation.

Of course, if this was the case ($\alpha = 1, \rho = \tau = 0$), then, due to constantly absorbing energy, the black body would continuously increase its temperature. Hence, **a black body that is in thermodynamic equilibrium and consequently in constant temperature,** should **re-emit** electromagnetic radiation. This radiation is called **black body radiation** and conserves the equilibrium of energy. Black body radiation obeys the **Planck's law** (§2.2, §2.13, Figure 2.2) so that its spectrum depends only on temperature, regardless of the shape and composition of the body, the angle of emission, etc. A black body in thermodynamic equilibrium has the following remarkable properties [1]:

- (P1). It is an **ideal emitter**, i.e., it emits at each frequency at least as much energy as any other body at the same temperature.
- (P2). It is an **isotropic emitter**, i.e., the energy is radiated isotropically, independent of direction.

Real bodies emit only a fraction of the black body radiation. The **emission coefficient** or **emissivity**, ϵ, is the fraction of EM radiation that is re-emitted by a body. By definition, for a black body in thermodynamic equilibrium, ϵ is equal to one,

$$\epsilon_{\text{black body}}^{\text{in thermodynamic equilibrium}} := 1. \tag{2.2}$$

In summary, for the black body it holds that

$$\alpha = 1, \rho = \tau = 0, \epsilon = 1. \tag{2.3}$$

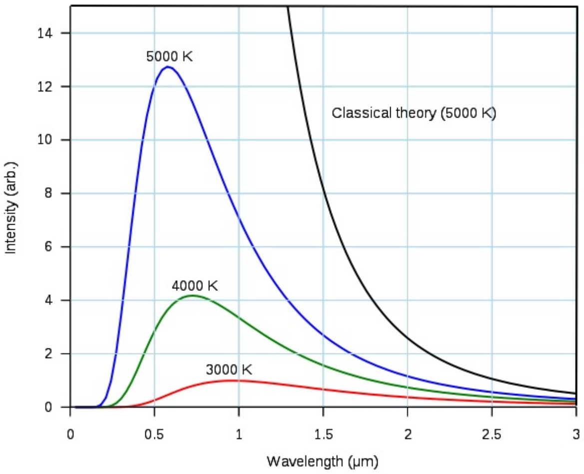

Figure 2.2: Black body radiation according to Planck's law (see §2.2 and §2.13). It depends only on temperature and not on the shape, body composition, angle of emission, etc..

A body with $\epsilon < 1$ is called a **gray body**. A body that reflects all incident radiation is called a **white body** ($\rho = 1$), thus $\alpha = \tau = 0$. All these supposedly hold regardless of frequency, direction or temperature. A body that transmits none of the EM radiation that reaches it ($\tau = 0$), thus $\alpha + \rho = 1$, is called an **opaque body**. A body that transmits all of the EM radiation that reaches it ($\tau = 1$), thus $\alpha = \rho = 0$ is called a **transparent body**. The above definitions are summarized in Table 2.1.

Table 2.1: Definition of bodies..

black body	$\alpha = 1, \rho = \tau = 0, \epsilon = 1$
gray body	$\alpha, \rho, \tau, \epsilon < 1$
white body	$\rho = 1, \alpha = \tau = 0$
opaque body	$\tau = 0, \alpha + \rho = 1$
transparent body	$\tau = 1, \alpha = \rho = 0$

Radiation from stars, planets and other bodies is commonly characterized by an **effective temperature**, i.e., by the temperature of a black body that **would emit the same total (meaning integrated over all frequencies) intensity of radiation**, I (units $[I] = \mathrm{W/m^2}$, §2.3).

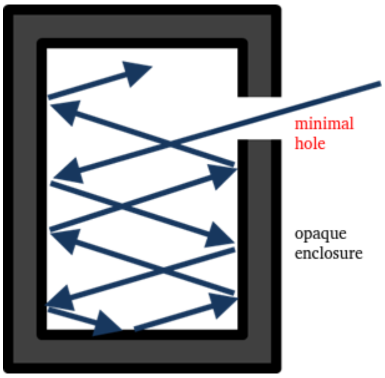

Figure 2.3: Cavity with a hole: an approximate realization of the black body by opening a minimal hole on the wall of an opaque enclosure.

An approximate realization of the black body can be seen in Figure 2.3. An approximate black body can be constructed by opening a small hole on the wall of an **opaque enclosure**, e.g., on a wall of a common box, thus creating a **cavity with a hole** [2]. In photonics, we sometimes refer to the term cavity implying the presence of this minimal hole. Due to the minimal size of the hole compared to the cavity, the light that enters the cavity is **(almost) reflected for ever or absorbed** and it is improbable that it will escape from the cavity, making our system an **almost ideal absorber**. **Whether** this system is in **thermodynamic equilibrium** and thus **the radiation it emits is black body radiation that follows the Planck's law** depends on the nature of the wall and the other contents of the enclosure [3]. **Let us now assume that the cavity is kept at constant temperature T and that the trapped radiation is in thermodynamic equilibrium with the enclosure**. Generally, the hole will let a fraction of radiation escape. If the hole is small enough, the incoming and outgoing radiations have negligible effect on the equilibrium of radiation inside the cavity. **The radiation that escapes will approximately be black body radiation, distributed according to the Planck's law characterized by its temperature T, and it will not depend on the properties of the cavity with a hole, at least for wavelengths adequately smaller than the size of the hole**. The cavity with a hole has been used at least since 1898, when it was described by Otto Lummer and Ferdinand Kurlbaum. Their design was a hole on a platinum box, with its interior blackened with iron oxide [4] or later with a mixture of chromium, nickel, and cobalt oxides [5]. Below, we mention some additional approximate realizations of the black body.

There is an interest in **near-black** bodies or materials for applications such as camouflage (mainly from radars), solar energy collectors, and infrared thermal detectors. As a perfect emitter of radiation, a hot material with nearly-black-body behavior would create an efficient infrared heater, particularly in space or in a vacuum, where conductive heat transport is impossible. Near-black bodies are also useful in telescopes and cameras as anti-reflection surfaces to reduce stray light, and in information-gathering about objects in areas with high optical contrast, e.g. to observe planets orbiting around their stars, where near-black materials absorb light that comes from the irrelevant sources. A first approximation of a black body is carbon black. It has been shown in recent years that nearly perfect black bodies ($\alpha \approx 0.99$) can be constructed using carbon nanotubes [6, 7], while the simple color black has $\alpha < 0.975$. The material "super black" has $\alpha \approx 0.996$ and $\rho \approx 0.004$. A few years ago it has been announced by Surrey NanoSystems that a material called Vantablack has been developed by carbon nanotubes, absorbing, according to the manufacturers, 99.96% of the incident light. An image of Vantablack on an aluminum foil can be seen in Figure 2.4. The name originates from vertically aligned nanotube arrays (VANTA) [8] and the word "black". Vertically aligned carbon nanotubes (CNTs) like a fuzzy forest of tiny trees has been recently used to develop a material that is one order of magnitude darker than other very black materials [9]. According to the authors [9], "the CNT-metal hierarchical architectures demonstrate omnidirectional blackbody photoabsorption with the reflectance of 1×10^{-5} over the range from ultraviolet to terahertz region, which is one order of magnitude lower than that of any previously reported broadband absorber material."

Figure 2.4: The material Vantablack composed by carbon nanotubes (Surrey NanoSystems) which, according to its manufacturers, absorbs 99.96% of incident light, on an aluminum foil.

Planck's law, formulated in 1900, describes the energy density of EM radiation, in an infinitesimal frequency interval, of a black body in thermodynamic equilibrium, $\rho(\nu, T)d\nu$. Specifically,

$$\rho(\nu, T)d\nu = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{\frac{h\nu}{k_B T}} - 1} d\nu. \tag{2.4}$$

The units of $\rho(\nu,T)$ are $[\rho(\nu,T)] = \frac{\mathrm{J}}{\mathrm{m^3Hz}}$. This is a formulation of Planck's law as a function of frequency. There are other formulations, too, which will be described later, e.g., as a function of the wavelength, λ, of the angular frequency, ω, and of the wavenumber, k.

2.2 Energy density of EM radiation in an infinitesimal frequency interval, of a black body in thermodynamic equilibrium: Planck's law and comparison with Rayleigh-Jeans and Wien approximations.

The energy density of EM radiation, in an infinitesimal frequency interval, of a black body in thermodynamic equilibrium, $\rho(\nu,T)d\nu$, was meant to become **one of the issues that revealed the quantization of EM radiation**. Below, we mention three equations that were introduced in search of an explanation for the experimental behavior; the Rayleigh-Jeans expression (theory, classical physics, 1900), the Wien's expression (fitting with experimental data of that era, at high frequencies, 1896), and eventually, the Planck's expression (theory, old quantum mechanics, 1900) that coincides with the experimental behavior in the whole frequency range. Hence, we have the Rayleigh-Jeans law (theory, classical physics, 1900),

$$\rho_{\mathrm{RJ}}(\nu,T) = \frac{8\pi\nu^2 k_{\mathrm{B}}T}{c^3} = \rho_{\mathrm{RJ}}, \tag{2.5}$$

the Wien's law (fitting with experimental data of that era, at high frequencies, 1896),

$$\rho_{\mathrm{W}}(\nu,T) = \frac{\alpha\nu^3}{e^{b\nu/T}} \overset{\text{constants from}}{\underset{\text{Planck's law}}{=\!=\!=\!=}} \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_{\mathrm{B}}T}} = \rho_{\mathrm{W}}, \tag{2.6}$$

where the notes above and below the "=" sign mean that before the sign we present the original expression that Wien proposed and after the sign we present the constants predicted by Planck's law in the asymptotic limit of high frequencies, in which Wien's law approximates Planck's law. Finally, the Planck's law (theory, old quantum mechanics, 1900) that coincides with the experimental behavior for all frequencies,

$$\boxed{\rho(\nu,T) = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_{\mathrm{B}}T}-1} = \rho} \tag{2.7}$$

Let us change the variables, defining

$$\boxed{x = \frac{h\nu}{k_{\mathrm{B}}T}} \tag{2.8}$$

Then,

$$\nu = \frac{k_{\mathrm{B}}T}{h}x \Rightarrow d\nu = \frac{k_{\mathrm{B}}T}{h}dx. \tag{2.9}$$

Then, the essential difference of the above laws is revealed:

$$\boxed{\rho_{\mathrm{RJ}}(x) = \rho_0 x^2} \tag{2.10}$$

$$\boxed{\rho_{\mathrm{W}}(x) = \rho_0\frac{x^3}{e^x}} \tag{2.11}$$

$$\boxed{\rho(x) = \rho_0\frac{x^3}{e^x-1}} \tag{2.12}$$

$$\boxed{\rho_0 := \frac{8\pi}{h^2}\left(\frac{k_{\mathrm{B}}T}{c}\right)^3} \tag{2.13}$$

The units are $[\rho_0] = \frac{\mathrm{Js}}{\mathrm{m}^3} = \frac{\mathrm{J}}{\mathrm{m}^3\mathrm{Hz}}$. Of course, 0 does not belong to the domain of Eq. 2.12, i.e., we do not refer to zero frequency or infinite temperature. An alternative notation found in the literature for $\rho(\nu, T)$ is $u(\nu, T)$.

As mentioned above, the Planck's law can alternatively be stated as a function, e.g., of the wavelength, λ, i.e., in the form $\rho(\lambda, T)$. This can be done by demanding

$$\int_0^\infty \rho(\lambda, T) d\lambda := \int_0^\infty \rho(\nu, T) d\nu \Rightarrow \tag{2.14}$$

$$\int_0^\infty \rho(\lambda, T) d\lambda = \int_0^\infty \frac{8\pi h}{c^3} \frac{\nu^3}{e^{\frac{h\nu}{k_\mathrm{B}T}} - 1} d\nu. \tag{2.15}$$

However,

$$c = \lambda\nu \Leftrightarrow \nu = \frac{c}{\lambda} \Rightarrow \frac{d\nu}{d\lambda} = -\frac{c}{\lambda^2}. \tag{2.16}$$

Hence,

$$\int_0^\infty \rho(\lambda, T) d\lambda = -8\pi hc \int_\infty^0 \frac{1}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_\mathrm{B}T}} - 1} d\lambda = 8\pi hc \int_0^\infty \frac{d\lambda}{\lambda^5 (e^{\frac{hc}{\lambda k_\mathrm{B}T}} - 1)} \Rightarrow \tag{2.17}$$

the Planck's law as a function of the wavelength and the temperature is

$$\boxed{\rho(\lambda, T) = \frac{8\pi hc}{\lambda^5 (e^{\frac{hc}{\lambda k_\mathrm{B}T}} - 1)}} \tag{2.18}$$

Defining

$$\boxed{\psi = \frac{hc}{\lambda k_\mathrm{B} T}} \tag{2.19}$$

and

$$\boxed{\rho_0' = 8\pi \frac{(k_\mathrm{B}T)^5}{(hc)^4}} \tag{2.20}$$

Eq. 2.18 is written as

$$\boxed{\rho(\psi) = \rho_0' \frac{\psi^5}{e^\psi - 1}} \tag{2.21}$$

The units of ρ_0' are $[\rho_0'] = \frac{\mathrm{J}}{\mathrm{m}^3\mathrm{m}}$. Hence, the units of $\rho(\lambda, T)$ are $[\rho(\lambda, T)] = \frac{\mathrm{J}}{\mathrm{m}^3\mathrm{m}}$, as well. **These differ from the units of** $\rho(\nu, T)$, which are $[\rho(\nu, T)] = \frac{\mathrm{J}}{\mathrm{m}^3\mathrm{Hz}}$. In other words, although we use the same symbol (ρ), it is not the same physical quantity. Of course, in Eq. 2.21, 0 does not belong to the domain of $\rho(\psi)$, i.e., the wavelength and the temperature cannot become infinite.

The three above expressions are compared in Figure 2.5. The once so-called *ultraviolet (UV) catastrophe*, i.e., the divergence of the classical Rayleigh-Jeans approximation increasing frequency, is more than evident. Hence, the classical approximation is satisfactory only in the regime of very small frequencies; then, as the frequency increases, it predicts an infinite ρ, in disastrous contradiction with the experimental data. The Wien's approximation has a problem on the opposite limit, i.e., for small frequencies, where it deviates from the experimental behavior, a fact once called *far-infrared (FIR) problem. These characterizations are related to the available experimental data around the 1900s and are, in this sense, deceptive.* In fact, the region where deviations begin to be significant obviously depends on the temperature of the black body: the expressions 2.10, 2.11, 2.12 differ only in the function of x, which according to Eq. 2.8 depends not only on frequency, ν, but also on temperature, T.

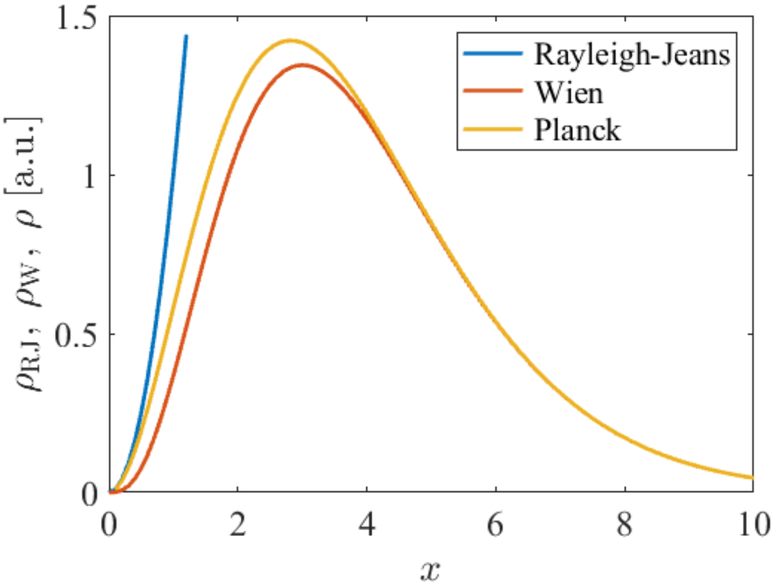

Figure 2.5: Comparison of the Rayleigh-Jeans (Eq. 2.10), Wien (Eq. 2.11), and Planck (Eq. 2.12) laws. We have set $\rho_0 = 1$ (Eq. 2.13), for simplicity, to make the plot. We observe the deviation of the classical Rayleigh-Jeans theory from Planck's law (which agrees with the experiment) very soon increasing $x = \frac{h\nu}{k_B T}$, as well as the deviation of the Wien fitting from Planck's law at low enough x. x includes both frequency, ν, and temperature, T.

2.3 Two formulations of the Stefan-Boltzmann law: (1) Energy density. (2) Intensity of radiation.

We present two common formulations of the Stefan-Boltzmann law, which refers to a black body at temperature T.

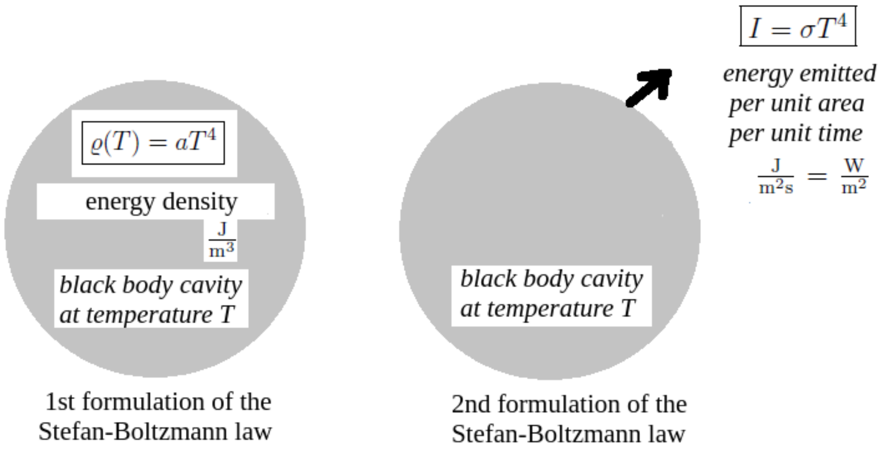

Figure 2.6: [**Left**] The 1st formulation of the Stefan-Boltzmann law refers to the energy density ϱ (units J/m^3) inside a black body in thermodynamic equilibrium at temperature T and has the form $\varrho(T) = aT^4$. $a = \frac{8\pi^5 k_B^4}{15c^3h^3} \approx 7.5657 \times 10^{-16} \frac{\mathrm{J}}{\mathrm{m}^3\mathrm{K}^4}$. [**Right**] The 2nd formulation of the Stefan-Boltzmann law refers to the energy emitted per unit area per unit time, i.e., to the power emitted per unit area or to the intensity of radiation I (units $\frac{\mathrm{J}}{\mathrm{m}^2\mathrm{s}} = \frac{\mathrm{W}}{\mathrm{m}^2}$), and has the form $I = \sigma T^4$. $\sigma = \frac{2\pi^5 k_B^4}{15c^2h^3} \approx 5.67 \times 10^{-8} \frac{\mathrm{W}}{\mathrm{m}^2\mathrm{K}^4}$.

In its first form, the Stefan-Boltzmann law defines the **energy density** (units J/m^3) **inside a black body** at temperature T. To calculate it, we have to integrate Eq. 2.7, i.e., $\rho(\nu, T)$, over all frequencies. Let us use Eq. 2.8. Briefly,

$$\varrho(T) := \int_0^\infty \rho(\nu, T)d\nu = \int_0^\infty \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_\mathrm{B}T} - 1}d\nu \overset{\text{Eq.2.8}}{=\!=} \frac{8\pi h}{c^3}\left(\frac{k_\mathrm{B}T}{h}\right)^3 \frac{k_\mathrm{B}T}{h} \underbrace{\int_0^\infty \frac{x^3}{e^x - 1}dx}_{\pi^4/15} \Rightarrow$$

$$\varrho(T) = \frac{8\pi^5 k_\mathrm{B}^4}{15c^3h^3}T^4. \tag{2.22}$$

Thus

$$\boxed{\varrho(T) = aT^4} \tag{2.23}$$

which is the Stefan-Boltzmann law in its 1st formulation. Here,

$$a = \frac{8\pi^5 k_\mathrm{B}^4}{15c^3h^3} \approx 7.5657 \times 10^{-16}\frac{\mathrm{J}}{\mathrm{m}^3\mathrm{K}^4}. \tag{2.24}$$

Of course, the units of $\varrho(T)$ are $[\varrho(T)] = \mathrm{J}/\mathrm{m}^3$ (energy density). The 1st formulation of the Stefan-Boltzmann law is depicted in Figure 2.6 (left). An alternative symbolism for $\varrho(T)$ is $\breve{u}(T)$.

In its 2nd form, the Stefan-Boltzmann law defines the **energy emitted per unit area per unit time**, i.e., the power emitted per unit area or the intensity of radiation I (units $\frac{\mathrm{J}}{\mathrm{m}^2\mathrm{s}} = \frac{\mathrm{W}}{\mathrm{m}^2}$). Let as take for granted from the kinetic theory of gases [10, 11, 12] that the number of particle collisions (here, photons) onto a wall per unit area and per unit time (units $\frac{1}{m^2s}$) or the flux of particles (here, photons) is

$$\Phi_\sigma = \frac{n}{4}\langle v\rangle, \tag{2.25}$$

where n is the particle density (units $1/\mathrm{m}^3$) and $\langle v\rangle$ is the mean velocity of the particles (here, photons). Thus, for photons,

$$\Phi_\gamma = \frac{n}{4}c. \tag{2.26}$$

But

$$I = \langle h\nu\rangle\Phi_\gamma, \tag{2.27}$$

where

$$\langle h\nu\rangle = \frac{\varrho}{n} \tag{2.28}$$

is the average value of energy each photon carries. From Eqs. 2.26, 2.27, 2.28 it follows that

$$I = \frac{c}{4}\varrho. \tag{2.29}$$

Hence, due to Eq. 2.23,

$$I = \left(\frac{2\pi^5 k_\mathrm{B}^4}{15c^2h^3}\right)T^4 \tag{2.30}$$

or

$$\boxed{I = \sigma T^4} \tag{2.31}$$

which is the 2nd and most common formulation of the Stefan-Boltzmann law. Here,

$$\sigma = \frac{2\pi^5 k_\mathrm{B}^4}{15c^2h^3} \approx 5.67 \times 10^{-8}\frac{W}{\mathrm{m}^2\mathrm{K}^4}. \tag{2.32}$$

The 2nd formulation of the Stefan-Boltzmann law is depicted in Figure 2.6 (right). In other words, the 2nd formulation of the Stefan-Boltzmann law states that the total intensity of radiation emitted by a black body at temperature T is proportional to the 4th power of temperature.

Some electromagnetic issues...

In order to prove Planck's law, but also to prove the classical Rayleigh-Jeans law, we need to know, among other things, the normal modes of EM field in a cavity and, more specifically, $g(\nu) = \frac{dN}{d\nu}$ that is, the infinitesimal number of EM field normal modes in an infinitesimal frequency range. Hence, we will need to address some electomagnetic issues...

2.4 Maxwell's equations. Formulation in terms of total charge and total current.

We know the Gauss's theorem

$$\oint_{S=\partial V} \vec{\Delta} \cdot d\vec{a} = \int_V \vec{\nabla} \cdot \vec{\Delta}\, dV, \tag{2.33}$$

and the Stokes' theorem

$$\oint_{L=\partial S} \vec{\Delta} \cdot d\vec{\ell} = \int_S \vec{\nabla} \times \vec{\Delta} \cdot d\vec{a}. \tag{2.34}$$

Here, $\vec{\Delta}$ denotes a vector field, such as the electric field, magnetic induction, etc., $S = \partial V$ denotes the surface S containing a volume V, $L = \partial S$ denotes the line L containing the surface S. Also, $d\vec{\ell}, d\vec{a}, dV$ denote infinitesimal length, infinitesimal area, and infinitesimal volume, respectively. These theorems allow us to pass from the differential form of Maxwell's equations

$$\boxed{\vec{\nabla} \cdot \vec{E} = \frac{\rho}{\varepsilon_0}} \quad \text{Gauss's law for electrism (1st)} \tag{2.35a}$$

$$\boxed{\vec{\nabla} \cdot \vec{B} = 0} \quad \text{Gauss's law for magnetism (2nd)} \tag{2.35b}$$

$$\boxed{\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}} \quad \text{Faraday's law of induction (3rd)} \tag{2.35c}$$

$$\boxed{\vec{\nabla} \times \vec{B} = \mu_0 \vec{J} + \mu_0 \varepsilon_0 \frac{\partial \vec{E}}{\partial t}} \quad \text{Ampère's law and Maxwell's correction (4th)} \tag{2.35d}$$

after some calculations,

$$\oint_{S=\partial V} \vec{E} \cdot d\vec{a} = \int_V \vec{\nabla} \cdot \vec{E}\, dV = \int_V \frac{\rho}{\varepsilon_0}\, dV = \frac{q_{\text{enclosed in } V}}{\varepsilon_0} \Rightarrow \tag{2.36a}$$

$$\oint_{S=\partial V} \vec{B} \cdot d\vec{a} = \int_V \vec{\nabla} \cdot \vec{B}\, dV = 0 \Rightarrow \tag{2.36b}$$

$$\oint_{L=\partial S} \vec{E} \cdot d\vec{\ell} = \int_S \vec{\nabla} \times \vec{E} \cdot d\vec{a} = -\int_S \frac{\partial \vec{B}}{\partial t} \cdot d\vec{a} = -\frac{\partial}{\partial t} \int_S \vec{B} \cdot d\vec{a} \Rightarrow \tag{2.36c}$$

$$\oint_{L=\partial S} \vec{B} \cdot d\vec{\ell} = \int_S \vec{\nabla} \times \vec{B} \cdot d\vec{a} = \int_S \left(\mu_0 \vec{J} + \mu_0 \varepsilon_0 \frac{\partial \vec{E}}{\partial t} \right) \cdot d\vec{a} = \mu_0 \int_S \vec{J} \cdot d\vec{a} + \mu_0 \varepsilon_0 \int_S \frac{\partial \vec{E}}{\partial t} \cdot d\vec{a} \Rightarrow \tag{2.36d}$$

to their integral form

$$\boxed{\Phi_{E,S=\partial V} := \oint_{S=\partial V} \vec{E}\cdot d\vec{a} = \frac{q_{\text{enclosed in } V}}{\varepsilon_0}} \quad \text{Gauss's law for electrism (1st)} \tag{2.37a}$$

$$\boxed{\Phi_{B,S=\partial V} := \oint_{S=\partial V} \vec{B}\cdot d\vec{a} = 0} \quad \text{Gauss's law for magnetism (2nd)} \tag{2.37b}$$

$$\boxed{\mathscr{E}_{\text{EMF}} := \oint_{L=\partial S} \vec{E}\cdot d\vec{\ell} = -\frac{\partial \Phi_{B,S}}{\partial t}} \quad \text{Faraday's law of induction (3rd)} \tag{2.37c}$$

$$\boxed{\oint_{L=\partial S} \vec{B}\cdot d\vec{\ell} = \mu_0 I_{\text{passing through } S} + \mu_0\varepsilon_0 \frac{\partial \Phi_{E,S}}{\partial t}} \quad \text{Ampère's law and Maxwell's correction (4th)} \tag{2.37d}$$

In 2.37d, $I_{\text{passing through } S}$ is the current passing through the surface S.

In vacuum, where $\rho = 0$ and $\vec{J} = \vec{0}$, Eqs. 2.35a-2.35d become

$$\vec{\nabla}\cdot\vec{E} = 0 \tag{2.38a}$$

$$\vec{\nabla}\cdot\vec{B} = 0 \tag{2.38b}$$

$$\vec{\nabla}\times\vec{E} = -\frac{\partial \vec{B}}{\partial t} \tag{2.38c}$$

$$\vec{\nabla}\times\vec{B} = \mu_0\varepsilon_0 \frac{\partial \vec{E}}{\partial t} \tag{2.38d}$$

2.5 Boundary conditions at interfaces.

We will now describe the boundary conditions at an interface. This information can also be found in a electromagnetism textbook [13, 14].

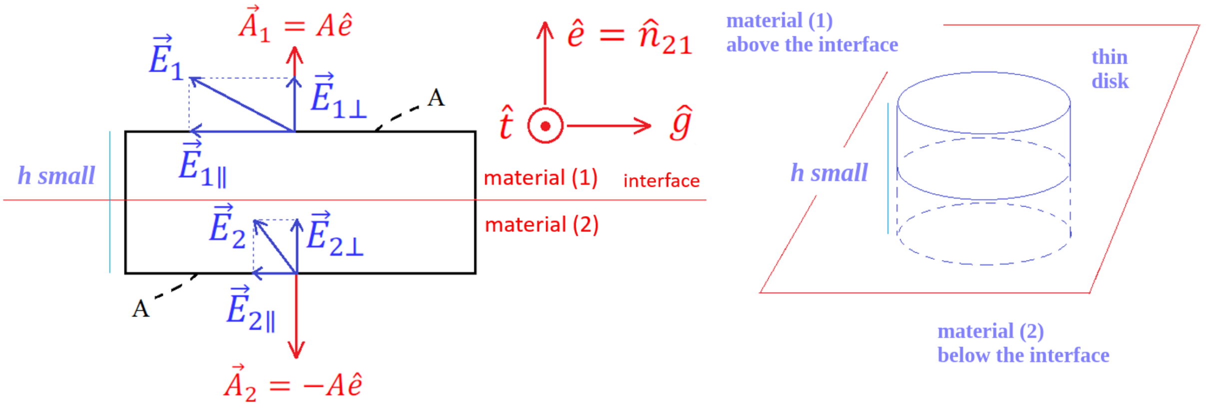

Figure 2.7: Boundary conditions for the 1st Maxwell's equation. The direction of vectors $\vec{E}_1$ and $\vec{E}_2$ has been chosen arbitrarily on purpose. Similarly we treat the 2nd Maxwell's equation, where $\vec{E}$ should be replaced by $\vec{B}$.

♣ Let us apply the 1st Maxwell's equation 2.37a on Figure 2.7, where an arbitrary direction of vectors $\vec{E}_1$ and $\vec{E}_2$ has been drawn on purpose.

$$\Phi_{E,S=\partial V} := \oint_{S=\partial V} \vec{E}\cdot d\vec{a} = \frac{q_{\text{enclosed in } V}}{\varepsilon_0} \Rightarrow$$

$$\Phi_{E,\text{ upper circle}} + \Phi_{E,\text{ lower circle}} + \Phi_{E,\text{ lateral}} = \frac{q_{\text{ enclosed in } V}}{\varepsilon_0}.$$

$\Phi_{E,\text{ upper circle}} = \vec{E}_1 \cdot \vec{A}_1 = E_{1\perp}A_1$ and $\Phi_{E,\text{ lower circle}} = \vec{E}_2 \cdot \vec{A}_2 = E_{2\perp}A_2$, where $E_{1\perp}, E_{2\perp}, A_1, A_2$ are algebraic values. Thus

$$\left.\begin{aligned} AE_{1\perp} - AE_{2\perp} + \int\limits_{A_{\text{lateral}}} \vec{E}\cdot d\vec{a} = \frac{\sigma \cdot A}{\varepsilon_0} \\ \text{But when } h \to 0 \Rightarrow A_{\text{lateral}} \to 0 \\ \Rightarrow \int\limits_{A_{\text{lateral}}} \vec{E}\cdot d\vec{a} \to 0 \end{aligned}\right\} \Rightarrow \begin{aligned} E_{1\perp} - E_{2\perp} = \frac{\sigma}{\varepsilon_0} \\ \text{and} \\ \text{if } \sigma = 0 \Rightarrow E_{1\perp} = E_{2\perp} \end{aligned}$$

We denoted $|\vec{A}_1| = |\vec{A}_2| = |\vec{A}| = A$. Hence, if, e.g., we have spread positive surface charge density σ on the interface, then $\vec{E}_{1\perp}$ and $\vec{E}_{2\perp}$ point outside of the interface. Concisely, we can write the alternative forms

$$\boxed{E_{1\perp} - E_{2\perp} = \frac{\sigma}{\varepsilon_0}} \tag{2.39a}$$

$$\text{or} \quad \boxed{(\vec{E}_1 - \vec{E}_2)\cdot\hat{e} = \frac{\sigma}{\varepsilon_0}} \qquad \hat{e} = \hat{n}_{21} \text{ (from 2 towards 1)} \tag{2.39b}$$

$$\text{or} \quad \boxed{(\vec{E}_1 - \vec{E}_2)\cdot\hat{n}_{21} = \frac{\sigma}{\varepsilon_0}} \tag{2.39c}$$

$$\text{or} \quad \boxed{(\vec{E}_2 - \vec{E}_1)\cdot\hat{n}_{12} = \frac{\sigma}{\varepsilon_0}} \qquad \hat{n}_{12} \text{ (from 1 towards 2)} \tag{2.39d}$$

◊ Similarly, let us now apply the 2nd Maxwell's equation 2.37b on Figure 2.7, by switching $\vec{E}$ to $\vec{B}$.

$$\Phi_{B,S=\partial V} := \oint\limits_{S=\partial V} \vec{B}\cdot d\vec{a} = 0.$$

In accordance with the above, we arrive at the following alternative expressions

$$\boxed{B_{1\perp} = B_{2\perp}} \tag{2.40a}$$

$$\text{or} \quad \boxed{(\vec{B}_1 - \vec{B}_2)\cdot\hat{e} = 0} \qquad \hat{e} = \hat{n}_{21} \text{ (from 2 towards 1)} \tag{2.40b}$$

$$\text{or} \quad \boxed{(\vec{B}_1 - \vec{B}_2)\cdot\hat{n}_{21} = 0} \tag{2.40c}$$

$$\text{or} \quad \boxed{(\vec{B}_2 - \vec{B}_1)\cdot\hat{n}_{12} = 0} \qquad \hat{n}_{12} \text{ (from 1 towards 2)} \tag{2.40d}$$

♡ Let us now apply the 3rd Maxwell's equation 2.37c on Figure 2.8.

$$\mathscr{E}_{\text{EMF}} := \oint\limits_{L=\partial S} \vec{E}\cdot d\vec{\ell} = -\frac{\partial \Phi_{B,S}}{\partial t} \Rightarrow$$

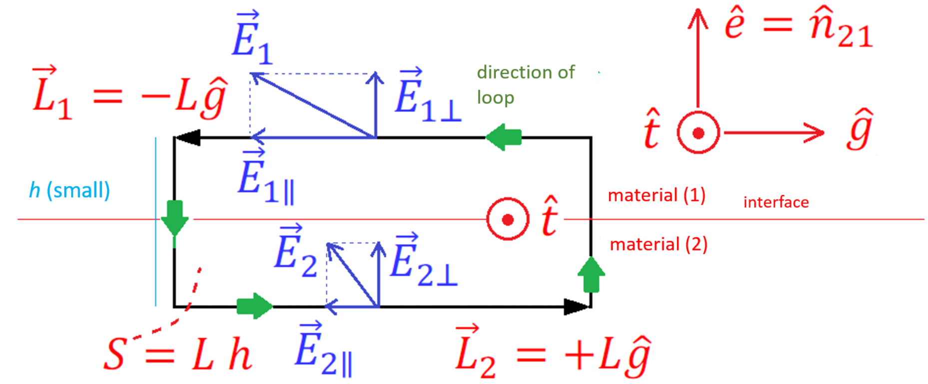

Figure 2.8: Boundary conditions for the 3rd Maxwell's equation. The direction of vectors $\vec{E}_1$ and $\vec{E}_2$ has been chosen arbitrarily on purpose. Here, the loop is on the plane $(\hat{e}, \hat{g})$.

$$\left.\begin{array}{ll} & \vec{E}_1 \cdot \vec{L}_1 + \int\limits_{\text{small left}}^{\text{h interval}} \vec{E} \cdot d\vec{\ell} + \vec{E}_2 \cdot \vec{L}_2 + \int\limits_{\text{small right}}^{\text{h interval}} \vec{E} \cdot d\vec{\ell} = -\frac{\partial}{\partial t} \int_S \vec{B} \cdot d\vec{a} \\ \text{but when} & h \to 0 \Rightarrow S = hL \to 0 \Rightarrow \int_S \vec{B} \cdot d\vec{a} \to 0 \\ \text{but when} & h \to 0 \Rightarrow \int\limits_{\text{small left}}^{\text{h interval}} \vec{E} \cdot d\vec{\ell} = 0 = \int\limits_{\text{small right}}^{\text{h interval}} \vec{E} \cdot d\vec{\ell} \end{array}\right\} \Rightarrow$$

$$\vec{E}_1 \cdot \vec{L}_1 + \vec{E}_2 \cdot \vec{L}_2 = 0 \Rightarrow E_{1\|} L_1 + E_{2\|} L_2 = 0 \Rightarrow -E_{1\|} L + E_{2\|} L = 0 \Rightarrow E_{1\|} = E_{2\|}.$$

Above, we denoted $|\vec{L}_1| = |\vec{L}_2| = |\vec{L}| = L$, while $E_{1\|}, E_{2\|}, L_1, L_2$ are algebraic values. Since

$$\vec{E}_1 \cdot \vec{L}_1 + \vec{E}_2 \cdot \vec{L}_2 = 0 \Rightarrow (\vec{E}_2 - \vec{E}_1) \cdot \hat{g} = 0.$$

$$\begin{array}{rl} \text{Hence, when the loop is on the plane } (\hat{e}, \hat{g}) \Rightarrow & \text{the difference } (\vec{E}_2 - \vec{E}_1) \perp \hat{g}. \\ \text{Similarly, when the loop is on the plane } (\hat{e}, \hat{t}) \Rightarrow & \text{the difference } (\vec{E}_2 - \vec{E}_1) \perp \hat{t}. \\ \text{That is,} & \text{the difference } (\vec{E}_2 - \vec{E}_1) \perp \text{interface} \\ \text{which can be written as} & (\vec{E}_2 - \vec{E}_1) \times \hat{e} = \vec{0}. \end{array}$$

Hence, concisely, we arrive at the alternative forms

$$\boxed{E_{2\|} = E_{1\|}} \tag{2.41a}$$

$$\boxed{(\vec{E}_2 - \vec{E}_1) \times \hat{e} = \vec{0}} \tag{2.41b}$$

♠ Let us now apply the 4th Maxwell's equation 2.37d on Figure 2.9.

$$\oint_{L=\partial S} \vec{B} \cdot d\vec{\ell} = \mu_0 I_{\text{passing through } S} + \mu_0 \varepsilon_0 \frac{\partial \Phi_{E,S}}{\partial t} \Rightarrow$$

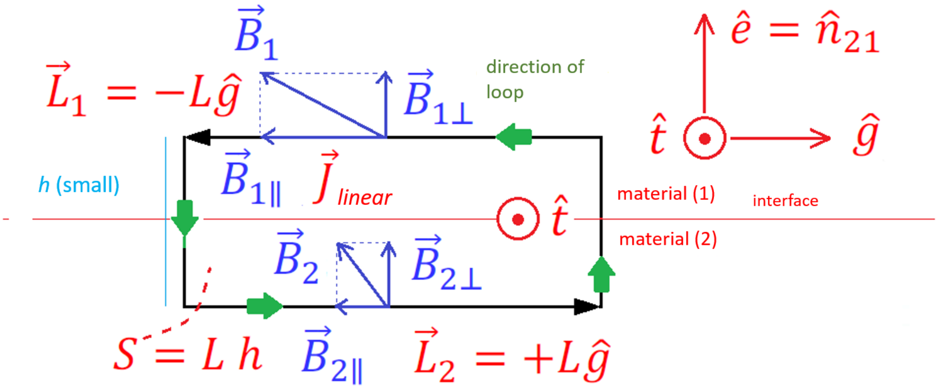

Figure 2.9: Boundary conditions for the 4th Maxwell's equation. The direction of vectors $\vec{B}_1$ and $\vec{B}_2$ has been chosen arbitrarily on purpose.

$$\left.\begin{array}{l}
\vec{B}_1\cdot\vec{L}_1 + \int\limits_{\text{small left}}^{\text{h interval}} \vec{B}\cdot d\vec{\ell} + \vec{B}_2\cdot\vec{L}_2 + \int\limits_{\text{small right}}^{\text{h interval}} \vec{B}\cdot d\vec{\ell} = \\
\mu_0 J_{\text{linear, passing through } S}\, L + \mu_0\varepsilon_0 \dfrac{\partial}{\partial t} \int\limits_{S=Lh} \vec{E}\cdot d\vec{a} \\
\text{but when} \qquad h \to 0 \Rightarrow \int\limits_{\text{small left}}^{\text{h interval}} \vec{B}\cdot d\vec{\ell} = 0 = \int\limits_{\text{small right}}^{\text{h interval}} \vec{B}\cdot d\vec{\ell} \\
\text{but when} \qquad h \to 0 \Rightarrow S = Lh \to 0 \Rightarrow \int\limits_{S=Lh} \vec{E}\cdot d\vec{a} \to 0
\end{array}\right\} \Rightarrow$$

$$-B_{1\|}L + B_{2\|}L = \mu_0 J_{\text{linear, passing through } S} L.$$

Hence, concisely, we can write the following alternative forms

$$\boxed{(\vec{B}_2 - \vec{B}_1)\times\hat{e} = \mu_0 \vec{J}_{\text{linear, passing through } S}} \tag{2.42a}$$

$$\boxed{B_{2\|} - B_{1\|} = \mu_0 J_{\text{linear, passing through } S}} \tag{2.42b}$$

If $J_{\text{linear, passing through } S} = 0 \Rightarrow B_{2\|} = B_{1\|}$. $B_{1\|}, B_{2\|}$ are algebraic values. We denoted $|\vec{L}_1| = |\vec{L}_2| = |\vec{L}| = L$. The units of $J_{\text{linear, passing through } S}$ are A/m. Thus, in Eq. 2.42a or 2.42b the units are T = $(\mathrm{N/A^2})(\mathrm{A/m})$.

2.6 Existence of EM waves in the absence of charge density and charge current.

Let's see how the Maxwell's equations are transformed when $\rho = 0, \vec{J} = \vec{0}$.

$$\left.\begin{array}{lr}
\vec{\nabla}\cdot\vec{E} = \dfrac{\rho}{\varepsilon_0} & \text{(1st)} \\
\vec{\nabla}\cdot\vec{B} = 0 & \text{(2nd)} \\
\vec{\nabla}\times\vec{E} = -\dfrac{\partial\vec{B}}{\partial t} & \text{(3rd)} \\
\vec{\nabla}\times\vec{B} = \mu_0\vec{J} + \mu_0\varepsilon_0\dfrac{\partial\vec{E}}{\partial t} & \text{(4th)}
\end{array}\right\}
\xrightarrow[\vec{J}=\vec{0}]{\rho=0}
\begin{array}{lr}
\vec{\nabla}\cdot\vec{E} = 0 & \text{(1st}') \\
\vec{\nabla}\cdot\vec{B} = 0 & \text{(2nd}') \\
\vec{\nabla}\times\vec{E} = -\dfrac{\partial\vec{B}}{\partial t} & \text{(3rd}') \\
\vec{\nabla}\times\vec{B} = \mu_0\varepsilon_0\dfrac{\partial\vec{E}}{\partial t} & \text{(4th}')
\end{array} \tag{2.43}$$

We will now use the identity

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{\Delta}) = \vec{\nabla}(\vec{\nabla} \cdot \vec{\Delta}) - \nabla^2 \vec{\Delta}, \tag{2.44}$$

where ∇^2 is the Laplacian, for $\vec{E}$ and for $\vec{B}$.

- For $\vec{E}$:

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{E}) = \vec{\nabla}(\vec{\nabla} \cdot \vec{E}) - \nabla^2 \vec{E} \quad \overset{(1\text{st}')}{\underset{(3\text{rd}')}{\Longrightarrow}} \tag{2.45}$$

$$\vec{\nabla} \times \left(- \frac{\partial \vec{B}}{\partial t} \right) = -\nabla^2 \vec{E} \quad \Rightarrow \tag{2.46}$$

$$-\frac{\partial}{\partial t}(\vec{\nabla} \times \vec{B}) = -\nabla^2 \vec{E} \quad \overset{(4\text{th}')}{\Longrightarrow} \tag{2.47}$$

$$\frac{\partial}{\partial t}\left(\mu_0 \varepsilon_0 \frac{\partial \vec{E}}{\partial t} \right) = \nabla^2 \vec{E} \quad \Rightarrow \tag{2.48}$$

$$\text{wave equation} \begin{cases} \nabla^2 \vec{E} = \varepsilon_0 \mu_0 \dfrac{\partial^2 \vec{E}}{\partial t^2}, & v_\phi = \dfrac{1}{\sqrt{\varepsilon_0 \mu_0}} = c \quad \Rightarrow \\ \nabla^2 \vec{E} = \dfrac{1}{c^2} \dfrac{\partial^2 \vec{E}}{\partial t^2} & \text{or} \\ \left[\nabla^2 - \dfrac{1}{c^2} \dfrac{\partial^2}{\partial t^2} \right] \vec{E} = \vec{0} & \text{or} \\ \Box \vec{E} = \vec{0} & \text{where } \Box \text{ is the so-called D' Alembertian.} \end{cases} \tag{2.49}$$

- For $\vec{B}$:

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{B}) = \vec{\nabla}(\vec{\nabla} \cdot \vec{B}) - \nabla^2 \vec{B} \quad \overset{(2\text{nd}')}{\underset{(4\text{th}')}{\Longrightarrow}} \tag{2.50}$$

$$\vec{\nabla} \times \left(\varepsilon_0 \mu_0 \frac{\partial \vec{E}}{\partial t} \right) = -\nabla^2 \vec{B} \quad \Rightarrow \tag{2.51}$$

$$\varepsilon_0 \mu_0 \frac{\partial}{\partial t}(\vec{\nabla} \times \vec{E}) = -\nabla^2 \vec{B} \quad \overset{(3\text{rd}')}{\Longrightarrow} \tag{2.52}$$

$$\varepsilon_0 \mu_0 \frac{\partial}{\partial t}\left(- \frac{\partial \vec{B}}{\partial t} \right) = -\nabla^2 \vec{B} \quad \Rightarrow \tag{2.53}$$

$$\text{wave equation} \begin{cases} \nabla^2 \vec{B} = \varepsilon_0 \mu_0 \dfrac{\partial^2 \vec{B}}{\partial t^2}, & v_\phi = \dfrac{1}{\sqrt{\varepsilon_0 \mu_0}} = c \quad \Rightarrow \\ \nabla^2 \vec{B} = \dfrac{1}{c^2} \dfrac{\partial^2 \vec{B}}{\partial t^2} & \text{or} \\ \left[\nabla^2 - \dfrac{1}{c^2} \dfrac{\partial^2}{\partial t^2} \right] \vec{B} = \vec{0} & \text{or} \\ \Box \vec{B} = \vec{0} & \text{where } \Box \text{ is the so-called } \mathit{D'Alembertian}. \end{cases} \tag{2.54}$$

2.7 Fields inside an ideal conductor.

A good conductor is a material that reflects most of the energy of an EM wave that impinges on it [14]. We define as an ideal conductor a material that reflects all the energy of an EM wave that impinges on it [14]. Since the energy density of an EM wave is

$$U = \frac{\varepsilon_0}{2}E^2 + \frac{1}{2\mu_0}B^2 = \frac{\varepsilon_0}{2}\left[E^2 + c^2B^2\right], \tag{2.55}$$

with units $[U] = \frac{\mathrm{J}}{\mathrm{m}^3}$, it follows that

$$\boxed{\text{inside an ideal conductor,} \quad \vec{E} = \vec{0} \quad \text{and} \quad \vec{B} = \vec{0}} \tag{2.56}$$

2.8 Fields at the boundary of an ideal conductor.

Let us remember the boundary conditions at an interface between two materials and further assume that materal (1) is an ideal conductor while material (2) is vacuum or, in approximation, air.

$$\left.\begin{aligned} E_{1\perp} - E_{2\perp} &= \frac{\sigma}{\varepsilon_0} \qquad \underline{\text{GBC}} \\ B_{1\perp} &= B_{2\perp} \\ E_{1\parallel} &= E_{2\parallel} \\ B_{2\parallel} - B_{1\parallel} &= \mu_0 \underbrace{J^{\text{linear}}_{\text{passing through } S}}_{\text{units } [A/m]} \end{aligned}\right\} \Longrightarrow \tag{2.57}$$

$$\left.\begin{aligned} &\text{if} \\ &\text{material (1) is an ideal conductor } (\vec{B}_1 = \vec{0} \text{ and } \vec{E}_1 = \vec{0}) \\ &\text{material (2) is vacuum or air} \end{aligned}\right\} \Longrightarrow \tag{2.58}$$

$$\left.\begin{aligned} -E_{2\perp} &= \frac{\sigma}{\varepsilon_0} \qquad \underline{\text{SBC}} \\ &\boxed{B_{2\perp} = 0} \\ &\boxed{E_{2\parallel} = 0} \\ B_{2\parallel} &= \mu_0 J^{\text{linear}}_{\text{passing through } S} \end{aligned}\right\} \tag{2.59}$$

GBC stands for general boundary conditions and SBC means specific boundary conditions. Also, let us denote SBC* the subset of boundary conditions we will use more often.

$$\left.\begin{aligned} &\boxed{B_{2\perp} = 0} \qquad \underline{\text{SBC}^*} \\ &\boxed{E_{2\parallel} = 0} \end{aligned}\right\} \tag{2.60}$$

2.9 Fields inside cavities.

We learned above that the largest fraction of the energy of an EM wave that impinges on the surface of a good conductor is reflected; actually, if the conductor is ideal, then all the energy is reflected. Hence,

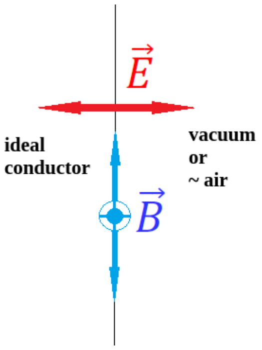

Figure 2.10: On the surface of an ideal conductor, the component of $\vec{B}$ that is perpendicular to its surface and the component of $\vec{E}$ that is parallel to its surface vanish, so the fields can only have some of the orientations presented in this figure.

we can store EM energy in the form of standing waves inside a cavity with walls made of an ideal (or, in approximation, good) conductor.

We also saw the $\underline{\text{SBC}}$ and focused on the $\underline{\text{SBC}^*}$

$$\begin{aligned} B_{2\perp} &= 0 \\ E_{2\parallel} &= 0, \end{aligned}$$

i.e., for an ideal conductor, the component of $\vec{B}$ that is perpendicular to its surface and the component of $\vec{E}$ that is parallel to its surface vanish, as shown in Figure 2.10. Thus, the possible $\underline{\text{patterns}}$ and $\underline{\text{frequencies}}$ of the standing waves that are preserved inside a cavity are $\underline{\text{determined}}$ by the $\underline{\text{shape of that cavity}}$. Schematically,

$$\text{(normal) modes} \begin{cases} \text{patterns} \\ \text{and} \\ \text{frequencies} \end{cases}$$

2.10 Normal EM modes inside rectangular parallelepiped cavity.

Let us assume a rectangular parallelepiped cavity such as the one shown in Figure 2.11.

Inside the cavity $\rho = 0, \vec{J} = \vec{0} \overset{\cdots}{\Longrightarrow}$

$$\boxed{\nabla^2 \vec{E} = \frac{1}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} \qquad \underline{\text{WEE}}} \tag{2.61}$$

and

$$\boxed{\nabla^2 \vec{B} = \frac{1}{c^2} \frac{\partial^2 \vec{B}}{\partial t^2} \qquad \underline{\text{WEB}}} \tag{2.62}$$

$\underline{\text{WEE}}$ means wave equation for $\vec{E}$ and $\underline{\text{WEB}}$ means wave equation for $\vec{B}$. Since the walls of the cavity are perfectly (ideally) conducting, in each one of its faces, the perpendicular component of the magnetic field and the parallel component of the electric field must vanish (conditions SBC*), i.e.,

$$\boxed{B_\perp = 0} \tag{2.63a}$$

$$\boxed{E_\parallel = 0} \tag{2.63b}$$

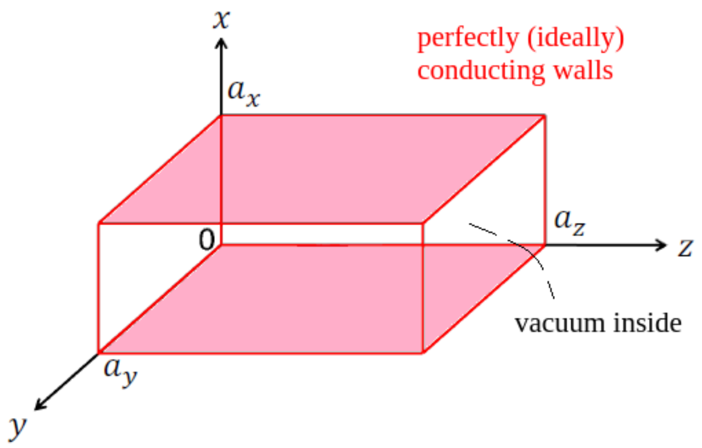

Figure 2.11: A rectangular parallelepiped cavity with perfectly (ideally) conducting walls. Inside the cavity there is vacuum or, in approximation, air. To make a clear picture, only the lower ($x = 0$) and upper ($x = a_x$) faces have been colored, but all six faces are made of perfectly (ideally) conducting walls.

Plane waves in free space do not satisfy these boundary conditions. We can, however, search for solutions by separating the variables $\vec{r}, t$, i.e., of the form

$$\boxed{\vec{E}(x, y, z, t) = \overset{\text{space}}{\vec{E}_{\vec{r}}(x, y, z)}\overset{\text{time}}{e^{-i\omega t}}} \tag{2.64}$$

Due to Eq. 2.64, the WEE becomes

$$\cancel{e^{-i\omega t}}\nabla^2\vec{E}_{\vec{r}} = \frac{1}{c^2}(-i\omega)^2\cancel{e^{-i\omega t}}\vec{E}_{\vec{r}} \Rightarrow$$

$$\boxed{\nabla^2\vec{E}_{\vec{r}} + \frac{\omega^2}{c^2}\vec{E}_{\vec{r}} = \vec{0}} \tag{2.65}$$

Then, we separate the variables x, y, z, of $\vec{r}$. After several calculations [14] that will be omitted here, we have:

$$E_x = E_{x0}\cos(k_x x)\sin\left(k_y y\right)\sin(k_z z)e^{-i\omega t} \Rightarrow \text{becomes zero for } y = 0 \text{ and } z = 0 \tag{2.66}$$

$$E_y = E_{y0}\sin(k_x x)\cos\left(k_y y\right)\sin(k_z z)e^{-i\omega t} \Rightarrow \text{becomes zero for } x = 0 \text{ and } z = 0 \tag{2.67}$$

$$E_z = E_{z0}\sin(k_x x)\sin\left(k_y y\right)\cos(k_z z)e^{-i\omega t} \Rightarrow \text{becomes zero for } x = 0 \text{ and } y = 0 \tag{2.68}$$

where

$$\boxed{k_x^2 + k_y^2 + k_z^2 = \frac{\omega^2}{c^2}} \tag{2.69}$$

In Figure 2.11, the lower and upper faces (where $x = 0$ and $x = a_x$, respectively) have been colored, but all six faces are made of perfectly (ideally) conducting walls. As it is evident from Eqs. 2.66, 2.67, 2.68, in the lower face, the electric field has only x-component, i.e., it is perpendicular to this face. Similarly, the electric field has only y-component in the back face and only z-component in the left face; it is thus perpendicular to these faces. In the same manner, the electric field, must have only x-component in the

upper face, y-component in the front face, and z-component in the right face, i.e., it must be perpendicular to these faces, as well.
Since E_x must vanish for both $y = a_y$ and $z = a_z \Rightarrow$

$$\sin\left(k_y a_y\right) = 0 \Rightarrow k_y a_y = m_y \pi$$
$$\sin(k_z a_z) = 0 \Rightarrow k_z a_z = m_z \pi$$

Since E_y must vanish for both $x = a_x$ and $z = a_z \Rightarrow$

$$\sin(k_x a_x) = 0 \Rightarrow k_x a_x = m_x \pi$$
$$\sin(k_z a_z) = 0 \Rightarrow k_z a_z = m_z \pi$$

Since E_z must vanish for both $x = a_x$ and $y = a_y \Rightarrow$

$$\sin(k_x a_x) = 0 \Rightarrow k_x a_x = m_x \pi$$
$$\sin\left(k_y a_y\right) = 0 \Rightarrow k_y a_y = m_y \pi$$

Concisely, in the upper and lower faces the electric field has only x-component, i.e., it is perpendicular to these faces, in the back and front faces the electric field has only y-component, i.e., it is perpendicular to these faces, and in the left and right faces the electric field has only z-component, i.e., it is perpendicular to these faces.

Additionally, it occurs that

$$k_x = \frac{m_x \pi}{a_x}, \quad k_y = \frac{m_y \pi}{a_y}, \quad k_z = \frac{m_z \pi}{a_z}, \tag{2.70}$$

where $m_x, m_y, m_z \in \mathbb{Z}$.

Furthermore, from the $(1\mathrm{st}')$ Maxwell's equation, $\vec{\nabla} \cdot \vec{E} = 0 \Rightarrow$

$$k_x E_{x0} + k_y E_{y0} + k_z E_{z0} = 0, \tag{2.71}$$

while, from the $(3\mathrm{rd}')$ Maxwell's equation, $\vec{\nabla} \times \vec{E} = -\dfrac{\partial \vec{B}}{\partial t} \Rightarrow$

$$B_x = \frac{i}{\omega}\left(E_{y0} k_z - E_{z0} k_y\right) \sin(k_x x) \cos\left(k_y y\right) \cos(k_z z) e^{-i\omega t} \tag{2.72}$$
$$B_y = \frac{i}{\omega}\left(E_{z0} k_x - E_{x0} k_z\right) \cos(k_x x) \sin\left(k_y y\right) \cos(k_z z) e^{-i\omega t} \tag{2.73}$$
$$B_z = \frac{i}{\omega}\left(E_{x0} k_y - E_{y0} k_x\right) \cos(k_x x) \cos\left(k_y y\right) \sin(k_z z) e^{-i\omega t} \tag{2.74}$$

Checking whether $\vec{B}$ satisfies the SBC* on the walls as well as the $(2\mathrm{nd}')$, $\vec{\nabla} \cdot \vec{B} = 0$, and $(4\mathrm{th}')$, $\vec{\nabla} \times \vec{B} = \varepsilon_0 \mu_0 \dfrac{\partial \vec{E}}{\partial t}$, Maxwell's equations is left for the reader.

From Eqs. 2.69 and 2.70 we can write

$$\omega_{m_x, m_y, m_z} = c\sqrt{\left(\frac{m_x \pi}{a_x}\right)^2 + \left(\frac{m_y \pi}{a_y}\right)^2 + \left(\frac{m_z \pi}{a_z}\right)^2}. \tag{2.75}$$

For a rectangular parallelepiped cavity,

$$\omega_{m_x,m_y,m_z} = \pi c \sqrt{\left(\frac{m_x}{a_x}\right)^2 + \left(\frac{m_y}{a_y}\right)^2 + \left(\frac{m_z}{a_z}\right)^2}, \tag{2.76}$$

for a tetragonal parallelepiped cavity $(a_x = a_y = a')$,

$$\omega_{m_x,m_y,m_z} = \pi c \sqrt{\frac{m_x^2 + m_y^2}{a'^2} + \frac{m_z^2}{a_z}^{2}}, \tag{2.77}$$

and, for a cubic cavity $(a_x = a_y = a_z = a)$,

$$\omega_{m_x,m_y,m_z} = \frac{\pi c}{a} \sqrt{m_x^2 + m_y^2 + m_z^2}. \tag{2.78}$$

Table 2.2: The values of $a\omega/\pi c$ occurring from Eq. 2.78 in the case of cubic cavity, for several values of the natural numbers m_x, m_y, m_z. Whether zero electric and magnetic field occurs from Eqs. 2.66, 2.67, 2.68 and 2.72, 2.73, 2.74, respectively, is also noted, in column "amplitude".

m_x	m_y	m_z	$a\omega/\pi c$	"amplitude"
0	0	0	0	0
0	0	1	1	0
0	1	1	$\sqrt{2}$	$\neq 0$
1	1	1	$\sqrt{3}$	$\neq 0$
2	0	0	2	0
2	1	0	$\sqrt{5}$	$\neq 0$

We can also choose $m_x, m_y, m_z \in \mathbb{N}$ (natural numbers) thus absorbing the sign change in E_{x0}, E_{y0}, E_{z0}, i.e., allowing E_{x0}, E_{y0}, E_{z0} to take positive or negative values such that they agree with the boundary conditions. In Table 2.2 we present some $\frac{a\omega}{\pi c}$ occurring from Eq. 2.78 for the cubic cavity for several values of m_x, m_y, m_z. Whether zero electric and magnetic field occurs from Eqs. 2.66, 2.67, 2.68 and 2.72, 2.73, 2.74, respectively, is also noted, in column "amplitude".

2.11 Infinitesimal number of EM field normal modes per infinitesimal frequency interval.

Below, we will prove that

$$\boxed{g(\nu) = \frac{dN}{d\nu} = \frac{8\pi\nu^2 V}{c^3}} \tag{2.79}$$

where dN is the infinitesimal number of modes in an infinitesimal frequency interval $d\nu$ and V is the volume of the cavity, which is a 3D box. In other words, we are interested in the quantity

$$g(\nu) = \frac{dN}{d\nu} = \frac{d(\text{number of normal modes})}{d(\text{frequency})}$$

$$[g(\nu)] = \frac{1}{\text{Hz}}$$

The proof will be provided for periodic boundary conditions and for the rectangular parallelepiped cavity of the previous Section 2.10.

2.11.1 1st case: Periodic boundary conditions.

Let us suppose that the electric field is subject to periodic boundary conditions, i.e., that

$$\left.\begin{aligned} \vec{E}(\vec{r},t) &= \vec{E}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t+\phi)} \\ \vec{E}(0,t) &= \vec{E}_0 e^{i(-\omega t+\phi)} \\ \vec{E}((a_x,0,0),t) &= \vec{E}_0 e^{i(k_x a_x-\omega t+\phi)} \end{aligned}\right\} \Rightarrow e^{ik_x a_x} = 1 \Leftrightarrow k_x a_x = 2\pi n_x, \quad n_x \in \mathbb{Z}$$

Thus

$$\boxed{\begin{aligned} & & k_x &= \frac{2\pi n_x}{a_x}, & n_x &\in \mathbb{Z} \\ &\text{similarly,} & k_y &= \frac{2\pi n_y}{a_y}, & n_y &\in \mathbb{Z} \\ & & k_z &= \frac{2\pi n_z}{a_z}, & n_z &\in \mathbb{Z} \end{aligned}} \tag{2.80}$$

As seen in Eq. 2.80, the possible values of k are discrete. The step defining the discreteness in k-space is $\Delta k_x = \frac{2\pi}{a_x}$ in the x-axis, $\Delta k_y = \frac{2\pi}{a_y}$ in the y-axis, and $\Delta k_z = \frac{2\pi}{a_z}$ in the z-axis. These points in k-space are drawn in Figure 2.12. Note that in Figure 2.12 only one octant of the k-space is shown; however, k covers all eight octants, i.e., the whole k-space. From Eq. 2.80 it occurs that the infinitesimal k-volume is $\frac{8\pi^3}{V}$, where

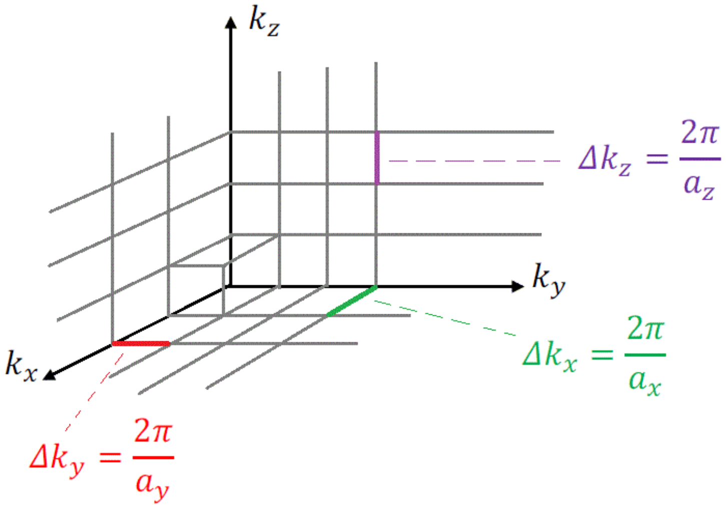

Figure 2.12: The possible values of k are discrete and the infinitesimal k-volume is $\frac{8\pi^3}{V}$, where V is the volume of the cavity (Eq.2.80). In each of the 8 vertices of this infinitesimal volume lies one k-state which belongs to it by 1/8, since it is shared by 8 similar adjoining infinitesimal rectangular parallelepipeds.

V is the volume of the cavity. In each of the 8 vertices of this infinitesimal volume lies one k-state which belongs to it by 1/8, since it is shared by 8 similar adjoining infinitesimal rectangular parallelepipeds. Let us also consider the infinitesimal volume from k to $k + dk$, i.e. the spherical shell of radius k and thickness dk, which is equal to $4\pi k^2 dk$, and denote by dN_k the number of k-states inside this spherical shell. Hence,

$$\left.\begin{array}{lll} \text{in } k\text{-space } \dfrac{(2\pi)^3}{a_x a_y a_z} = \dfrac{8\pi^3}{V} & & \exists\ 8\dfrac{1}{8} = 1\ k\text{-state} \\ \text{in } k\text{-space } \ k \rightarrow k + dk \ \text{ i.e. } \ 4\pi k^2 dk & & \exists\ dN_k \quad k\text{-states} \end{array}\right\} \Rightarrow$$

$$\left.\begin{aligned} dN_k &= \frac{4\pi k^2 dkV}{8\pi^3} = \frac{1}{2\pi^2}k^2 dkV \\ c = \lambda\nu &= \frac{2\pi}{k}\nu \Rightarrow k = \frac{2\pi}{c}\nu \Rightarrow dk = \frac{2\pi}{c}d\nu \end{aligned}\right\} \Rightarrow dN_\nu = \frac{1}{2\pi^2}\frac{4\pi^2\nu^2 2\pi d\nu V}{c^2 \quad c} = \frac{4\pi V}{c^3}\nu^2 d\nu$$

However, there are two possible polarizations of the electric field perpendicular to $\vec{k}$, as shown in Figure 2.13. Therefore, the number of states is

$$dN = \frac{8\pi V}{c^3}\nu^2 d\nu, \tag{2.81}$$

hence,

$$g(\nu) = \frac{dN}{d\nu} = \frac{8\pi\nu^2 V}{c^3},$$

which is Eq. 2.79 that was to be proven.

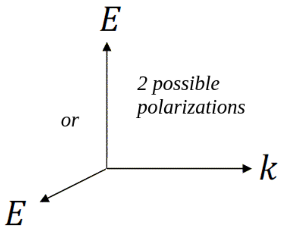

Figure 2.13: There are two possible polarizations of the electric field perpendicular to $\vec{k}$.

2.11.2 2nd case: Rectangular parallelepiped cavity.

From Eq. 2.66, if we suppose that, for symmetry reasons, the electric field should point towards the same side of the upper and lower faces of the rectangular parallelepiped, i.e., if $E_x(x = 0) = -E_x(x = a_x)$, it is implied that $1 = -\cos(k_x a_x) \Rightarrow \cos(k_x a_x) = -1 \Rightarrow k_x = \frac{(2m_x+1)\pi}{a_x}, \quad m_x \in \mathbb{Z}$. Thus, the step that defines the discreteness in k-space in the x-axis is $\Delta k_x = \frac{2\pi}{a_x}$ (similar considerations hold also for the y- and z-axes.). Hence, the infinitesimal k-volume is $\frac{8\pi^3}{V}$, where V is the volume of the cavity. Hence, just as in the previous Subsection 2.11.1, Eq. 2.79, which was to be proven, occurs.

2.12 Proof of the classical Rayleigh-Jeans law using the equipartition theorem and the infinitesimal number of EM field normal modes per infinitesimal frequency interval.

As shown below, $\rho(\nu, T)$ is the energy density per unit volume per unit frequency, while $\frac{g(\nu)}{V}$ is the density of normal modes per unit volume per unit frequency. Hence, for a given $\frac{g(\nu)}{V}$, we have to multiply it by the average energy of each normal mode, $\bar{E}$ to obtain $\rho(\nu, T)$.

$$\begin{aligned} g(\nu) &= \frac{dN}{d\nu} = \frac{8\pi\nu^2 V}{c^3} \Rightarrow & [g(\nu)] &= \frac{1}{\mathrm{Hz}} = \mathrm{s} \\ \frac{g(\nu)}{V} &= \frac{8\pi\nu^2}{c^3} & \left[\frac{g(\nu)}{V}\right] &= \frac{1}{\mathrm{Hz\,m^3}} = \frac{\mathrm{s}}{\mathrm{m^3}} \\ \rho(\nu, T) &= \bar{E}\frac{g(\nu)}{V} & [\rho(\nu, T)] &= \frac{\mathrm{J}}{\mathrm{m^3 Hz}} = \frac{\mathrm{Js}}{\mathrm{m^3}} \end{aligned}$$

According to the classical equipartition theorem [10, 11, 12], in thermal equilibrium, we attribute to each degree of freedom of the building block of the system the average energy $\overline{E(T)} = \frac{1}{2}k_B T$. Thus, e.g., in a system of N building blocks, each having M degrees of freedom, the energy is $\frac{NM}{2}k_B T$. The average energy of each normal mode is

$$\overline{E(T)} = M \times \frac{1}{2}k_B T. \tag{2.82}$$

Hence,

in a 3D ideal gas $\quad \bar{E}_{\text{KIN}} = \frac{3}{2}k_B T \Rightarrow \bar{E} = \frac{3}{2}k_B T$

in a 1D ideal gas $\quad \bar{E}_{\text{KIN}} = \frac{1}{2}k_B T \Rightarrow \bar{E} = \frac{1}{2}k_B T$

in a 1D simple harmonic oscillator (SHO) $\quad \bar{E}_{\text{POT}} = \bar{E}_{\text{KIN}} = \frac{1}{2}k_B T \Rightarrow \bar{E} = k_B T$

$\bar{E}_{\text{POT}}$ ($\bar{E}_{\text{KIN}}$) is the average potential (kinetic) energy. Therefore, supposing an ensemble of SHOs with $\bar{E} = k_B T$, we conclude that

$$\boxed{\rho(\nu, T) = \frac{8\pi\nu^2}{c^3}k_B T} \qquad \text{Rayleigh-Jeans law} \tag{2.83}$$

Hence, for $\nu \to \infty \Rightarrow \rho(\nu, T) \to \infty$, that is, we have great problem increasing frequency, because this behaviour contradicts emphatically experimental data: The limit to infinity disagrees with experimental data, i.e., we have "catastrophic" disagreement with the experiment at higher frequencies. This behaviour was named in the past "ultraviolet catastrophy" because it was first observed in the ultraviolet regime. This issue was addressed in Section 2.2. Let us notice that if we did not assume two degrees of freedom so that to obtain $\bar{E} = \frac{2}{2}k_B T = k_B T$ but M degrees of freedom, then the only thing that would change would be a constant, because we would obtain $\bar{E} = \frac{M}{2}k_B T$ and we would arrive to $\rho(\nu, T) = \frac{8\pi\nu^2}{c^3}\frac{M}{2}k_B T$. The extremely problematic behavior ν^2 that increasing ν leads to infinite $\rho(\nu, T)$ would not change at all.

2.13 Proof of the Planck's law the way Planck did it.

We will follow here the assumptions Planck was forced to make in 1900 in order to prove the equation known today as the "Planck's law" [15], which agrees with experimental data on black body radiation. The problem of black body radiation had been opened at least since 1859 by Kirchhoff. Planck was involved with the problem of black body radiation from 1894. The Wien's law, which provides an equation that just happens to fit the experimental data at high frequencies, was proposed in 1896. The Rayleigh-Jeans law, which emerges from classical physics, can describe the black body radiation only at very low frequencies, i.e., it fails miserably, as we have just seen above. Thus, a consistent theoretical explanation covering all frequencies was missing.

After several failed attempts, Planck proposed in 1900 a proof involving the assumption that EM energy **can only be a discrete, "quantized", multiple of the quantity** $h\nu$, where h is what we now call "the Planck's constant" and ν is the radiation frequency. Furthermore, he utilized the statistical Boltzmann distribution. He was definitely not happy with these assumptions; however they were imposed to him by the need to explain the experimental data. Soon, in 1905, Einstein [16] explained the photoelectric effect by assuming that such quanta of light exist. The term "photon" was written for the first time in 1926 by G. N. Lewis [17].

Planck was essentially forced to introduce the notion of the **resonator**, which has discrete, that is, not continuous but depending on a natural number, n, in other words, "quantized", allowed values of its energy,

E_n, for a given frequency, ν. Then he had to assume that the energy corresponding to a given frequency, ν, and temperature, T, is in reality an average value, $\overline{E(\nu, T)}$, of the energies of a large number of identical resonators, each of which is at a different energy level, E_n, while the occupation probability of the levels, p_n, is given by Boltzmann statistics.

So, we will assume that the EM energy of a resonator with frequency ν inside a black body cavity can only take discrete values, i.e., it is "quantized" and, actually, that it takes the form

$$E_n = h\nu n, \quad n = 0, 1, 2, 3, \ldots \tag{2.84}$$

We underline that if, instead of this relation, we set $E_n = h\nu(n + \frac{1}{2})$, as we know today for the quantum simple harmonic oscillator, we do not obtain the Planck's law... We notice that classically, according to the equipartition theorem, in thermal equilibrium we attribute an average energy $\overline{E(T)} = \frac{1}{2}k_{\mathrm{B}}T$ to each degree of freedom of the building block of the system. Hence, e.g., in a system with N building blocks, each having M degrees of freedom, the energy is $\frac{NM}{2}k_{\mathrm{B}}T$. In contrast, here we will assume that the average energy of a normal mode depends not only on temperature, but also on frequency

$$\overline{E(\nu, T)} = \sum_n E_n p_n \tag{2.85}$$

and that the probability that the building block has energy E_n is p_n, given by Boltzmann statistics, i.e.,

$$p_n = \frac{e^{\frac{-E_n}{k_{\mathrm{B}}T}}}{Z}, \tag{2.86}$$

$$Z = \sum_n e^{\frac{-E_n}{k_{\mathrm{B}}T}}. \tag{2.87}$$

Z is called "the partition function". Let us define

$$x := \frac{h\nu}{k_{\mathrm{B}}T}. \tag{2.88}$$

From Eqs. 2.84, 2.85, 2.86, 2.87, 2.88, it follows that

$$\overline{E(\nu, T)} = \sum_n n x k_{\mathrm{B}}T \frac{e^{-nx}}{Z} = \frac{k_{\mathrm{B}}Tx}{Z} \underbrace{\sum_n n e^{-nx}}_{\mathscr{A}}, \tag{2.89}$$

$$Z = \sum_n e^{-nx} = \frac{1}{1 - e^{-x}}, \tag{2.90}$$

since we have an infinite sum of terms of the geometric progression $a_n = e^{-nx}$ with initial value $a_0 = e^{-0x} = 1$ and ratio $\text{ϡ} = \frac{a_{n+1}}{a_n} = e^{-x} < 1$. [Here, we used the archaic Greek letter sampi ("san pi", which means "like a π").] Let us now also try to express $\mathscr{A}$ as a function of x. From Eq. 2.90 it occurs that

$$\frac{\partial Z}{\partial x} = -\sum_n n e^{-nx} = -\frac{e^{-x}}{(1 - e^{-x})^2} \Rightarrow \tag{2.91}$$

$$\mathscr{A} = \frac{e^{-x}}{(1 - e^{-x})^2}. \tag{2.92}$$

Consequently, from Eqs. 2.89, 2.90, 2.92 we obtain

$$\overline{E(\nu,T)} = k_B T x \frac{e^{-x}}{1-e^{-x}} = k_B T x \frac{1}{e^x - 1}. \tag{2.93}$$

And, if we remember how x was defined (Eq. 2.88), we arrive at

$$\overline{E(\nu,T)} = \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1}. \tag{2.94}$$

In analogy with what we did in Section 2.12,

$$\begin{aligned} g(\nu) &= \frac{dN}{d\nu} = \frac{8\pi\nu^2 V}{c^3} \Rightarrow & [g(\nu)] &= \frac{1}{\mathrm{Hz}} = \mathrm{s} \\ \frac{g(\nu)}{V} &= \frac{8\pi\nu^2}{c^3} & \left[\frac{g(\nu)}{V}\right] &= \frac{1}{\mathrm{Hz\,m^3}} = \frac{\mathrm{s}}{\mathrm{m^3}} \\ \rho(\nu,T) &= \overline{E(\nu,T)}\frac{g(\nu)}{V} & [\rho(\nu,T)] &= \frac{\mathrm{J}}{\mathrm{m^3Hz}} = \frac{\mathrm{Js}}{\mathrm{m^3}} \end{aligned}$$

Now $\overline{E(\nu,T)}$ depends not only on temperature T but also on frequency ν. Actually, it is given by Eq. 2.94, therefore,

$$\rho(\nu,T) = \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1}\frac{8\pi\nu^2}{c^3}. \tag{2.95}$$

Consequently, the energy density per unit frequency of the EM radiation of a black body in thermodynamic equilibrium, $\rho(\nu,T)$, with units $\frac{\mathrm{J}}{\mathrm{m^3Hz}}$, is

$$\boxed{\rho(\nu,T) = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{\frac{h\nu}{k_B T}} - 1}} \tag{2.96}$$

In other words, we have obtained the Planck's law (Eq. 2.7).

2.14 Proof of the Wien's displacement law.

For Planck's law in the form $\rho(\nu,T)$, proven above, we will find the –as a function of temperature– frequency, $\nu_0(T)$, where we have maximum of $\rho(\nu,T)$, i.e., Eq. 2.98. Let us remember the form of the Planck's law after the change of variables (Eq. 2.8), i.e., after we have set

$$x = \frac{h\nu}{k_B T} \Rightarrow \nu = \frac{k_B T}{h}x \Rightarrow d\nu = \frac{k_B T}{h}dx.$$

Then, Eq. 2.12 occurs,

$$\rho = \rho_0 \frac{x^3}{e^x - 1},$$

where, according to Eq. 2.13,

$$\rho_0 = \frac{8\pi}{h^2}\left(\frac{k_B T}{c}\right)^3$$

with units

$$[\rho_0] = \frac{\mathrm{Js}}{\mathrm{m^3}} = \frac{\mathrm{J}}{\mathrm{m^3Hz}}.$$

Of course, $x = 0$ does not belong to the domain of the function $\rho(x)$, i.e., we do not refer to zero frequency of infinite temperature. Therefore,

$$\frac{d\rho}{dx} = \rho_0 \frac{3x^2(e^x - 1) - x^3 e^x}{(e^x - 1)^2} = \rho_0 x^2 \frac{3(e^x - 1) - xe^x}{(e^x - 1)^2}. \tag{2.97}$$

Since we are looking for extrema, the derivative $\frac{d\rho}{dx}$ should become zero, thus,

$$\frac{d\rho}{dx} = 0 \Rightarrow 3(e^x - 1) - xe^x = 0 \Rightarrow (\text{since } x \neq 0) \quad x_0 \sim 3.$$

x_0 is the desired root and ν_0 the respective frequency, i.e. $x_0 = \frac{h\nu_0}{k_B T}$. More precisely, a graphical or numerical solution gives $x_0 \approx 2.821439$. The graphical solution is presented in Figure 2.14. Finally,

$$\nu_0 = \frac{k_B T x_0}{h} \approx \frac{k_B T\ 2.821439}{h} \approx (58.789\ \text{GHz/K})\ T \Rightarrow$$

$$\boxed{\frac{\nu_0}{T} \approx 58.789\ \text{GHz/K}} \tag{2.98}$$

Eq. 2.98 shows how the frequency at which we have a maximum of $\rho(\nu, T)$ is shifted as a function of temperature T, it is thus a “displacement law”, although it is expressed in terms of frequency and not wavelength, as the usual “Wien’s displacement law”, of Eq. 2.101, which is proven below.

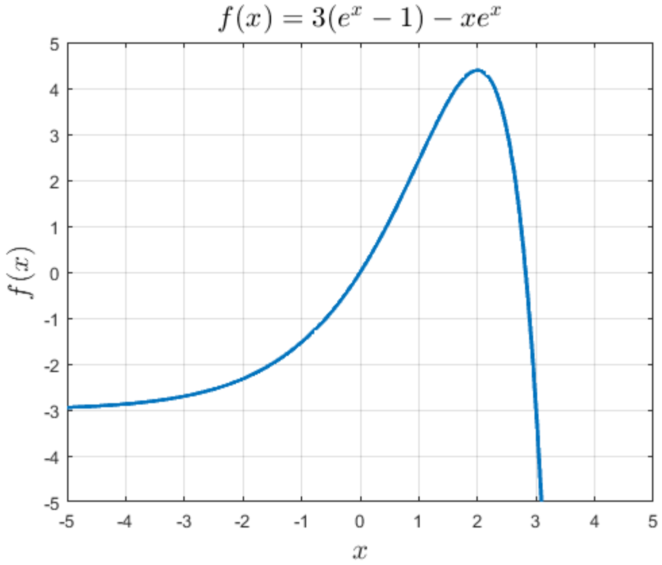

Figure 2.14: Graphical solution of equation $3(e^x - 1) - xe^x = 0$. The first root is $x_0 = 0$, which does not belong to the domain of $\rho(x)$. The other root is $x_0 \approx 2.821439$.

Next, using Planck’s law as a function of wavelength, $\rho(\lambda, T)$, in the form of Eq. 2.21, we will find the –as a function of temperature– wavelength, $\lambda_0(T)$, where we have maximum of $\rho(\lambda, T)$, that is Eq. 2.101 below. Taking the derivative of Eq. 2.21, we obtain

$$\frac{d\rho}{d\psi} = \rho_0' \frac{5\psi^4(e^\psi - 1) - \psi^5 e^\psi}{(e^\psi - 1)^2} = \rho_0' \psi^4 \frac{5(e^\psi - 1) - \psi e^\psi}{(e^\psi - 1)^2}. \tag{2.99}$$

Since we are looking for extrema, the derivative $\frac{d\rho}{d\psi}$ should become zero, thus,

$$\frac{d\rho}{d\psi} = 0 \Rightarrow 5(e^\psi - 1) - \psi e^\psi = 0 \Rightarrow (\text{since } \psi \neq 0) \quad \psi_0 \sim 5.$$

ψ_0 is the desired root and λ_0 the respective wavelength, i.e. $\psi_0 = \frac{hc}{\lambda_0 k_B T}$. More precisely, a graphical solution gives $\psi_0 \approx 4.965114$. The graphical solution is presented in Figure 2.15. Finally,

$$\lambda_0 = \frac{hc}{\psi_0 k_B T} \approx \frac{hc}{4.965114 k_B T} \Rightarrow \tag{2.100}$$

$$\boxed{\lambda_0 T \approx 2.897772 \times 10^{-3}\ \mathrm{m\,K}} \tag{2.101}$$

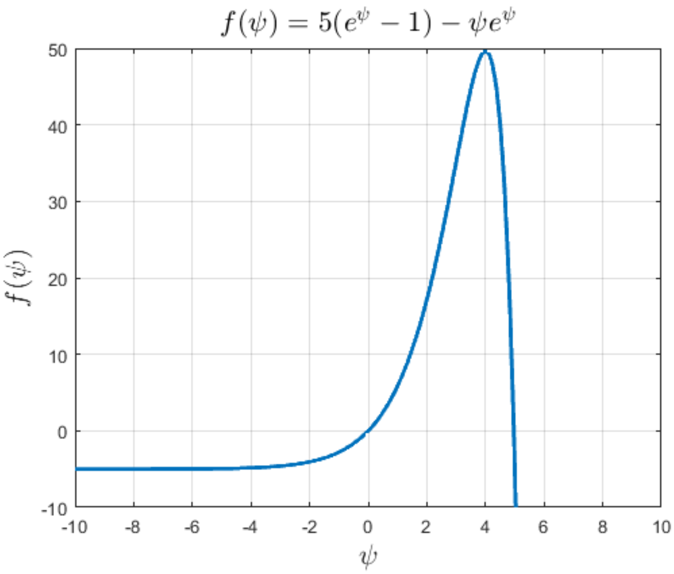

Figure 2.15: Graphical solution of equation $5(e^{\psi} - 1) - \psi e^{\psi} = 0$. The first root is $\psi_0 = 0$, which does not belong to the domain of $\rho(\psi)$. The other root is $\psi_0 \approx 4.965114$.

Eq. 2.98 shows how the wavelength at which there is maximum of $\rho(\lambda, T)$ is shifted as a function of temperature T, it is thus a "displacement law", the so-called "Wien's displacement law". This is the "contemporary form" of Wien's displacement law; it was derived by W. Wien in 1893 with the phraseology that the black body radiation for different temperatures peaks at a wavelength inversely proportional to its temperature, i.e.:

$$\lambda_0 T = \text{constant} \tag{2.102}$$

This behavior, although it can be derived by Planck's law, as shown above, leading to Eq. 2.101, it was discovered by W. Wien some years before Planck's proof of his law (Eq. 2.12 ή Eq. 2.18). Planck's law in the form $\rho(\lambda, T)$ for $T = 1595$ K as well as λ_0 of Wien's displacement law are depicted in Figure 2.16. We chose this value of T with reference to Figure 2 of the historic article by W. W. Coblentz [18], which contains experimental data and comparison with Planck's law at this temperature.

Planck's law for several black body temperatures is depicted in Figure 2.17. We notice a shift of the spectrum towards smaller wavelengths, as the temperature increases, which is expressed by Wien's displacement law. For these temperatures, the corresponding λ_0, at which there is a peak of $\rho(\lambda, T)$ is also shown. Furthermore, the visible region of the EM spectrum is depicted, which will be useful in some exercises on bodies emitting EM radiation, where we assume that they can be approximated by black bodies of some "effective temperature". The effective temperature of a body is the temperature of the black body that would emit the same *total* amount of EM radiation. However, this does not mean that the distribution of radiation as a function of wavelength or frequency essentially follows Planck's law. Planck's law, $\rho(\nu, T)$, for some black body temperatures is shown in Figure 2.18. We observe the shift of the spectrum to higher frequencies, as we increase the black body absolute temperature, T, which is what Wien's displacement law expresses. We also observe that generally the whole distribution $\rho(\nu, T)$ is increased, as we increase the temperature T.

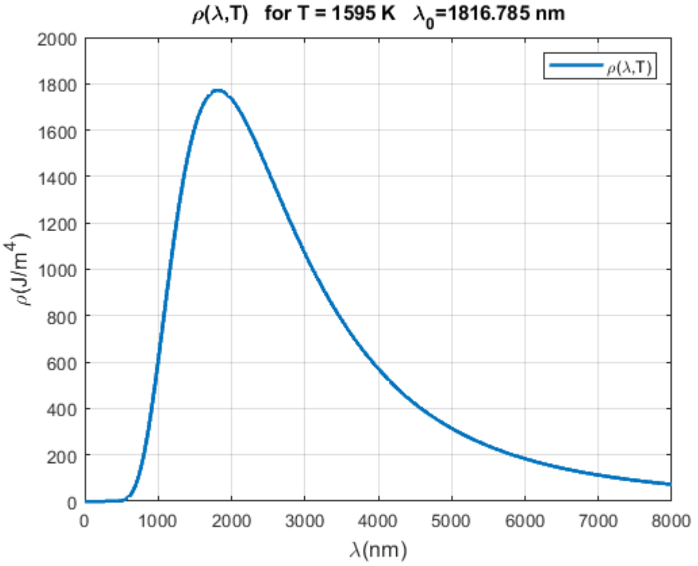

Figure 2.16: Planck's law in the form $\rho(\lambda, T)$ for $T = 1595$ K as well as λ_0 of Wien's displacement law. This value of T was chosen with reference to Figure 2 of the historic article by W. W. Coblentz [18].

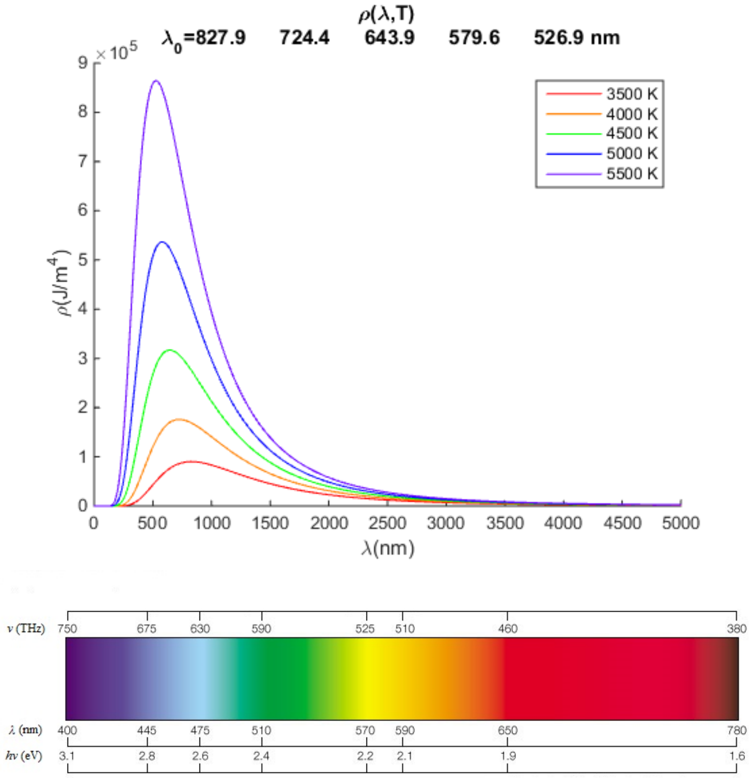

Figure 2.17: [Top] Planck's law $\rho(\lambda, T)$ for several black body temperatures. We notice a shift of the spectrum towards smaller wavelengths, as the temperature increases, which is expressed by Wien's displacement law. The corresponding λ_0, at which there is a peak of $\rho(\lambda, T)$ is also included. We observe that generally the whole distribution $\rho(\lambda, T)$ is increased, as we increase the temperature, T. [Bottom] The visible part of the EM spectrum.

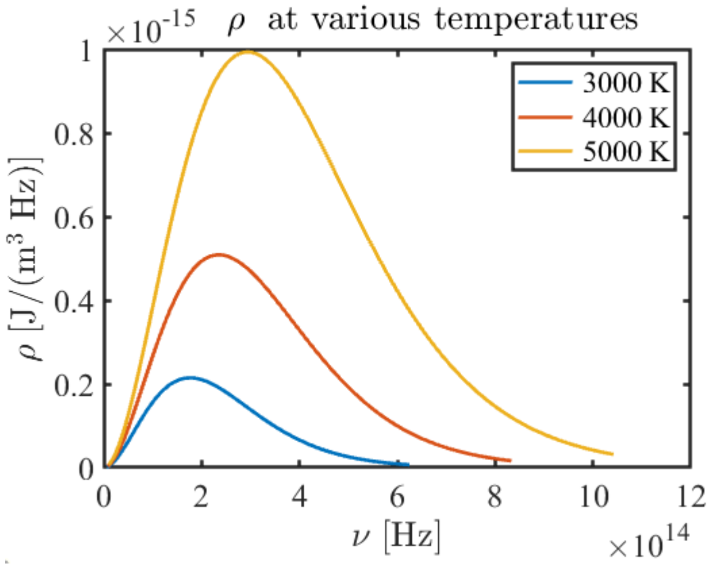

Figure 2.18: Planck's law, $\rho(\nu, T)$, for some characteristic black body temperatures. We observe the shift of the spectrum to higher frequencies, as the black body absolute temperature T is increased, which is what Wien's displacement law expresses. We also observe that generally the whole distribution $\rho(\nu, T)$ is increased, as we increase the temperature T.

2.15 Photoelectric effect.

The photoelectric effect (PEE) is the emission of electrons from a material that has absorbed energy from EM radiation, usually in the visible or ultraviolet regime. It was observed by H. Hertz [19] in 1887, who showed that it is easier to create electric sparks when ultraviolet light shines on the electrodes. To occur, the photoelectric effect needs photons with energies of the order of 1 eV to 1 MeV (in materials with large atomic number). The study of the photoelectric effect led to the acceptance of the quantum nature of light and of the wave-particle duality. In 1905, A. Einstein explained the PEE by hypothesizing that light is composed of discrete packets ("quanta") instead of continuous waves [16]. Those discrete packets are now called photons, a term attributed to G. N. Lewis [17] that came to common use much later.

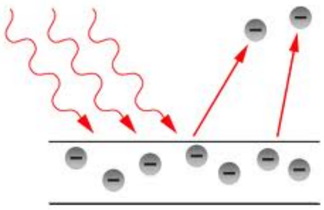

Figure 2.19: A schematic representation of the photoelectric effect.

Einstein used Planck's theory of black body radiation and assumed that the energy of each photon, E, is proportional to its frequency, ν, with the proportionality constant being what was later named "the Planck's constant", h, i.e., he assumed that $E = h\nu$. This is how he explained the PEE: a photon with frequency larger than a threshold value contains the necessary energy to eject a single electron from the material. For his explanation of the PEE, which lead to the quantum revolution, Einstein was honored with the 1921 Nobel Prize in Physics. He proposed that, under certain conditions, light is equivalent to a flow of particles (light quanta, today called photons). He discovered this result by analyzing the thermodynamics of black body radiation in the Wien's regime. Among the consequences of his proposition was the explanation of several puzzling characteristics of the photoelectric effect.

So, when visible or UV radiation hits a metallic surface, electrons begin to be ejected, if the frequency of EM radiation is high enough. For example, when monochromatic light impinges on the cathode of a discharge tube, current between the anode and the cathode is created, due to the displacement of ejected electrons from the cathode towards the anode. In the setup of Figure 2.20, the voltage between the anode and the cathode can be either positive or negative. When it is positive, electrons accelerate, thus the current is increased, while, when it is negative, electrons decelerate, thus the current is decreased. For an adequately negative voltage, $-V_0$, the current vanishes. V_0 is called threshold voltage or potential difference.

One of the puzzling aspects of the PEE was that, irrespective of the intensity of the incident monochromatic radiation, the threshold voltage always remains the same. The existence of a voltage that can stop electric current implies a maximum kinetic energy that electrons ejected from the cathode can gain. This maximum kinetic energy is equal to the threshold voltage V_0 multiplied by the elementary charge, e. Thus,

$$\frac{m_e u^2}{2}\Big|_{max} = eV_0. \tag{2.103}$$

In other words, the kinetic energy the electrons obtain when ejected from the metallic surface has a maximum value which always remains the same, regardless the intensity of monochromatic EM radiation. Every metal has a work function W_0, which means an electron inside a metal has to obtain energy at least equal to W_0 to be removed. If it obtains exactly W_0, then it "goes out" with zero velocity, while, if it obtains

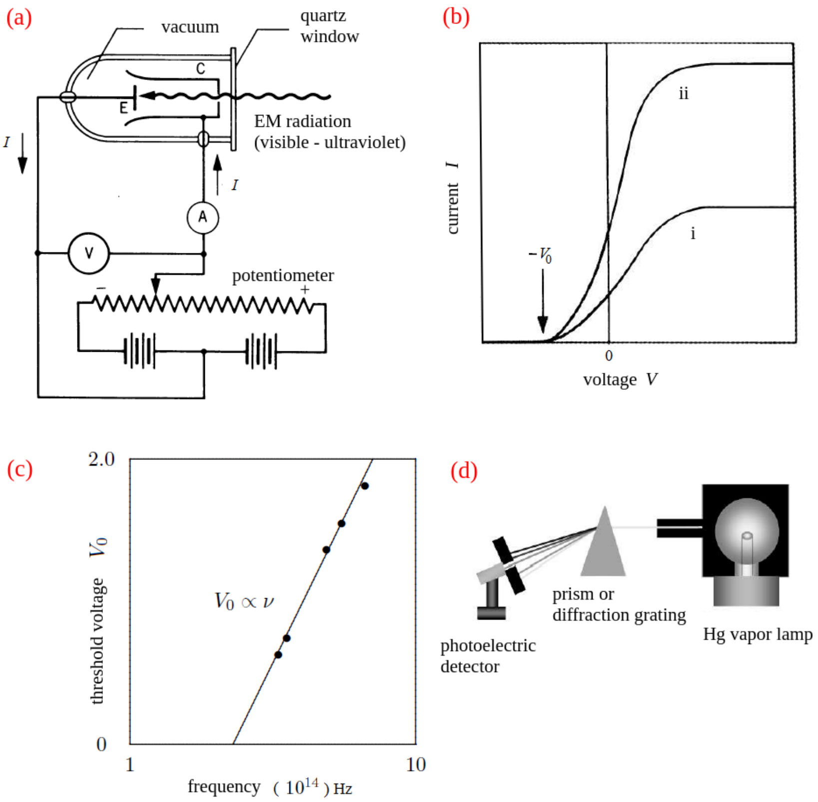

Figure 2.20: (a) The setup needed to study the energy of electrons emitted during the photoelectric effect (PEE). (b) The shape of the characteristic current-voltage curve, $I(V)$, for two different intensities of incident EM radiation. In case ii, the intensity of EM radiation is larger than in case i. We observe that there is a voltage, $-V_0$, at which the current, I, vanishes at both cases, i.e., V_0 does not depend on the intensity of incident radiation. (c) The relation $V_0(\nu)$. (d) The setup used to demonstrate the frequency dependence within the PEE.

$E > W_0$, it uses the excess amount as kinetic energy. Hence,

$$E = W_0 + \frac{m_e u^2}{2}. \tag{2.104}$$

So, Einstein [16] hypothesized that light is composed of "packets" or otherwise "particles" or otherwise "quanta", each of which carries energy equal to $h\nu$. Thus, if we assume that an electron absorbs the energy of the photon, the previous equation can be written as

$$h\nu = W_0 + \frac{m_e u^2}{2}. \tag{2.105}$$

Hence, applying the previous relationship to the maximum kinetic energy, we have

$$h\nu = W_0 + eV_0. \tag{2.106}$$

Therefore,

$$V_0 = \frac{h}{e}\nu - \frac{W_0}{e}. \tag{2.107}$$

Thus, if we plot the threshold voltage, V_0, as a function of frequency, ν, we will obtain a straight line; see Figure 2.20(c). According to Einstein, the increase of monochromatic EM radiation intensity means an increase in the number of electrons with kinetic energy $\frac{m_e u^2}{2}$ but not an increase in this kinetic energy. In Figure 2.20(d), the setup used to demonstrate the frequency dependence within the PEE is presented. The light source is a mercury vapor lamp emitting 5 intense lines from yellow to the UV regime, as seen in Table 2.3.

Table 2.3: The photoelectric effect using a mercury vapor lamp as a light source.

Emission line	**Frequency** ν ($\times 10^{14}$ Hz)	**Threshold voltage** V_0 (V)
ultraviolet 2	8.22	1.807
ultraviolet 1	7.41	1.546
bright blue	6.88	1.359
green	5.49	0.738
yellow	5.19	0.624

This setup ensures the separation of emission lines, and a photoelectric detector counts the energies of ejected electrons. The results of a typical experiment, plotted in Figure 2.20(c) are shown in Table 2.3. According to Eq. 2.107, the line's slope is $\frac{h}{e}$. So, according to the aforementioned data, we have $\frac{h}{e} = (0.400 \pm 0.016) \times 10^{-14}$ Js/C, while, today we know that this ratio is approximately $\frac{h}{e} = 0.414 \times 10^{-14}$ Js/C. The predictions of Einstein's theory were verified later, with the most important moment being the experiments by R. Millikan [20, 21]. The second one [21] is far more detailed.

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CHAPTER 3

INTERACTION PROCESSES BETWEEN A PHOTON AND A TWO-LEVEL SYSTEM

In this Chapter:

We describe the interaction mechanisms or processes between a photon and a two-level system (2LS). These processes are usually called Einstein mechanisms or processes: spontaneous emission, stimulated emission, (stimulated) absorption. This way we also introduce the relevant Einstein coefficients A and B. Of course, from them, only stimulated emission was introduced by Einstein. The other two processes were already known, but nobody had up to then seen them as an integral whole, if I am not mistaken. Here the Planck law is proven, with a proof almost identical to that of Einstein himself, with the help of these processes and the Boltzmann statistics. A comparison between Maxwell-Boltzmann, Fermi-Dirac, and Bose-Einstein statistics, which is followed by classical particles, fermions, and bosons, respectively, is included. We also compare spontaneous with stimulated emission as well as the stimulated processes between them.

Prerequisite knowledge: Basic knowledge of Physics and Mathematics as well as a little bit of Statistical Physics.

3.1 Interaction processes between a photon and a two-level system (2LS). (Stimulated) Absorption. Spontaneous Emission. Stimulated Emission. Einstein coefficients A and B.

LASER is an acronym that means Light Amplification by Stimulated Emission of Radiation. Einstein set the theoretical foundations of the LASER in 1916-1917, through a re-derivation, that is a new proof, of the Planck's law for black body radiation. His proof was based on the so-called today "Einstein processes or mechanisms", which describe the probabilities of (Stimulated) Absorption, Spontaneous Emission and Stimulated Emission. These are the processes involved in the interaction between EM radiation and matter or, more precisely, between a photon and a two-level system, e.g., within an atom, molecule, quantum dot, nonoparticle etc.

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Hence, we will deal with the interaction of EM radiation or, better, light quanta (photons) with a two-level system, e.g., focusing on two energy levels of an atom, E_1 and $E_2 > E_1$. We will suppose that this two-level system has a sole electron. According to Einstein [1, 2], there are three processes that affect this interaction: Spontaneous Emission, Stimulated Absorption and, finally, Stimulated Emission. The latter was introduced by Einstein [1, 2]. A process is called "stimulated" when it needs the influence of EM radiation, i.e., of photons, on the 2LS to occur. A process is called "spontaneous" when it does not need the influence of EM radiation, i.e., of photons, on the 2LS to occur. The word "stimulated" is often omitted in the term Stimulated Absorption, since it is implied; any absorption is stimulated, needing EM radiation to happen. Below we will examine in detail what exactly Stimulated Emission and the rest two processes (i.e., Spontaneous Emission and Stimulated Absorption) are. The mechanisms or processes of interaction between EM radiation and a two-level system are analyzed in articles [1, 2], which were published during 1916-1917. In the same articles, together with the definition of these processes, the derivation of the Planck's law using them is included. So, concisely

Stimulated Emission	due to $\rho(\nu, T)$
Stimulated Absorption	due to $\rho(\nu, T)$
Spontaneous Emission	

A. Einstein had already (1905) explained the photoelectric effect [3] assuming that there exist light quanta with energy $E = h\nu$, these would later be termed photons. [Probably the word was introduced in 1926 by G. N. Lewis [4].] It is worth noting here that it was only several decades later –mainly in the 1950s and 1960s– and after international efforts by many prominent or not physicists that it became possible to construct the first MASERs ("M" stands for Microwaves) and LASERs. In 1964, Charles Townes, Nikolay Basov and Aleksandr Prokhorov shared the Nobel Prize in Physics "for (their) fundamental work in the field of quantum electronics, which has led to the construction of oscillators and amplifiers based on the maser-laser principle".

We will suppose that we are inside a black body in thermodynamic equilibrium. The mechanisms or processes of interaction between photons and a two-level system are explained below. As it will become clear later, for the so-called Einstein coefficients A_{21}, B_{12}, B_{21} we use A for the spontaneous process and B for the stimulated processes.

In Sections 3.1.1, 3.1.2, 3.1.3, as an example of a two-level system, we focus on two energy levels, E_1 and E_2, of an atom.

3.1.1 (Stimulated) Absorption.

The Stimulated Absorption of a photon with energy E_{ph} and momentum p_{ph}, between two energy levels E_1 and E_2 of an atom where we focus on, is illustrated in Figure 3.1. Let us suppose that initially the atom is motionless. Additionally, let us assume that the probability, $dW_{\text{ab}}^{\text{st}}$, that the atom absorbs a photon in time dt is given by

$$\boxed{dW_{\text{ab}}^{\text{st}} = B_{12}\rho(\nu, T)dt} \tag{3.1}$$

i.e., it is proportional to the time interval dt and the EM energy density in an infinitesimal frequency interval, $\rho(\nu, T)$, with a constant of proportionality B_{12}, where the index 12 means that after the absorption the electron will jump from level 1 to level 2.

We apply the laws of Conservation of Energy and Momentum.

Conservation of Energy $$E_1 + h\nu = E_2 + \overset{\text{supposedly negligible}}{\cancel{\frac{p_{\text{at}}^2}{2m_{\text{at}}}}} \Rightarrow E_2 - E_1 = h\nu$$

Conservation of Momentum $$p_{\text{ph}} = p_{\text{at}} \Rightarrow p_{\text{at}} = \frac{h\nu}{c} = \frac{hc}{\lambda c} = \frac{h}{\lambda} = \frac{h2\pi}{2\pi\lambda} = \hbar k \Rightarrow p_{\text{at}} = \frac{h}{\lambda} = \hbar k$$

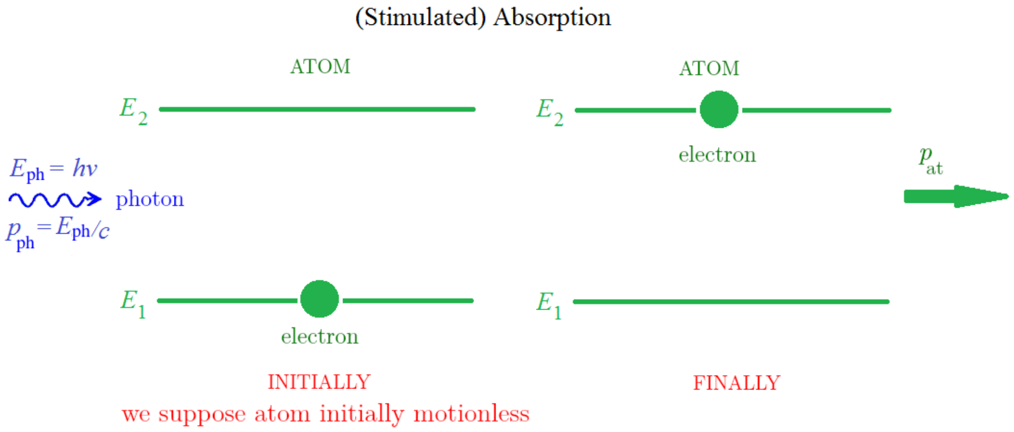

Figure 3.1: Stimulated Absorption of a photon with energy E_{ph} and momentum p_{ph}, accompanied with an electron transfer between two energy levels E_1 and E_2 of an atom.

Let us now check whether the kinetic energy of the atom after the absorption, $\frac{p_{\text{at}}^2}{2m_{\text{at}}}$, is indeed negligible compared to the photon energy, E_ϕ, by calculating their ratio, Λ.

$$\Lambda = \frac{\frac{p_{\text{at}}^2}{2m_{\text{at}}}}{E_\phi} = \frac{h^2 \quad \lambda}{\lambda^2 2m_{\text{at}} hc} = \frac{h}{2\lambda c m_{\text{at}}}.$$

For Λ to increase, m_{at} must decrease. Hence, let us set m_{at} equal to the mass of the smallest possible atom, hydrogen.

$$\left.\begin{array}{l} m_{\text{at}} \approx m_p + m_e \\ m_p \approx 1.673 \cdot 10^{-27}\,\text{kg} \\ m_e \approx 9.109 \cdot 10^{-31}\,\text{kg} \end{array}\right\} \Rightarrow m_{\text{at}} \simeq 1.673 \cdot 10^{-27}\,\text{kg}$$

We wrote $m_{\text{at}} \approx m_p + m_e$ instead of $m_{\text{at}} = m_p + m_e$ because there is a (small) “mass defect”, i.e., the binding energy of the electron and the proton in the hydrogen atom. Let us consider a typical green photon with $\lambda \approx 500$ nm. Then,

$$\Lambda = \frac{6.626 \cdot 10^{-34}\text{Js} \quad \text{s}}{2 \cdot 500 \cdot 10^{-9}\text{m} \;\; 3 \cdot 10^{8}\text{m} \;\; 1.673 \cdot 10^{-27}\text{kg}} \approx 1.320 \cdot 10^{-9}.$$

Hence, in our example, the kinetic energy of the atom is indeed negligible compared to the photon energy.

Question: For which wavelength λ, does the ratio Λ become equal to 0.05 in the hydrogen atom?
Answer:

$$\Lambda = \frac{h}{2\lambda c m_{\alpha\tau}} = 0.05 \Rightarrow$$

$$\lambda = \frac{h}{2cm_{\alpha\tau}\Lambda} = \frac{6.626 \cdot 10^{-34}\text{Js} \cdot \text{s}}{2 \cdot 3 \cdot 10^{8}\,\text{m} \cdot 1.673 \cdot 10^{-27}\,\text{kg} \cdot 0.05} \approx 13.2 \cdot 10^{-15}\,\text{m} = 13.2\text{fm}.$$

This is an extremely tiny wavelength. Even γ-rays have typical wavelengths below pm (10×10^{-12} m), but, here we are at the fm regime, that is at the 10^{-15} m regime. Even the diameter of the atomic nuclei varies from 1.75 fm = 1.75×10^{-15} m for hydrogen (the diameter of a proton) to ≈ 15 fm for some of the heaviest atoms like uranium. Thus, our assumption that the kinetic energy of the atom is negligible compared to the photon energy is valid nearly across the whole EM spectrum.

3.1.2 Spontaneous Emission.

The Spontaneous Emission is illustrated in Figure 3.2. Let us assume that the probability, $dW_{\text{em}}^{\text{sp}}$, that the atom spontaneously emits a photon at time dt is given by

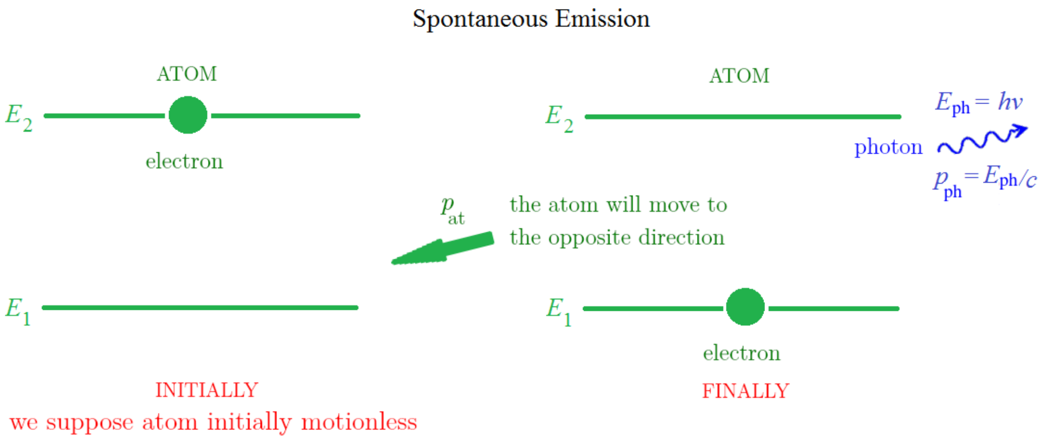

Figure 3.2: Spontaneous Emission of a photon with energy E_{ph} and momentum p_{ph}, accompanied with an electron transfer between two energy levels E_2 and E_1 of an atom.

$$\boxed{dW_{\text{em}}^{\text{sp}} = A_{21}dt} \tag{3.2}$$

i.e., it is proportional to the time interval, dt, with a constant of proportionality A_{21}, where the index 21 means that with the emission of the photon, the electron will fall from level 2 to level 1. We note that since this process is spontaneous, $dW_{\text{em}}^{\text{sp}}$ does not depend on the EM energy density in an infinitesimal frequency interval, $\rho(\nu, T)$. We can define the lifetime of level 2 as the time it takes for the photon to be emitted spontaneously *with certainty* (hence the electron is transferred from level 2 to level 1). If we denote it by $\tau_2 = \tau$, then, from Eq. (3.2), we obtain $1 = A_{21}\tau$. Thus,

$$\tau_2 = \tau = \frac{1}{A_{21}}. \tag{3.3}$$

We now apply the laws of Conservation of Energy and Momentum, supposing that the atom is initially motionless. Hence, when a photon is emitted, it will move towards the opposite direction.

$$\begin{array}{rl} \text{Conservation of Energy} & E_2 = E_1 + E_{\text{ph}} + \dfrac{p_{\text{at}}^2}{2m_{\text{at}}} \\ \text{Conservation of Momentum} & p_{\text{at}} + p_{\text{ph}} = 0 \end{array}$$

Since this process is spontaneous, photons are emitted towards a random direction, i.e., without directionality, and with a random phase, i.e., without coherence. In other words, they are incoherent photons. **Directionality** means that EM radiation is emitted towards a certain direction. **Coherence is a constant relationship between the phase of waves with the same frequency**. For example, two light beams are coherent when the phase difference between them remains constant, while they are incoherent when there is a random or varying phase difference between them. **Stable forms of interference** are created only by **coherent beams**. In fact, they usually come from a single beam which is separated into two or more beams. A LASER, unlike an incandescent light source, produces a light beam the components of which have constant relationship between their phases. Similarly, two photons with a constant phase relationship are coherent.

3.1.3 Stimulated Emission.

The Stimulated Emission is illustrated in Figure 3.3. In this process, before the electron falls spontaneously from level 2 to level 1, a stimulating photon causes it to fall. Let us suppose that the atom is initially motionless. Let us consider as positive the initial direction of the stimulating photon. Let us further suppose that the probability, $dW^{\mathrm{st}}_{\mathrm{em}}$, that the atom emits a photon in time dt via this process is given by

$$\boxed{dW^{\mathrm{st}}_{\mathrm{em}} = B_{21}\rho(\nu,T)dt} \tag{3.4}$$

i.e., it is proportional to the time interval dt and the EM energy density in an infinitesimal frequency interval, $\rho(\nu,T)$, with a constant of proportionality B_{21}, where the index 21 means that after the emission of the photon, the electron will fall from level 2 to level 1.

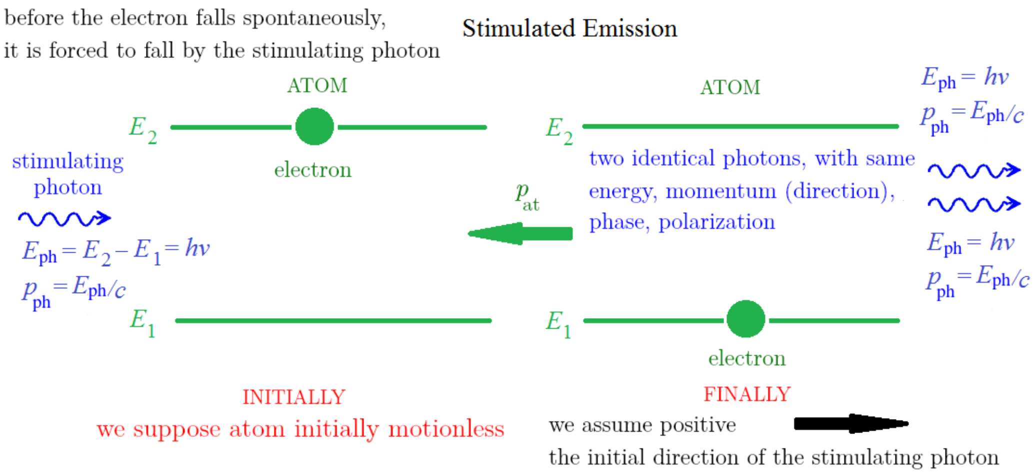

Figure 3.3: Stimulated Emission of a photon with energy E_{ph} and momentum p_{ph}, accompanied with an electron transfer between two energy levels E_2 and E_1 of an atom. An initial stimulating photon causes the creation of another photon with identical characteristics (energy, momentum, phase, polarization).

The two photons, i.e., the initial stimulating photon and the photon that is emitted by the atom, are identical, indistinguishable, i.e., they have the same energy (→ monochromaticity), momentum, hence direction (→ directionality), phase (→ coherence), polarization (→ polarized light).

$$\left.\begin{array}{r}\text{monochromaticity}\\ \text{directionality}\\ \text{coherence}\\ \text{polarization}\end{array}\right\}\text{are properties of a LASER}$$

Although the two photons involved in the process of Stimulated Emission have the same polarization, i.e., the electric field of these photons is in the same direction, the rest two processes, Spontaneous Emission and (Stimulated) Absorption, are still present in the effective medium of a LASER device. However, in Spontaneous Emission, the emitted photons have random direction, phase, and polarization (while their energy, in a strictly two-level system is the same). Thus, overall, the photons present inside the effective medium of a LASER device, do not have a specific polarization. On the other hand, the light of a LASER device can become polarized by attaching a polarizer (a material that lets only light of specific polarization pass) or a "Brewster window" at the exit of the LASER device.

When a light beam impinges on the interface between two media, its reflected part and its transmitted (in other words, refracted) part are described by the Fresnel Equations and depend on the polarization of the incident light and the angle of incidence. Thus, p-polarized light (electric field polarized in the plane defined by the incident beam and the normal to the interface) will not be reflected if the angle of incidence is $\theta_B = \arctan(n_2/n_1)$, where n_1, n_2 are the refraction indices of the initial and the other medium. This equation is known as the Brewster's law and the angle θ_B is referred to as the Brewster's angle. We discuss the Fresnel Equations and the Brewster's angle in detail in Section 12.1, and the emission of a polarized beam in Section 12.3. In practice, the light of some LASER devices is largely polarized (e.g., in gas LASERs), while the light of some other LASER devices is polarized to a lesser extent (e.g., in diode LASERs). LASER devices have a cavity that confines the effective medium and creates a competition between the EM modes and between polarizations. In the end, the mode and polarization with the smallest losses dominate. However, there are also LASERs with many modes or polarizations.

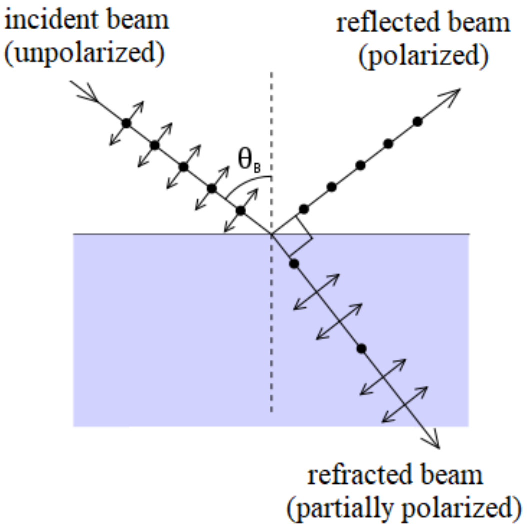

Figure 3.4: The Brewster angle.

Let us notice that:

- What is mentioned above about same phase and polarization is not discussed in Einstein articles [1, 2] nor they do play any role in the derivation of Planck's law therein, derivation presented below, too.
- Photons are bosons, thus two or more photons can have the same energy, momentum (hence, direction), and phase.
- We need to assume that the initial stimulating photon, with energy $E_{ph} = E_2 - E_1 = h\nu$, is not at all affected during Stimulated Emission.
- We could state that the initial stimulating photon determines the phase and the polarization of the emitted photon just as the stimulating force determines the phase and the polarization of a forced or stimulated oscillation.

We now apply the laws of Conservation of Energy and Momentum, supposing that the atom is initially motionless. According to what we have discussed up to now

$$\begin{aligned} &\text{Conservation of energy} \qquad && E_2 + E_{ph} = 2E_{ph} + E_1 + \cancelto{\text{small}}{\frac{p_{at}^2}{2m_{at}}} \\ &\text{Conservation of momentum} \qquad && \vec{p}_{ph} = 2\vec{p}_{ph} + \vec{p}_{at} \end{aligned}$$

We could, of course, attempt to consider that the two photons might have different energy and momentum, e.g., to write

Conservation of energy

$$E_2 + \cancel{E_{\mathrm{ph}}} = E_1 + \cancel{E_{\mathrm{ph}}} + E'_{\mathrm{ph}} + \overset{\text{small}}{\cancel{\frac{p_{\mathrm{at}}^2}{2m_{\mathrm{at}}}}} \Rightarrow$$

$$E'_{\mathrm{ph}} = E_2 - E_1 = E_{\mathrm{ph}}$$

the photons have the same energy

Let us assume the initial direction of the stimulating photon as positive, that is $p_\phi > 0$.

Conservation of momentum $\quad \cancel{\vec{p}_{\mathrm{ph}}} = \cancel{\vec{p}_{\mathrm{ph}}} + \vec{p}'_{\mathrm{ph}} + \vec{p}_{\mathrm{at}} \Rightarrow \vec{p}'_{\mathrm{ph}} = -\vec{p}_{\mathrm{at}}$

If we assume that the stimulating photon determines the direction of the new photon, then

$$p'_{\mathrm{ph}} > 0 \quad p'_{\mathrm{ph}} = \frac{E'_{\mathrm{ph}}}{c} = \frac{E_{\mathrm{ph}}}{c} = p_{\mathrm{ph}} \Rightarrow \text{the photons have the same momentum}$$

In brief, because the photons have same energy, the outgoing light will have monochromaticity and because the photons have momentum in the same direction, the outgoing light will have directionality.

3.2 Derivation of Planck's law via emission and absorption processes and Boltzmann statistics. Relationship between Einstein coefficients A and B.

Let us consider the interaction between the EM field and matter in thermodynamic equilibrium, so that the temperature T = constant. Let us denote by N_i the population of the level i, i.e., the average number of atoms with the electron at level i, for which we assume that it follows the Boltzmann distribution, which is

(1) with same statistical weights
(simpler form)

$$N_i = N_{\mathrm{tot}} \underbrace{\frac{e^{-\frac{E_i}{k_{\mathrm{B}}T}}}{Z}}_{p_i}$$

$$Z = \sum_i e^{-\frac{E_i}{k_{\mathrm{B}}T}}$$

or

(2) with different statistical weights
(general form)

$$N_i = N_{\mathrm{tot}} \underbrace{\frac{g_i e^{-\frac{E_i}{k_{\mathrm{B}}T}}}{Z}}_{p_i}$$

$$Z = \sum_i g_i e^{-\frac{E_i}{k_{\mathrm{B}}T}}$$

Here, p_i is the occupation probability for level i. The Boltzmann distribution is defined using the **partition function**, Z, which plays a central role in the description of the statistical properties of a system in thermodynamic equilibrium (see a statistical physics textbook, e.g., [5]). Since we have assumed thermodynamic equilibrium, the variations of the level populations in time dt will be equal, i.e., the number of atoms where electrons jump from 1 to 2 will be equal to the number of atoms where electrons drop from 2 to 1, i.e.,

$$dN_{1\to 2} = dN_{2\to 1}. \tag{3.5}$$

$dN_{1\to 2}$ will be equal to the population N_1 multiplied by the transition probability from 1 to 2 in time dt. This probability is associated with (Stimulated) Absorption, and is given by Eq. 3.1. $dN_{2\to 1}$ will be equal to the population N_2 multiplied by the transition probability from 2 to 1 in time dt. This probability is associated with Spontaneous Emission, given by Eq. 3.2, and Stimulated Emission, given by Eq. 3.4. Thus,

$$N_1 dW_{\text{ab}}^{\text{st}} = N_2(dW_{\text{em}}^{\text{sp}} + dW_{\text{em}}^{\text{st}}). \tag{3.6}$$

(1) To begin with, let us make calculations with same statistical weights. Due to Eqs. 3.1, 3.2, 3.4, Eq. 3.6 becomes

$$\begin{aligned}
& N_{\text{tot}}\frac{e^{-\frac{E_1}{k_\text{B}T}}}{Z}B_{12}\rho(\nu,T)dt = N_{\text{tot}}\frac{e^{-\frac{E_2}{k_\text{B}T}}}{Z}\Big(A_{21}dt + B_{21}\rho(\nu,T)dt\Big) \Rightarrow \\
& B_{12}e^{-\frac{E_1}{k_\text{B}T}}\rho(\nu,T) - B_{21}e^{-\frac{E_2}{k_\text{B}T}}\rho(\nu,T) = A_{21}e^{-\frac{E_2}{k_\text{B}T}} \Rightarrow \\
& \rho(\nu,T) = \frac{A_{21}e^{-\frac{E_2}{k_\text{B}T}}}{B_{12}e^{-\frac{E_1}{k_\text{B}T}} - B_{21}e^{-\frac{E_2}{k_\text{B}T}}}.
\end{aligned}$$

However, we already know (cf. e.g. Figure 2.18) that

$$\begin{aligned}
\lim_{T\to\infty}\rho(\nu,T) &= \infty \Rightarrow \\
\frac{A_{21}}{B_{12}-B_{21}} &= \infty \Rightarrow B_{12} = B_{21} := B \\
& \qquad\qquad\qquad A_{21} := A.
\end{aligned}$$

Hence,

$$\rho(\nu,T) = \frac{\frac{A}{B}}{e^{\frac{(E_2-E_1)}{k_\text{B}T}} - 1}.$$

Comparing with Planck's law (or even, dimensionally, with Wien's law), we have

$$\text{up to now} \quad \boxed{\rho(\nu,T) = \frac{\frac{A}{B}}{e^{\frac{(E_2-E_1)}{k_\text{B}T}} - 1}} \qquad \text{Planck's law} \quad \boxed{\rho(\nu,T) = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{\frac{h\nu}{k_\text{B}T}} - 1}}$$

Thus,

$$\boxed{\frac{A}{B} = \frac{8\pi h\nu^3}{c^3}} \tag{3.7}$$

$$\boxed{E_2 - E_1 = h\nu} \tag{3.8}$$

(2) Let us now make calculations with different statistical weights. Due to Eqs. 3.1, 3.2, 3.4, Eq. 3.6 becomes

$$\begin{aligned}
& N_{\text{tot}}\frac{g_1\, e^{-\frac{E_1}{k_\text{B}T}}}{Z}B_{12}\rho(\nu,T)dt = N_{\text{tot}}\frac{g_2\, e^{-\frac{E_2}{k_\text{B}T}}}{Z}\Big(A_{21}dt + B_{21}\rho(\nu,T)dt\Big) \Rightarrow \\
& \Big(g_1\, e^{-\frac{E_1}{k_\text{B}T}}B_{12} - g_2\, e^{-\frac{E_2}{k_\text{B}T}}B_{21}\Big)\rho(\nu,T) = g_2\, e^{-\frac{E_2}{k_\text{B}T}}A_{21} \Rightarrow \\
& \rho(\nu,T) = \frac{g_2\, A_{21}\, e^{-\frac{E_2}{k_\text{B}T}}}{g_1\, B_{12}e^{-\frac{E_1}{k_\text{B}T}} - g_2\, B_{21}e^{-\frac{E_2}{k_\text{B}T}}}.
\end{aligned}$$

However, we already know that

$$\lim_{T\to\infty} \rho(\nu,T) = \infty \Rightarrow$$

$$\frac{g_2\,A_{21}}{g_1\,B_{12} - g_2\,B_{21}} = \infty \Rightarrow$$

$$\boxed{g_1\,B_{12} = g_2\,B_{21}} \tag{3.9}$$

Hence, comparing with Planck's law

$$\text{up to now} \quad \boxed{\rho(\nu,T) = \frac{\frac{A_{21}}{B_{21}}}{e^{\frac{E_2-E_1}{k_B T}} - 1}} \qquad \text{Planck's law} \quad \boxed{\rho(\nu,T) = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{\frac{h\nu}{k_B T}} - 1}}$$

Thus,

$$\boxed{\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}} \tag{3.10}$$

$$\boxed{E_2 - E_1 = h\nu} \tag{3.11}$$

3.3 Comparison between emissions.

Let us compare Spontaneous Emission with Stimulated Emission.

$$\boxed{\frac{\overset{\text{incoherent process}}{dW^{\mathrm{sp}}_{\mathrm{em}}}}{\underset{\text{coherent process}}{dW^{\mathrm{st}}_{\mathrm{em}}}} = \frac{A_{21}dt}{B_{21}\rho(\nu,T)dt} = \frac{\frac{8\pi h\nu^3}{c^3}}{\frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_B T}-1}} = e^{\frac{h\nu}{k_B T}} - 1}$$

Since Spontaneous Emission is an incoherent process, i.e., the produced photons are not coherent (they do not have a constant phase relation), and Stimulated Emission is a coherent process, i.e., the produced photons are coherent (they have the same phase), seeking COHERENCE implies that we need as much as possible (1) larger T, (2) smaller ν (or larger λ). [See Figure 3.5, where the function $f(x) = e^x - 1$ is depicted. Here, $x = h\nu/k_B T$.] Thus, in this sense, it seems easier to create a coherent beam, for example, in

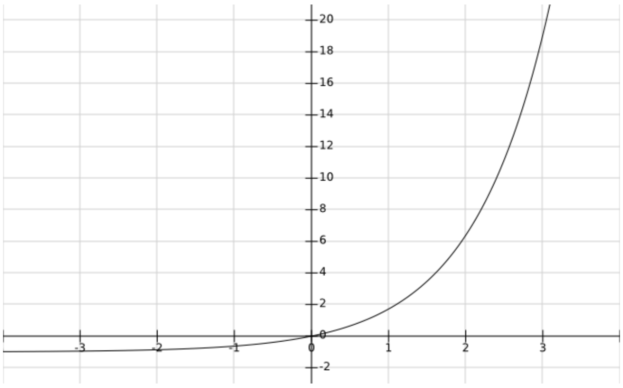

Figure 3.5: Graphical representation of $f(x) = e^x - 1$. Here, $x = h\nu/k_B T$.

microwaves than in the visible regime. Maybe this is why some of the first attempts to create a device that produces coherent EM waves were focused on microwaves and led to the creation of the MASER [Microwave Amplification by Stimulated Emission of Radiation] as a predecessor of LASER [Light Amplification by Stimulated Emission of Radiation]. However, today, the acronym LASER is used even for the invisible parts of the EM spectrum. For example, the terms infrared laser, ultraviolet laser, X-ray laser, etc, are used. Today, the term atom-laser is used, too, to describe a device which produces coherent beams of atoms that are bosons, such as ${}^{87}_{37}\mathrm{Rb}$ [6]. Because the MASER was developed prior to the LASER, devices functioning in the microwaves are still commonly referred to as MASERs instead of microwave lasers or radio lasers. The first MASER was created in 1953 by Charles Townes, James Gordon and Herbert Zeiger. Schematically,

MASER ($\lambda \sim 1$ cm)	LASER ($\lambda \sim 500$ nm)
easier to achieve coherence	harder to achieve coherence

Let us assume, for example, that we want the ratio $\dfrac{dW_{\rm em}^{\rm sp}}{dW_{\rm em}^{\rm st}} = 1$, and examine at which temperatures this is possible, (a) in the visible region, e.g., for $\lambda \sim 700$ nm, and (b) in the microwaves, e.g., for $\lambda \sim 1$ cm. We have

$$\frac{dW_{\rm em}^{\rm sp}}{dW_{\rm em}^{\rm st}} = 1 \Rightarrow e^{\frac{h\nu}{k_{\rm B}T}} - 1 = 1 \Rightarrow e^{\frac{h\nu}{k_{\rm B}T}} = 2 \Rightarrow \frac{h\nu}{k_{\rm B}T} = \ln 2 \Rightarrow$$

$$\boxed{T = \frac{h\nu}{k_{\rm B}\ln 2}} \quad \text{ή} \quad \boxed{T = \frac{hc}{\lambda k_{\rm B}\ln 2}}$$

(a) For $\lambda = 700$ nm (red light).

$$T = \frac{6.626\cdot 10^{-34}\mathrm{Js}\ \ 3\cdot 10^{8}\ \mathrm{m}\ \ \mathrm{K}}{700\cdot 10^{-9}\mathrm{m}\ \ 1.38\cdot 10^{-23}\mathrm{Js}\ \ \ln 2} \simeq \frac{6.626\cdot 3}{7\cdot 1.38}\,\frac{10^{-34+30+8}\ \mathrm{K}}{\ln 2} \simeq 29687\,\mathrm{K}.$$

Hence, in thermodynamic equilibrium, this is practically unachievable. For example, the Sun's photosphere has an effective temperature of ~ 6000 K, while temperatures ~ 30000 K can only be found in the surface of stars with 20 times the Sun's mass (Figure 3.6). This practical impossibility has lead researchers to seek for solutions outside thermodynamic equilibrium, such as the population inversion through pumping. These will be addressed in Chapter 11.

(b) For $\lambda = 1$ cm (microwaves).
Similarly, we find $T \sim 2.078$ K, i.e., although low, an experimentally achievable temperature.

3.4 Comparison between stimulated processes.

Let us now compare the two stimulated processes.

$$\frac{dW_{\rm ab}^{\rm st}}{dW_{\rm em}^{\rm st}} = \frac{B_{12}\cancel{\rho(\nu,T)dt}}{B_{21}\cancel{\rho(\nu,T)dt}} = 1,$$

for a system with equal statistical weights ($g_1 = g_2$).

$$\left.\begin{array}{l} \text{However, in thermodynamic equilibrium, } N_2 << N_1 \\ dN_{2\to 1}^{\rm st} = N_2\cdot dW_{\rm em}^{\rm st} \\ dN_{1\to 2}^{\rm st} = N_1\cdot dW_{\rm ab}^{\rm st} \end{array}\right\} \Rightarrow dN_{2\to 1}^{\rm st} << dN_{1\to 2}^{\rm st}.$$

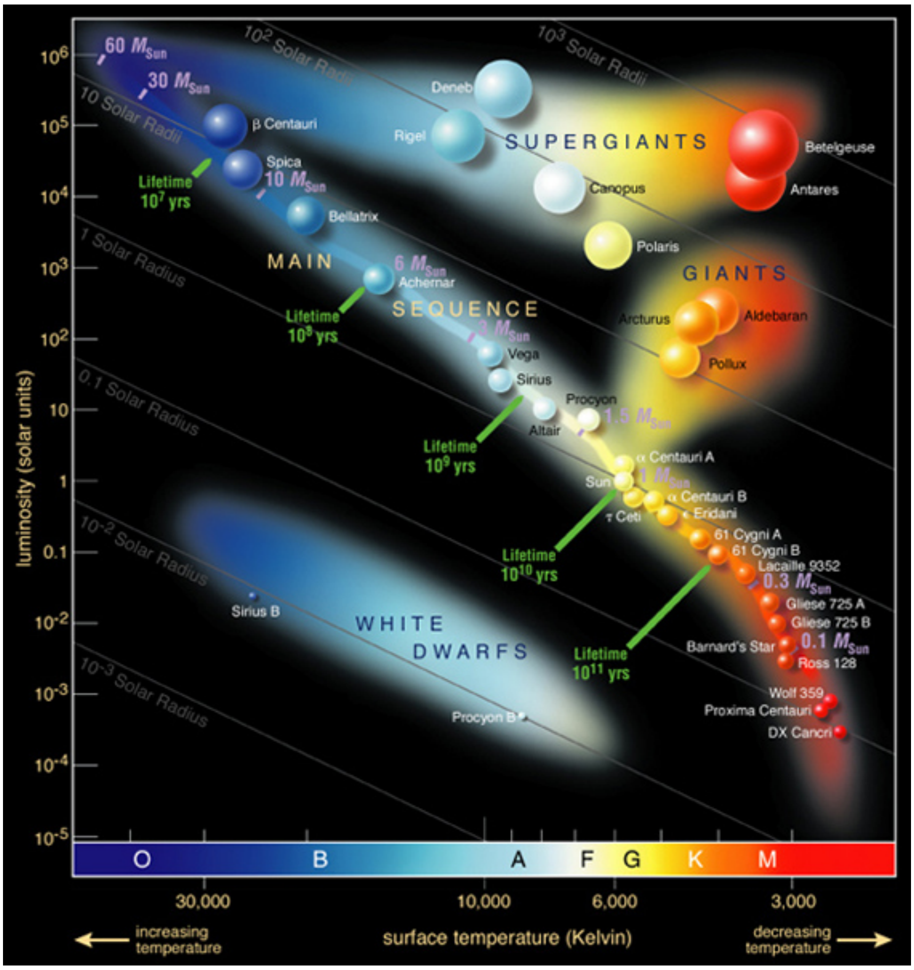

Figure 3.6: The Hertzsprung-Russell diagram, showing the relation between a stars' luminosity and surface temperature [7].

Hence, through the stimulated processes, the population of level 2 increases, therefore, the EM radiation density decreases. Then, spontaneous emission, which is accompanied by an electron dropping from level 2 to level 1, increases the incoherent EM radiation. This problem (caused by the fact that, in thermodynamic equilibrium, $N_2 << N_1$) can be solved by population inversion through pumping, which will be addressed in Chapter 11. There are many kinds of pumping. Pumping means that one somehow uploads electrons in level 2 so that $N_2 > N_1$.

Now, let as check, from a quantitative point of view, what does exactly $N_2 << N_1$ in thermodynamic equilibrium mean (see also Exercise 5 of the present Chapter in Appendix A). Let us consider an ensemble of hydrogen atoms in thermodynamic equilibrium. The eigenenergies of each atom are given by the well-known Bohr relation, $E_n \approx {}^{-\mathrm{Ry}}\!/_{n^2}$, where $\mathrm{Ry} \approx -13.6$ eV is the Rydberg energy. We will examine the population ratio of the first two levels. Given that

$$N_i = \frac{N_{\mathrm{tot}} e^{-\beta E_i}}{Z}, \tag{3.12}$$

this ratio will be

$$\frac{N_2}{N_1} = \frac{e^{-\beta E_2}}{e^{-\beta E_1}} = e^{\beta(E_1 - E_2)}. \tag{3.13}$$

At room temperature ($T = 300$ K), this ratio yields $e^{-394.5} \approx 4.7 \cdot 10^{-172}$. It is thus evident that, in thermal equilibrium, the population of the next level is overwhelmingly smaller than the population of the previous level.

3.5 Comparison between Maxwell-Boltzmann, Fermi-Dirac and Bose-Einstein statistics.

Previously, in Sec. 3.2, we derived the Planck's law via the emission and absorption processes, assuming that the populations of the electronic levels obey the Maxwell-Boltzmann statistics. It would be reasonable to wonder why this distribution was used instead of the Fermi-Dirac distribution, given that electrons are fermions. Well, this happened because in 1916-1917, when Einstein formulated his theory on the interaction processes between EM radiation and a two-level system, the Fermi-Dirac distribution was not known, it was only introduced in 1926. Additionally, as we will see below, at large temperatures or at low concentrations, the Fermi-Dirac distribution converges to the Maxwell-Boltzmann distribution. Let us compare with somehow higher detail [8] the Maxwell-Boltzmann [9, 14, 15, 16, 17, 18, 19, 20, 21, 10, 11, 12, 13], Fermi-Dirac [22, 23, 24] and Bose-Einstein [25, 26, 27] distributions, which are obeyed by classical particles, fermions and bosons, respectively.

In what follows, we denote the average number of particles at state i, with energy E_i, by $\bar{n}_i$, while, we denote the total number of particles by N. We assume that $\#i >> N$, in other words, the number of energy levels is much greater than the total number of particles. Moreover, μ is the chemical potential, while $\beta = {}^{1}\!/\!_{k_BT}$.

- The Maxwell-Boltzmann (MB) statistics describes classical particles for which we consider no quantized energy levels, such as the building blocks of the classical ideal gas. It has the form

  $$\bar{n}_i = \frac{1}{e^{\beta(E_i-\mu)}}. \tag{3.14}$$

  We notice that μ is determined by the relation

  $$\sum_i \bar{n}_i = N. \tag{3.15}$$

  Thus,

  $$\sum_i e^{-\beta E_i} e^{\beta\mu} = N \Rightarrow e^{\beta\mu} = \frac{N}{\sum_i e^{-\beta E_i}}. \tag{3.16}$$

  Hence,

  $$\bar{n}_i = \frac{Ne^{-\beta E_i}}{\sum_i e^{-\beta E_i}}. \tag{3.17}$$

- The Fermi-Dirac (FD) statistics describes quantum particles which obey the Pauli exclusion principle that a quantum state cannot be occupied by more than one particle. These particles are called fermions and their spin is a half-integer (half-natural) multiple (½, ³⁄₂, ⁵⁄₂, …) of the quantity $\hbar$. Such particles are, e.g., electrons, protons, and neutrons. For the FD statistics, it holds that

  $$\bar{n}_i = \frac{1}{e^{\beta(E_i-\mu)}+1}. \tag{3.18}$$

- The Bose-Einstein (BE) statistics describes quantum particles with the property that a quantum state can be occupied by any number of particles. These particles are called bosons and their spin is an integer (natural) multiple (0, 1, 2, …) of the quantity $\hbar$. Such particles are, e.g., photons, ${}^4_2$He atoms, and ${}^4_2$He atomic nuclei. For the BE statistics, it holds that

  $$\bar{n}_i = \frac{1}{e^{\beta(E_i-\mu)}-1}. \tag{3.19}$$

In FD and BE systems with a constant N, μ is also determined by the requirement of Eq. 3.15. Overall, we can concisely write

$$\boxed{\bar{n}_i = \frac{1}{e^{\beta(E_i-\mu)} \begin{array}{ll} +1 & \text{(FD)} \\ -1 & \text{(BE)} \\ \text{or } 0 & \text{(MB)} \end{array}}} \quad \text{and the relationship} \quad \boxed{\sum_i \bar{n}_i = N} \quad \text{determines} \quad \mu. \tag{3.20}$$

The MB, FD and BE distributions are illustrated in Figure 3.7.

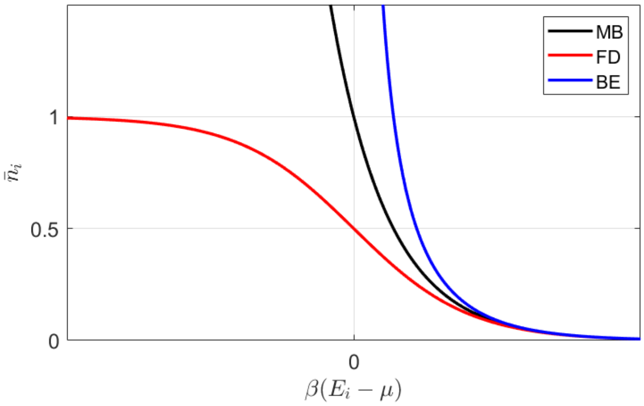

Figure 3.7: Representation of the Maxwell-Boltzmann, Fermi-Dirac and Bose-Einstein distributions.

The FD and BE distributions converge to the MB distribution in each of the following cases:

(a) The concentration of particles n is small compared to the quantum concentration

$$n_Q = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{\frac{3}{2}}, \tag{3.21}$$

i.e., when $n < n_Q$. For example, at room temperature ($T = 300$ K), and for protons, $n_Q \approx 1000$ nm^{-3}, while for electrons, $n_Q \approx 0.015$ nm^{-3}. Convergence in low concentrations occurs since

$$N \text{ very small} \quad \Rightarrow \quad \bar{n}_i << 1, \forall i \quad \Rightarrow \quad e^{\beta(E_i-\mu)} >> 1, \forall i.$$

(b) The temperatures are high enough, since then, the distribution covers energetically a broader range, with smaller occupation probabilities. Hence, $e^{\beta(E_i-\mu)} >> 1, \ \forall i$. Many levels with higher energy, even with $E_i > \mu$, are partially occupied.

In both cases, since

$$e^{\beta(E_i-\mu)} >> 1, \ \forall i, \tag{3.22}$$

$$\bar{n}_i = \frac{1}{e^{\beta(E_i-\mu)} \pm 1} \approx \frac{1}{e^{\beta(E_i-\mu)}}, \tag{3.23}$$

i.e., both the FD and the BE distribution converge to the MB distribution.

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[7] Hertzsprung-Russel Diagram identifying many well known stars in the Milky Way galaxy. ESO - Hertzsprung-Russell Diagram. This photograph was produced by European Southern Observatory (ESO). Their website states: “All ESO still and motion pictures, with the exception of the ESO Logo, are released under the Creative Commons Attribution 4.0 International License, unless the credit byline indicates otherwise.” 2021.

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CHAPTER 4

CONTINUOUS AND DISCRETE SPECTRUM

In this Chapter:

We deal with continuous and discrete energy spectrum. The discrete energy spectrum refers, crudely, to atoms, molecules, quantum dots (which are, in a way, artificial atoms and molecules), color centers etc., the discrete-continuous spectrum refers to quantum wires and wells, and finally, the continuous spectrum refers to solids. We focus on color centers and use a simplistic three-dimensional infinite quantum well model to describe them, hence, we present a complete solution of the infinite quantum well. We refer to quantum dots and use, exempli gratia, a simple three-dimensional finite square quantum well to describe them, hence, we present a complete solution of the finite square quantum well. Moreover, we describe the transition from single-level systems to one two-level or three level or four-level system, with three gradual variations of the tight-binding method. The discrete-continuous energy spectrum refers to cases with free motion in 2 (or 1) dimensions and bound states in 1 (or 2) dimensions, i.e., quantum wells (or quantum wires): From the free motion we have continuous energy spectrum with subbands, while, from the bound states we have levels. We utilize the Slater theorem, the Envelope Function Approach and the Effective Mass Approximation.

Prerequisite knowledge: Basic knowledge of Quantum Physics and Mathematics.

4.1 Continuous spectrum: solids. Discrete spectrum: atoms and molecules, color centers, artificial atoms and molecules.

Atoms and molecules have discrete energy spectrum. In other words, there exist some allowed energy levels, separated by energy gaps, where the presence of electrons is forbidden. On the other hand, solids have continuous energy spectrum, composed of allowed bands, separated by energy gaps inside which the presence of electrons is forbidden. These are depicted simplistically in Figure 4.1. In a discrete, e.g. molecular, system, the highest occupied level is called **HOMO** (highest occupied molecular orbital), while the lowest empty level is called **LUMO** (lowest unoccupied molecular orbital). In a continuous system, e.g. a

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Kallipos, Open Academic Editions. https://dx.doi.org/10.57713/kallipos-186

solid, the respective quantities are the **top of the valence band**, E_V, and the **bottom of the conduction band**, E_C. The difference $E_\mathrm{C} - E_\mathrm{V} := E_\mathrm{g}$ defines the **fundamental band gap**. Materials for which $E_\mathrm{g} = 0$ are metals. For relatively small values of E_g we have semiconductors, while for large values of E_g we have insulators.

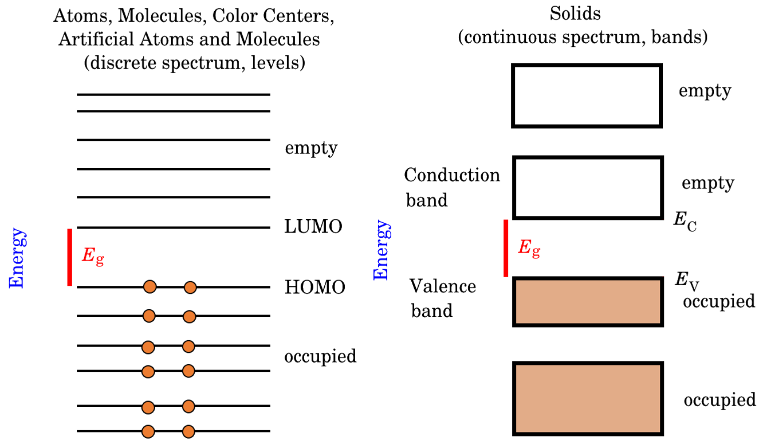

Figure 4.1: Simplistic representation of the energy structure. Left: Discrete spectrum. Right: Continuous spectrum.

We could assume that an approximation of a two-level system (2LS) could be **a simple atom** (and what is simpler than the hydrogen atom) for which we restrict ourselves to the lowest two levels. However, there are also cases where there may exist a discrete energy spectrum inside a solid. This happens when there are perturbations in the order of the solid (in periodicity, when a periodic crystal is concerned) either due to impurities, defects, etc, or by construction, for example in heterostructures. [Heterostructures are structures made up of different materials, so that there is partial order (or when periodic crystals are concerned, partial periodicity). Such changes in order or periodicity are commonly of the order of, very roughly, 1 nm - 1000 nm.]. **Color centers** are characteristic examples of the former category, while **quantum dots**, which are also commonly called nanoparticles, since these are particles of the order of some nanometers, are examples of the latter category. Therefore, we could assume, as an approximation of a 2LS, a color center or a quantum dot for which we restrict ourselves to the lowest two energy levels.

In Section 4.2 we discuss color centers, in a somewhat simplistic manner. In this discussion, it is useful to know the full solution of the infinite square well; this is done in § 4.2.1. Similarly, in Section 4.3 we discuss quantum dots. In this discussion, it is useful to know the full solution of the finite square well; this is done in § 4.3.1.

4.2 Color centers.

An *ideal crystal* extends to infinity. [Here, when we refer to crystals, we mean periodic crystals. There are also quasicrystals etc.] As known, just as solid = lattice + motif, crystal = crystal lattice + motif. The crystal lattice, i.e., a collection of mathematical points with spatial periodicity, is created by an integer linear combination of the primitive lattice vectors. The crystal is created by placing the motif (a collection of atoms, molecules, ions with well-defined orientation) at each crystal lattice point. A *monocrystal* is the simplest approximation of an ideal crystal. It differs from the latter in that periodicity is terminated on the crystal surfaces. However, even in such a crystal, there are deviations from periodicity. Each deviation from the perfect crystalline structure is a **defect**. Some common defects include impurities, vacancies, interstitial atoms, etc. In the case of impurities, the crystal within which these occur is called the **host crystal**. The properties of the material depend on both the host crystal and the defects.

Here, we will focus on a type of defect called **color center** of **F-center** (from the German word Farbe = color), which is a light-absorbing defect. These defects have taken their name from the characteristic color they give to alkaline halide crystals. Every defect in the crystal structure related to a "trapped" electron can be characterized as a color center if it absorbs approximately in the visible region of the EM spectrum. Color centers can easily be formed inside ionic crystals of alkaline halides (e.g. KCl) using ionizing radiation, such as X-rays (e.g. from a powder diffractometer or a synchrotron; a Tesla coil can be also used). A powerful source of γ-rays, such as ^{60}Co, could also be an appropriate ionizing radiation source. Ionizing radiation can release an electron from a halide anion (e.g. Cl^-). The now "free" electron can wander inside the crystal until it is finally trapped in a position of a missing halide anion, i.e., in an anion **vacancy**. In a KCl crystal, a vacancy has 6 K^+ cations as is first neighbors [Figure 4.2(left)]. In a rather simplistic approximation, the potential energy at a color center is $\approx -\frac{6e^2}{4\pi\varepsilon\varepsilon_0 r} < 0$, where $r = a/2$ is the neighboring anion-cation distance, a is the **lattice constant** or **lattice parameter**, and ε is the dielectric constant. A simple model that can describe the situation is a particle in a 3D potential well, since there is trapping in three dimensions. A 2D representation of a color center in a KCl crystal is shown in Figure 4.2(right). Apart from electron centers, hole centers, impurity centers, etc, can also occur.

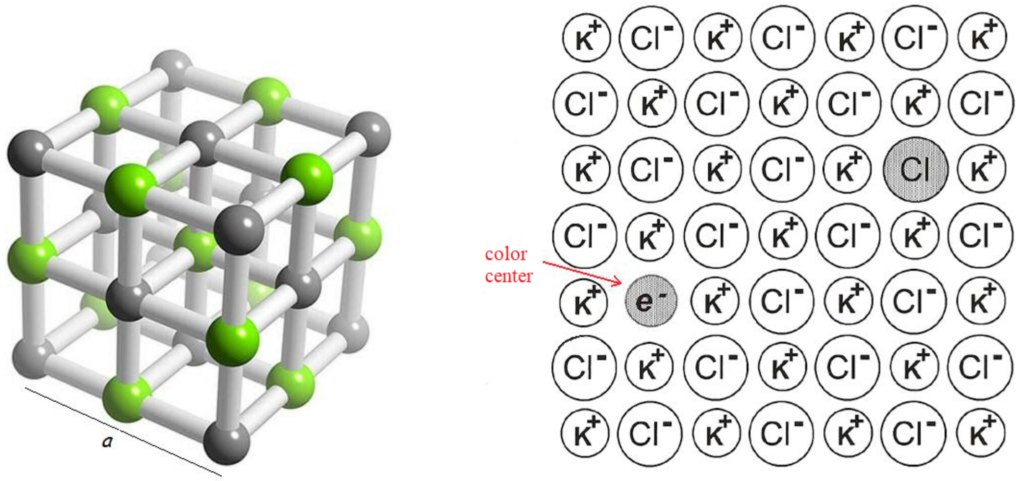

Figure 4.2: (Left) A potassium chloride crystal (KCl). Its structure can be described by a face-centered cubic (fcc) lattice with a diatomic basis (a cation-anion pair). For example, we place (i) a cation exactly on a lattice point and (ii) an anion on a point at a distance $(a/2)(\hat{x}+\hat{y}+\hat{z})$, where a is the lattice constant. For example, on the lattice point at the origin $[(0,0,0)]$ there is a cation and the corresponding anion is placed at the center of the conventional cubic cell. For example, any occurrent vacancy of chloride anion has 6 potassium cations as its first neighbors. (Right) A two-dimensional representation of a color center with a trapped electron in a Cl^- vacancy. An electron has left a Cl^- anion, e.g., due to irradiation. The distribution of the electron's wavefunction is determined by the shape of the 3D quantum well created inside the vacancy.

The color depends on the size of the vacancy, i.e., finally, on the type of the missing halogen atom, since the narrower the quantum well, the more separated become the allowed energy states inside it, while, the wider the quantum well, the more they approach each other. In a very rough approximation of the color center, let us remember the infinite quantum well. In a 1D –along the x-axis– infinite potential energy well of width L, with potential energy

$$U(x) = \begin{cases} 0, & 0 < x < L \\ \infty, & \text{elsewhere} \end{cases} \tag{4.1}$$

the discrete energy spectrum is

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}, \tag{4.2}$$

where $n = 1, 2, 3, \dots$ and m is the particle mass (in our case, the particle is an electron). Since the electron does not move in free space but inside a crystal, the mass m should be replaced by the so-called **effective mass** m^*. The effective mass is a useful approximation relative to the dispersion relation of electrons inside a crystal, e.g., close to the bottom of its conduction band. Schematically,

$$E(k) = \frac{\hbar^2 k^2}{2m} \quad \text{(free electrons)} \tag{4.3}$$

$$E(k) = \frac{\hbar^2 k^2}{2m^*} \quad \text{(electrons in a crystal)} \tag{4.4}$$

where k is the wavenumber. This approximation is based on the fact that, for small k (e.g., close to the bottom of the conduction band, where there is a minimum), the dispersion relation of electrons inside the crystal can be approximated by the parabolic form of the dispersion relation of free electrons, since

$$E(k) = E(0) + \underbrace{E'(0)}_{=0} k + E''(0)\frac{k^2}{2} + \dots . \tag{4.5}$$

Thus, choosing the origin such that $E(0) = 0$ and ignoring higher-order terms,

$$E(k) \approx \frac{E''(0)}{2} k^2 := \frac{\hbar^2}{2m^*} k^2 \Rightarrow m^* = \frac{\hbar^2}{E''(0)}. \tag{4.6}$$

Hence, returning to our square well, we have

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2m^* L^2}. \tag{4.7}$$

Thus, the distance between consecutive energy levels is

$$E_{n+1} - E_n = \frac{\hbar^2 \pi^2}{2m^* L^2}(2n+1) \quad n = 1, 2, 3, \dots \tag{4.8}$$

i.e. inversely proportional to the square of the width of the well.
Let us now remember that the wavefunction for the energy level n is

$$\psi_n(x) = \begin{cases} \sqrt{\dfrac{2}{L}} \sin\left(\dfrac{n\pi x}{L}\right), & 0 < x < L \\ 0, & \text{elsewhere} \end{cases} \tag{4.9}$$

thus, the respective probability density to find the particle positioned at x is

$$P_n(x) = \begin{cases} \dfrac{2}{L} \sin^2\left(\dfrac{n\pi x}{L}\right), & 0 < x < L \\ 0, & \text{elsewhere} \end{cases} \tag{4.10}$$

In color centers, the coloring is due to photon **absorption** by the trapped electron and the consequent **excitation** of the latter from the ground state to an excited state. The energy difference between these states is given by Eq. 4.8. Hence, using this simple 1D model, we predict that an increase (decrease) in

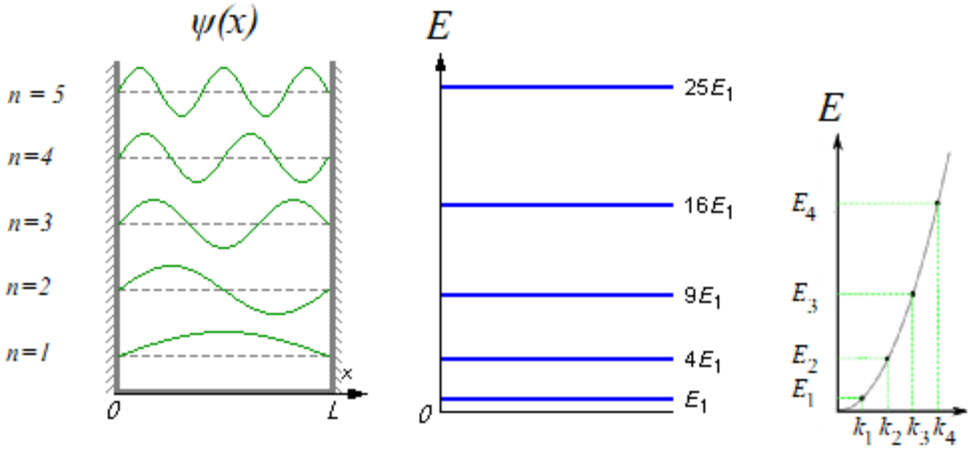

Figure 4.3: Eigenfunctions, eigenerergies, and energy dispersion ($k_n = n\pi/L, n = 1, 2, 3, \dots$) of the particle in the simplistic model of the infinite well. In the panel depicting the energy dispersion, the continuous gray line represents a particle moving freely inside the crystal.

L leads to absorption of photons with smaller (larger) energy. In other words, the spectrum is shifted towards red (blue). This is called **redshift**(**blueshift**).

The problem is somewhat more complex in 3D. However, an increase in the lattice constant a increases the space around the vacancy, where the color center is created. If we assume, reasonably, that $L \propto a$, then, as evident from the above equations, the absorption spectrum is shifted towards lower energies, that is, larger wavelengths. For example, since $a_{\mathrm{NaCl}} < a_{\mathrm{KCl}} < a_{\mathrm{KBr}}$, their absorption spectra are ordered in the manner depicted in Figure 4.4(left). The dependence of the absorption peak on the lattice constant, a, in alkaline halide crystals is presented in Figure 4.4(right).

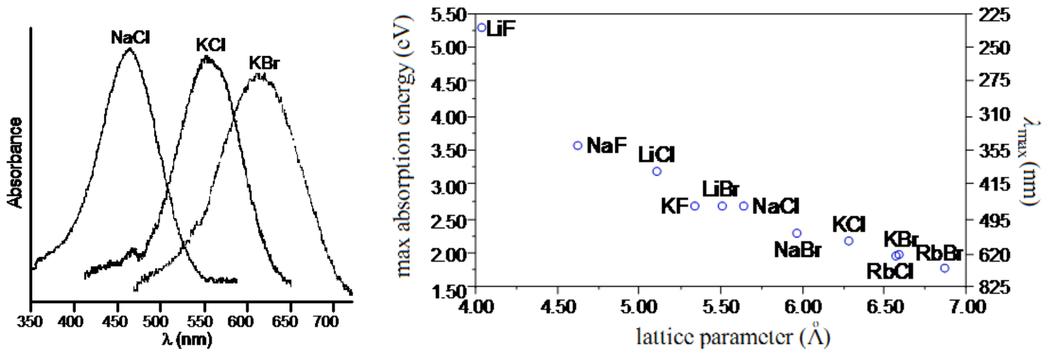

Figure 4.4: (Left) Color-center absorption spectra obtained on air, in 298 K, at the UV-visible, by NaCl, KCl, and KBr crystals radiated using a Tesla coil. [1]. The color depends on the size of the space left by the defect, i.e., by the lattice parameter or lattice constant, a. The peak of the absorption spectrum is shifted this way because $a_{\mathrm{NaCl}} < a_{\mathrm{KCl}} < a_{\mathrm{KBr}}$. (Right) Dependence of the absorption peak on a in alkaline halide crystals [1]. The increase in a creates larger vacancies when an ion is missing; thus there is a wider potential energy well. This leads to a decrease in the energy distance between the ground and first excited level, hence the energy (wavelength) of the photon that corresponds to this transition is smaller (larger).

Several theoretical models have been proposed to explain the optical properties of color centers [2]. All of them consider that, in the region of the vacancy, the potential energy is represented by a 3D well responsible for the electron binding, which in turn leads to a change in optical properties, e.g., in absorption or emission. Below, we will describe a simplistic **3D infinite well model**. We assume that the color center of an alkaline halide crystal is a 3D infinite potential energy well along the x, y, z axes, respectively,

$U_1(x)$, $U_2(y)$, $U_3(z)$, such that

$$U(\vec{r}) = U_1(x) + U_2(y) + U_3(z), \tag{4.11}$$

where all U_i are infinite wells. We further assume that the width of the well in each axis, L_i, should be or the order of the lattice constant a. Let us investigate the energy of the photons corresponding to a transition from the ground level to the 1st excited level, for example, in LiF and NaCl crystals. Due to the form of the potential energy, the variables can be fully separated and the energy spectrum of such an infinite well is

$$E_{n_1,n_2,n_3} = \frac{\hbar^2\pi^2 n_1^2}{2m_1^* L_x^2} + \frac{\hbar^2\pi^2 n_2^2}{2m_2^* L_y^2} + \frac{\hbar^2\pi^2 n_3^2}{2m_3^* L_z^2}. \tag{4.12}$$

If we also assume that $L_x = L_y = L_z = L$ and $m_1^* = m_2^* = m_3^* = m^*$, then

$$E_{n_1,n_2,n_3} = \frac{\hbar^2\pi^2}{2m^* L^2}(n_1^2 + n_2^2 + n_3^2). \tag{4.13}$$

Thus, the ground level (GL, $n_1 = n_2 = n_3 = 1$) and the 1st excited level (1stEL, one of n_i is equal to 2 and the two rest are equal to 1) have, respectively, eigenenergy

$$\left.\begin{aligned} E_{\mathrm{GL}} &= \frac{3\hbar^2\pi^2}{2m^* L^2} \\ E_{\mathrm{1stEL}} &= \frac{6\hbar^2\pi^2}{2m^* L^2} \end{aligned}\right\} \tag{4.14}$$

Hence, the photon energy which is, e.g., absorbed in order for the electron to jump from GL to 1stEL is

$$h\nu = \frac{3\hbar^2\pi^2}{2m^* L^2}. \tag{4.15}$$

If we now suppose that $L = \frac{a}{2}$,

$$h\nu = \frac{6\hbar^2\pi^2}{m^* a^2}. \tag{4.16}$$

In NaCl, where $a \approx 0.565$ nm, $m^* \approx 1.13\ m_e$, the energy is $h\nu \approx 12.498$ eV. If we used $L = a$, we would find

$$h\nu = \frac{3\hbar^2\pi^2}{2m^* a^2}, \tag{4.17}$$

thus $h\nu \approx 3.1245$ eV. The experimental value for the absorption peak of NaCl is $h\nu_{\mathrm{exp}} \approx 2.7$ eV. This means that the deviation of our simple model's prediction from the experimental value is ≈ 16%, not very far. This 2.7 eV corresponds to $\lambda \approx 460$ nm, i.e., to the blue. It is obvious that all these are very approximative. However, apart from numerical factors, it occurs that

$$h\nu \propto \frac{1}{a^2}, \tag{4.18}$$

hence $h\nu$ decreases when a increases. This is a qualitative explanation of Figure 4.4. For LiF, the effective mass can be assumed, in a fair approximation (Equation 2.72 of Reference [2]), $m^* \approx 1.5\ m_e$. Thus, from Eq. 4.17, for LiF it holds that $h\nu \approx 4.62$ eV, a value deviating from the experimental value by just 12%. On the other hand, of course, the value of the effective mass can be rather different; for example, according to Reference [3], for LiF it holds that $m^* \approx m_e$. It is of no use to try to fit our simplistic theoretical approach exactly to the experiment by playing with the value of the effective mass. We will restrict ourselves to noting that something that simple can come so close to experimental results, and can actually predict the approximate a^{-2} dependence. This model, which was employed here as an effortless guess, has actually been used in roughly the same form to study color centers [2], giving satisfactory results. Specifically, the formula

$$h\nu \approx \frac{0.97}{(a \text{ in nm})^{1.772}} \text{ eV} \tag{4.19}$$

can be used to fit all the experimental data for alkaline halides [2] (see Figure 4.4).

A careful eye might have noticed that, even though we refer to transitions between discrete levels **the spectra of Figure 4.4 are not delta functions; on the contrary, they have a rather large width**. The reason for this is that, up to now, we have taken into account only the discrete levels stemming from spatial localization. Generally, we distinguish two types of broadening: **homogeneous broadening** and **inhomogeneous broadening**. If the physical cause of broadening is the same for every absorber or emitter (here, for every 2LS) then it is called homogeneous. An example of homogeneous broadening is the one related to the lifetime of the energy level (lifetime broadening). In particular, the lifetime, τ, of an excited level, corresponding to Spontaneous Emission to a lower level, is related to the uncertainty in the energy of the excited level, ΔE, i.e., $\tau \;\; \Delta E \propto h$. [We remind the reader of the definition of lifetime, for Spontaneous Emission from level 2 to level 1, according to the relation 3.2, $dW_{\text{em}}^{\text{sp}} = A_{21}dt \Rightarrow 1 = A_{21}\tau$, for a dilute gas of identical atoms.] A small lifetime means large uncertainty in energy, hence broad emission. This type of broadening leads to a Lorentzian profile of the spectrum. Usually, in condensed matter physics, we have a large set of absorbers or emitters and the fluctuation ΔE is different for each absorber or emitter. The reason is that in a large system, such as a crystal, the environment of each absorber or emitter is rarely identical, due to the random presence of impurities, defects, etc. In other words, the quantum wells are not exactly the same (Figure 4.5, left). Inhomogeneous broadening commonly leads to a Gaussian profile. It should also be noted that broadening can be attributed to several causes, hence its shape is varying. There are additional causes that shape the energy spectrum, such as the vibrational degrees of freedom (Figure 4.5, right). Therefore, the spectra, mirroring this situation, will be broad. Moreover, all these are found inside a solid, hence the whole background of the latter will be also present. In practice (cf. upper Fig. 4.6), by absorbing a photon, an electron can be transferred, e.g., from the ground level to a higher level than the first excited level (let's say to a higher vibrational level), then relax at the first excited level by emitting one or more phonons (quanta of lattice vibrations), and finally fall back to the ground level by emitting a photon, this time, with energy smaller than the one of the initially absorbed photon by the energy of the phonon(s). The wavelength or frequency of energy difference between the position of the absorption and emission peak is called **Stokes shift** (Figure 4.6). If the emitted photon has a larger energy, this energy difference is called **anti-Stokes shift**. These differences are mostly due to lattice vibrations (phonons) [4].

Figure 4.5: Left: In a large system as e.g. in a crystal, the environment of each absorber or emitter is rarely identical, in other words, the quantum wells are not exactly the same. Right: Vibrational and spatial levels. The spectra, mirroring this situation, will be broad.

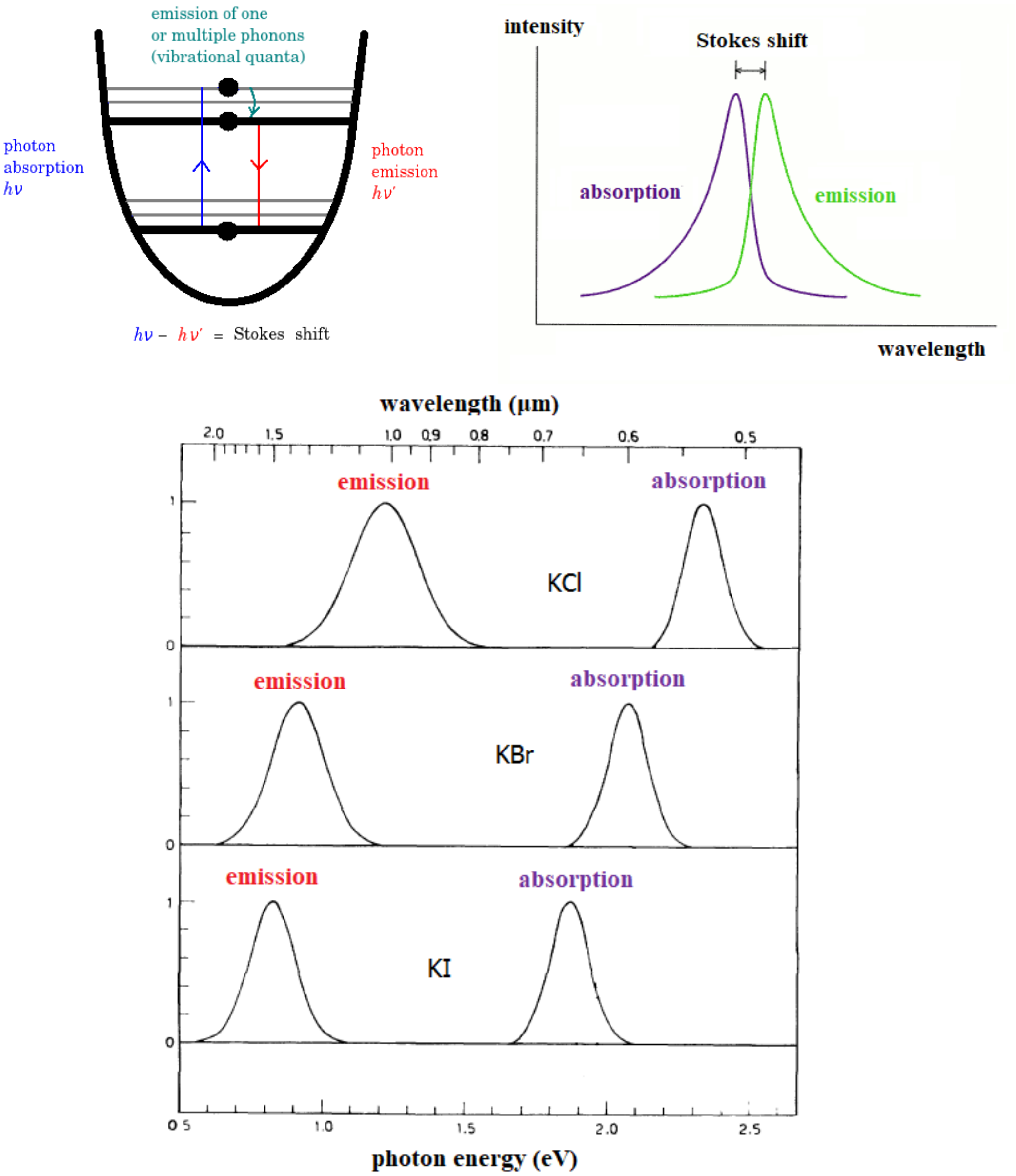

Figure 4.6: Upper: Explanation of the Stokes shift between absorption and emission. Lower: Stokes shifts of color centers in KCl, KBr and KI; figure adapted from Reference [5]. In accordance with Reference [6], the Stokes shift in KCl is ≈ 1.1 eV.

4.2.1 Full solution to the infinite square well.

We will try to give a a detailed solution of the infinite square quantum well. Let us think of the infinite square quantum well of potential energy shown in Figure 4.7. The one-dimensional –along the x-axis– infinite quantum well, of width L, is symmetrically extended from $-L/2$ to $L/2$. We distinguish the spatial regions I (left), II (medium) and III (right). Its potential energy is

$$U(x) = \begin{cases} \infty, & \qquad\qquad x < -L/2 \quad \text{region I} \\ 0, & -L/2 \leq x \leq \;\; L/2 \quad \text{region II} \\ \infty, & \qquad\qquad x > \;\; L/2 \quad \text{region III} \end{cases} \tag{4.20}$$

The particle cannot be found in regions I and III, because there the potential energy is infinite, hence,

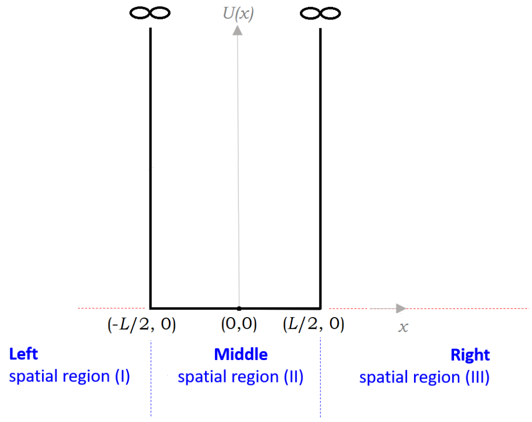

Figure 4.7: Schematic representation of an infinite square quantum well of potential energy.

its wavefunction will be $\psi(x) = 0$. In region II, the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\psi''(x) = E\psi(x). \tag{4.21}$$

Let us try solutions of the form

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad k \geq 0. \tag{4.22}$$

However, for $k = 0$, we obtain $\psi(x) = A + B$. Due to the demand that the wavefunction is continuous at the points $x = -L/2$ and $x = L/2$, since $\psi(-L/2) = 0 = \psi(L/2)$, it follows that $A + B = 0$, therefore $\psi(x) = 0$ everywhere, i.e., the particle is found nowhere. Therefore, we will assume below that $k > 0$. Hence,

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad k > 0. \tag{4.23}$$

Therefore, from Eqs. (4.21) and (4.23), it follows that

$$-\frac{\hbar^2}{2m}[Aikike^{ikx} + B(-ik)(-ik)e^{-ikx}] = E[Ae^{ikx} + Be^{-ikx}], \tag{4.24}$$

$$\frac{\hbar^2k^2}{2m}[Ae^{ikx}] + \frac{\hbar^2k^2}{2m}[Be^{-ikx}] = EAe^{ikx} + EBe^{-ikx}, \tag{4.25}$$

$$\left[\frac{\hbar^2k^2}{2m} - E\right]Ae^{ikx} + \left[\frac{\hbar^2k^2}{2m} - E\right]Be^{-ikx} = 0. \tag{4.26}$$

Consequently, since this holds $\forall\, x$, we obtain

$$E = \frac{\hbar^2k^2}{2m}. \tag{4.27}$$

Let us now use the boundary conditions.

$$\psi(-L/2) = 0 \Rightarrow Ae^{-ikL/2} + Be^{ikL/2} = 0 \Rightarrow -\frac{A}{B} = e^{ikL} \tag{4.28}$$

$$\psi(L/2) = 0 \Rightarrow Ae^{ikL/2} + Be^{-ikL/2} = 0 \Rightarrow -\frac{A}{B} = -e^{ikL}. \tag{4.29}$$

Consequently,

$$e^{ikL} = -e^{ikL} \Rightarrow e^{2ikL} = 1 = e^{i2\pi n}, \quad n \in \mathscr{Z}. \tag{4.30}$$

Hence,

$$k = \frac{\pi n}{L}, \quad n \in \mathscr{Z}. \tag{4.31}$$

However, we have noticed above that $k > 0$, hence

$$\boxed{k = \frac{\pi n}{L}, \quad n \in \mathscr{N}*} \tag{4.32}$$

Moreover, due to Eq. (4.27), it follows that

$$\boxed{E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}} \tag{4.33}$$

Now, due to Eq. (4.32) and because of

$$-\frac{A}{B} = e^{ikL}, \tag{4.34}$$

$$-\frac{A}{B} = -e^{ikL}, \tag{4.35}$$

we are led to

$$-\frac{A}{B} = e^{i\pi n} = e^{-i\pi n}. \tag{4.36}$$

Then, however,

$$\frac{A}{B} = -1, \quad \text{if } n \text{ even}, \tag{4.37}$$

$$\frac{A}{B} = +1, \quad \text{if } n \text{ odd}. \tag{4.38}$$

Well, therefore,

$$\psi_n(x) = Ae^{\frac{i\pi nx}{L}} + Ae^{-\frac{i\pi nx}{L}} = 2A\ \cos\left(\frac{\pi nx}{L}\right), \qquad \text{if } n \text{ odd}, \tag{4.39}$$

$$\psi_n(x) = Ae^{\frac{i\pi nx}{L}} - Ae^{-\frac{i\pi nx}{L}} = 2Ai\ \sin\left(\frac{\pi nx}{L}\right), \qquad \text{if } n \text{ even}. \tag{4.40}$$

Let us now proceed to normalization

$$\int_{-L/2}^{L/2} 4|A|^2 \cos^2\left(\frac{\pi nx}{L}\right) dx = 1, \qquad \text{if } n \text{ odd}, \tag{4.41}$$

$$\int_{-L/2}^{L/2} 4|A|^2 \sin^2\left(\frac{\pi nx}{L}\right) dx = 1, \qquad \text{if } n \text{ even}. \tag{4.42}$$

However, it holds that

$$\int_{-\pi/2}^{\pi/2} \cos(mz)\cos(\ell z)dz = \frac{\pi}{2}\delta_{m\ell}, \tag{4.43}$$

$$\int_{-\pi/2}^{\pi/2} \sin(mz)\sin(\ell z)dz = \frac{\pi}{2}\delta_{m\ell}. \tag{4.44}$$

Hence, with a change of variable, $z = \frac{\pi x}{L}$, the following must hold

$$|A|^2 = \frac{1}{2L}. \tag{4.45}$$

We can, therefore, choose,

$$A = \frac{1}{\sqrt{2L}}, \qquad \text{if } n \text{ odd}, \tag{4.46}$$

$$A = \frac{-i}{\sqrt{2L}}, \qquad \text{if } n \text{ even}. \tag{4.47}$$

After all this manipulation, we obtain

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{L}}\cos\left(\frac{\pi n x}{L}\right)} \qquad \text{if } n \text{ odd} \tag{4.48}$$

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi n x}{L}\right)} \qquad \text{if } n \text{ even} \tag{4.49}$$

The first four eigenfunctions of an infinite square quantum well are shown in Figure 4.8.

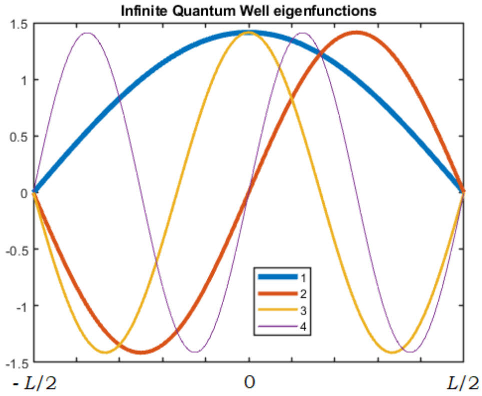

Figure 4.8: The first four eigenfunctions, $\psi_n(x)$, of an infinite square quantum well. The number of nodes is $n-1$.

Whereas, if we assumed the well in the region $x \in [0, L]$, the boundary conditions would be

$$0 = \psi(0) = A + B \Rightarrow B = -A, \tag{4.50}$$

$$0 = \psi(L) = Ae^{ikL} - Ae^{-ikL}. \tag{4.51}$$

Hence,

$$e^{2ikL} = 1 = e^{i2\pi n} \Rightarrow k = \frac{\pi n}{L}, n \in \mathcal{N}. \tag{4.52}$$

Therefore,

$$\psi_n(x) = Ae^{\frac{i\pi n x}{L}} - Ae^{-\frac{i\pi n x}{L}} = 2Ai\ \sin\left(\frac{\pi n x}{L}\right). \tag{4.53}$$

However, similarly, it holds that

$$\int_0^{\pi} \cos(mz)\cos(\ell z)dz = \frac{\pi}{2}\delta_{m\ell}, \tag{4.54}$$

$$\int_0^{\pi} \sin(mz)\sin(\ell z)dz = \frac{\pi}{2}\delta_{m\ell}. \tag{4.55}$$

Normalizing again, the following must hold

$$\int_0^{L} 4|A|^2 \sin^2\left(\frac{\pi n x}{L}\right) dx = 1. \tag{4.56}$$

According to the above, with a change of variable, $z = \frac{\pi x}{L}$, the following must hold

$$|A|^2 = \frac{1}{2L}. \tag{4.57}$$

We can, therefore, choose,

$$A = \frac{-i}{\sqrt{2L}}. \tag{4.58}$$

Hence,

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi n x}{L}\right)} \tag{4.59}$$

In other words, we obtain Eq. (4.9). We notice that moving the variable by $L/2$ and using trigonometric identities, we can, naturally, be transferred from Eq. (4.59) to Eqs. (4.48)-(4.49) and vice versa. We note that for $\mu \neq 0$, $\hat{A}\vec{v} = a\vec{v} \Leftrightarrow \hat{A}(\mu\vec{v}) = a(\mu\vec{v})$, and specifically, naturally it holds for $\mu \pm 1$.

4.3 Quantum Dots.

A typical, square, finite quantum well formed by a semiconductor heterostructure is presented in Figure 4.9 where we can see the well width L, the bottom of the conduction band E_{C}, the top of the valence band E_{V}, the conduction band offset ΔE_{C}, and the valence band offset ΔE_{V}. Depending on the materials that constitute the heterostructure, the quantum well has commonly ΔE_{C} and ΔE_{V} of the order of 0.01-10 eV and L is commonly in the range 0.1-100 nm.

Quantum confinement can occur in one dimension (1D), for which we use the expression **quantum well**, in two dimensions (2D), for which we use the expression **quantum wire**, or in three dimensions (3D), for which we use the expression **quantum dot**. See also Figure 4.10, where, in the case of quantum dots, the profile of the **density of states** (DOS) becomes discrete. Quantum dots are also referred to as **artificial atoms**, when they are single, or **artificial molecules**, when they are coupled.

In a square, finite 1D quantum well, there is at least one bound state [7]. In Figure 4.9 we have assumed that the well of the conduction band has two levels, while the well of the valence band has one. A quantum well of width L contains [7]

$$n = 1 + \mathrm{Int}\left[\sqrt{\frac{2m^* U_b L^2}{\pi^2\hbar^2}}\right] \tag{4.60}$$

bound energy states or "levels". Int(ξ) is the integer part of ξ, U_b is the discontinuity of the conduction or valence band (ΔE_{C} or ΔE_{V}, respectively) between the two materials, and m^* is the electron or hole effective mass. Hence, in a quantum dot we can choose as a two-level system one level of the conduction

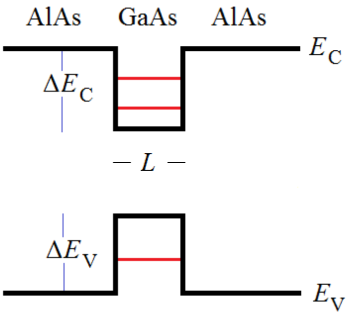

Figure 4.9: A square, finite quantum well, e.g. in an AlAs/GaAs/AlAs heterostructure. The well width L, the bottom of the conduction band E_C, the top of the valence band E_V, the conduction band offset ΔE_C, and the valence band offset ΔE_V, are shown. The wells have been drawn, schematically, as square; in fact, their shape depends on several factors, factors beyond the scope of this book.

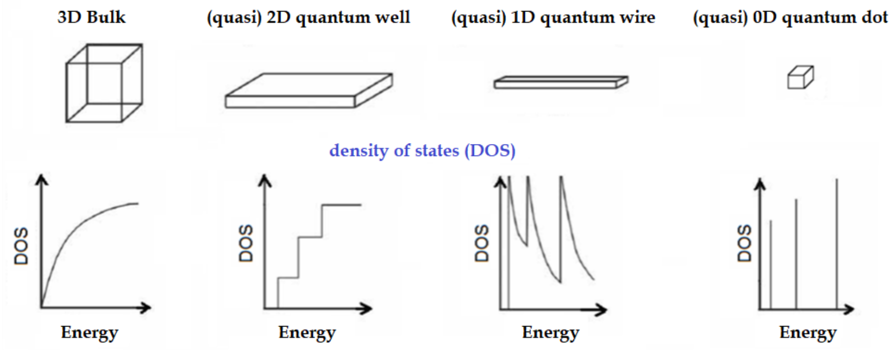

Figure 4.10: Quantum confinement in 0D, 1D, 2D and 3D (top) and the respective densities of states (bottom).

band and one level of the valence band, two levels of the conduction band, or two levels of the valence band. In the two latter cases there is, of course, the restriction of Eq. 4.60; i.e., there might be only one level in the valence or conduction band. In the following, we will prove Eq. 4.60 by fully solving the problem of the finite square well.

4.3.1 Full solution to the finite square well.

We will try to give a detailed solution of the finite square quantum well [8]. Let us assume the finite square quantum well of Figure 4.11.
⊟ Let us examine the regions with $E < 0$ [regions (m) and (l)], where bound states may exist.

- Spatial regions I and III. In these regions, the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\Psi''(x) = E\Psi(x) \iff \Psi''(x) + \frac{2mE}{\hbar^2}\Psi(x) = 0. \tag{4.61}$$

Since $E < 0$, we can assume that $\frac{2mE}{\hbar^2} \overset{\text{def}}{=} -q^2$; also, let $q > 0$. Hence, the above equation takes the form

$$\Psi''(x) - q^2\Psi(x) = 0. \tag{4.62}$$

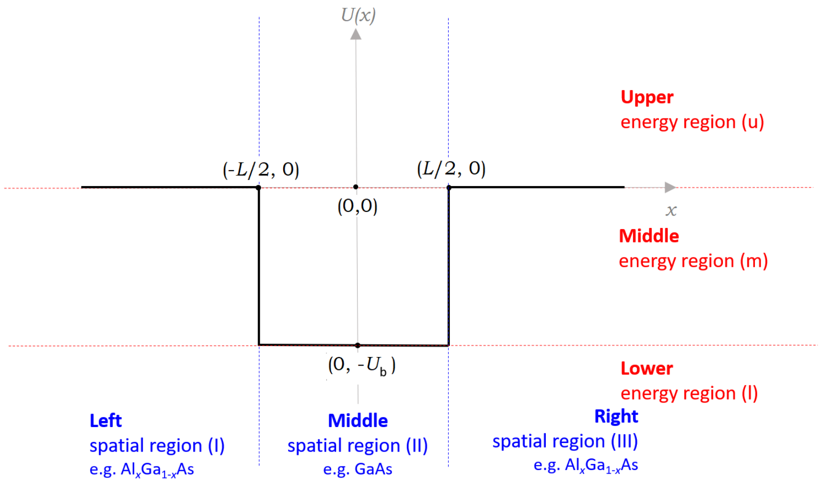

Figure 4.11: Schematic representation of a finite square quantum well of potential energy.

Let us now try solutions of the form

$$\Psi(x) = Ae^{-qx} + Be^{qx} \Rightarrow \tag{4.63}$$

$$\Psi'(x) = -Aqe^{-qx} + Bqe^{qx} \Rightarrow \tag{4.64}$$

$$\Psi''(x) = Aq^2e^{-qx} + Bq^2e^{qx}, \tag{4.65}$$

which, as it can be easily verified, satisfy the Schrödinger equation. Additionally, since $\Psi(x)$ must be square-integrable, it should hold that

$$\lim_{x\to\infty} \Psi(x) = 0 \Rightarrow \Psi_{\text{III}}(x) = Ae^{-qx} \tag{4.66}$$

$$\lim_{x\to-\infty} \Psi(x) = 0 \Rightarrow \Psi_{\text{I}}(x) = Be^{qx}. \tag{4.67}$$

Consequently,

$$\boxed{\Psi_{\text{I}}(x) = Be^{qx}} \tag{4.68}$$

$$\boxed{\Psi_{\text{III}}(x) = Ae^{-qx}} \tag{4.69}$$

- Spatial region II. There are two cases.
  - Energy region l. In this region, the time-independent Schrödinger equation is

    $$-\frac{\hbar^2}{2m}\Psi''(x) - U_b\Psi(x) = E\Psi(x) \iff \Psi''(x) + \frac{2m}{\hbar^2}(E + U_b)\Psi(x) = 0. \tag{4.70}$$

    Since $E < -U_b \iff E + U_b < 0$, we can assume that $\frac{2m(E+U_b)}{\hbar^2} \overset{\text{def}}{=} -Q^2$; also, let $Q > 0$. Hence, the above equation takes the form

    $$\Psi''(x) - Q^2\Psi(x) = 0. \tag{4.71}$$

    We try solutions of the form

    $$\Psi(x) = \Gamma e^{-Qx} + \Delta e^{Qx} \Rightarrow \tag{4.72}$$

    $$\Psi'(x) = -\Gamma Qe^{-Qx} + \Delta Qe^{Qx} \Rightarrow \tag{4.73}$$

    $$\Psi''(x) = \Gamma Q^2e^{-Qx} + \Delta Q^2e^{Qx}, \tag{4.74}$$

    which, as it can be easily verified, satisfy the Schrödinger equation. Thus,

    $$\boxed{\Psi_{\text{II}}(x) = \Gamma e^{-Qx} + \Delta e^{Qx}} \tag{4.75}$$

– Energy region m. In this region, the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\Psi''(x) - U_b\Psi(x) = E\Psi(x) \iff \Psi''(x) + \frac{2m}{\hbar^2}(E + U_b)\Psi(x) = 0. \tag{4.76}$$

Since $0 > E > -U_b \iff E + U_b > 0$, we can assume that $\frac{2m(E+U_b)}{\hbar^2} \overset{\text{def}}{=} k^2$; also, let $k > 0$. Hence, the above equation takes the form

$$\Psi''(x) + k^2\Psi(x) = 0. \tag{4.77}$$

We try solutions of the form

$$\begin{aligned}
\Psi(x) &= \Gamma e^{ikx} + \Delta e^{-ikx} \Rightarrow & (4.78)\\
\Psi'(x) &= ik\Gamma e^{kx} - ik\Delta e^{-ikx} \Rightarrow & (4.79)\\
\Psi''(x) &= -k^2\Gamma e^{ikx} - k^2\Delta e^{-ikx}, & (4.80)
\end{aligned}$$

or of the form

$$\begin{aligned}
\Psi(x) &= \Gamma\cos(kx) + \Delta\sin(kx) \Rightarrow & (4.81)\\
\Psi'(x) &= -\Gamma k\sin(kx) + \Delta k\cos(kx) \Rightarrow & (4.82)\\
\Psi''(x) &= -k^2\Gamma\cos(kx) - k^2\Delta\sin(kx), & (4.83)
\end{aligned}$$

which, as it can be easily verified, both satisfy the Schrödinger equation. Thus, we can choose either

$$\boxed{\Psi_{\text{II}}(x) = \Gamma e^{ikx} + \Delta e^{-ikx}} \tag{4.84}$$

or

$$\boxed{\Psi_{\text{II}}(x) = \Gamma\cos(kx) + \Delta\sin(kx)} \tag{4.85}$$

To sum up, in spatial region II there are two different solutions: Eq. 4.84 or Eq. 4.85 for energy region m, and Eq. 4.75 for energy region l.

◎ To find the full solution, we must, as we know, equate the wave functions and their first derivatives at the borders of the spatial regions, i.e., for $x = \pm\frac{L}{2}$.

◎ Let us try to equate the solutions of Eqs. 4.68, 4.69, and 4.75, i.e., in energy region l, for $x = \pm\frac{L}{2}$.

* For $x = -\frac{L}{2}$, we have

$$\left.\begin{aligned}
\Psi_{\text{I}}\left(-\tfrac{L}{2}\right) &= Be^{-q\frac{L}{2}}\\
\Psi_{\text{II}}\left(-\tfrac{L}{2}\right) &= \Gamma e^{Q\frac{L}{2}} + \Delta e^{-Q\frac{L}{2}}
\end{aligned}\right\} \Rightarrow Be^{-q\frac{L}{2}} = \Gamma e^{Q\frac{L}{2}} + \Delta e^{-Q\frac{L}{2}} \tag{4.86}$$

and

$$\left.\begin{aligned}
\Psi'_{\text{I}}\left(-\tfrac{L}{2}\right) &= Bqe^{-q\frac{L}{2}}\\
\Psi'_{\text{II}}\left(-\tfrac{L}{2}\right) &= -\Gamma Qe^{Q\frac{L}{2}} + \Delta Qe^{-Q\frac{L}{2}}
\end{aligned}\right\} \Rightarrow Bqe^{-q\frac{L}{2}} = -\Gamma Qe^{Q\frac{L}{2}} + \Delta Qe^{-Q\frac{L}{2}} \tag{4.87}$$

Dividing the above relations by parts, it occurs that

$$\begin{aligned} q &= \frac{-\Gamma Q e^{Q\frac{L}{2}} + \Delta Q e^{-Q\frac{L}{2}}}{\Gamma e^{Q\frac{L}{2}} + \Delta e^{-Q\frac{L}{2}}} \Rightarrow \\ \Gamma q e^{Q\frac{L}{2}} + \Delta q e^{-Q\frac{L}{2}} &= -\Gamma Q e^{Q\frac{L}{2}} + \Delta Q e^{-Q\frac{L}{2}} \Rightarrow \\ \Gamma(q+Q)e^{Q\frac{L}{2}} &= \Delta(Q-q)e^{-Q\frac{L}{2}} \Rightarrow \\ &\boxed{\frac{\Gamma}{\Delta} = \frac{Q-q}{Q+q}e^{-QL}} \end{aligned} \tag{4.88}$$

∗ For $x = \frac{L}{2}$, we have

$$\left.\begin{aligned} \Psi_{\text{III}}\left(\frac{L}{2}\right) &= Ae^{-q\frac{L}{2}} \\ \Psi_{\text{II}}\left(\frac{L}{2}\right) &= \Gamma e^{-Q\frac{L}{2}} + \Delta e^{Q\frac{L}{2}} \end{aligned}\right\} \Rightarrow Ae^{-q\frac{L}{2}} = \Gamma e^{-Q\frac{L}{2}} + \Delta e^{Q\frac{L}{2}} \tag{4.89}$$

and

$$\left.\begin{aligned} \Psi'_{\text{III}}\left(\frac{L}{2}\right) &= -Aqe^{-q\frac{L}{2}} \\ \Psi'_{\text{II}}\left(\frac{L}{2}\right) &= -\Gamma Q e^{-Q\frac{L}{2}} + \Delta Q e^{Q\frac{L}{2}} \end{aligned}\right\} \Rightarrow -Aqe^{-q\frac{L}{2}} = -\Gamma Q e^{-Q\frac{L}{2}} + \Delta Q e^{Q\frac{L}{2}} \tag{4.90}$$

Dividing the above relations by parts, it occurs that

$$\begin{aligned} -q &= \frac{-\Gamma Q e^{-Q\frac{L}{2}} + \Delta Q e^{Q\frac{L}{2}}}{\Gamma e^{-Q\frac{L}{2}} + \Delta e^{Q\frac{L}{2}}} \Rightarrow \\ -\Gamma q e^{-Q\frac{L}{2}} - \Delta q e^{Q\frac{L}{2}} &= -\Gamma Q e^{-Q\frac{L}{2}} + \Delta Q e^{Q\frac{L}{2}} \Rightarrow \\ \Gamma(Q-q)e^{-Q\frac{L}{2}} &= \Delta(Q+q)e^{Q\frac{L}{2}} \Rightarrow \\ &\boxed{\frac{\Gamma}{\Delta} = \frac{Q+q}{Q-q}e^{QL}} \end{aligned} \tag{4.91}$$

Combining Eqs. 4.88 and 4.91, we conclude that

$$\boxed{e^{-2QL} = \frac{(Q+q)^2}{(Q-q)^2}} \tag{4.92}$$

which is **absurd**, since for $Q, q > 0$, it holds that $e^{-2QL} < 1$, while $\frac{(Q+q)^2}{(Q-q)^2} > 1$. In other words, there is no solutions in the lower energy region l.

◎ Let us now try to equate the solutions of Eqs. 4.68, 4.69, and 4.84, i.e. in energy region m, for $x = \pm\frac{L}{2}$.

∗ For $x = -\frac{L}{2}$, we have

$$\left.\begin{aligned} \Psi_{\text{I}}\left(-\frac{L}{2}\right) &= Be^{-q\frac{L}{2}} \\ \Psi_{\text{II}}\left(-\frac{L}{2}\right) &= \Gamma e^{-ik\frac{L}{2}} + \Delta e^{ik\frac{L}{2}} \end{aligned}\right\} \Rightarrow Be^{-q\frac{L}{2}} = \Gamma e^{-ik\frac{L}{2}} + \Delta e^{ik\frac{L}{2}} \tag{4.93}$$

and

$$\left.\begin{aligned}\Psi'_{\mathrm{I}}\left(-\frac{L}{2}\right) &= Bqe^{-q\frac{L}{2}}\\ \Psi'_{\mathrm{II}}\left(-\frac{L}{2}\right) &= \Gamma ike^{-ik\frac{L}{2}} - \Delta ike^{ik\frac{L}{2}}\end{aligned}\right\} \Rightarrow Bqe^{-q\frac{L}{2}} = \Gamma ike^{-ik\frac{L}{2}} - \Delta ike^{ik\frac{L}{2}} \tag{4.94}$$

Dividing the above relations by parts, it occurs that

$$\begin{aligned}q = \frac{\Gamma ike^{-ik\frac{L}{2}} - \Delta ike^{ik\frac{L}{2}}}{\Gamma e^{-ik\frac{L}{2}} + \Delta e^{ik\frac{L}{2}}} &\Rightarrow\\ \Gamma qe^{-ik\frac{L}{2}} + \Delta qe^{ik\frac{L}{2}} = \Gamma ike^{-ik\frac{L}{2}} - \Delta ike^{ik\frac{L}{2}} &\Rightarrow\\ \Delta(ik+q)e^{ik\frac{L}{2}} = \Gamma(ik-q)e^{-ik\frac{L}{2}} &\Rightarrow\end{aligned}$$

$$\boxed{\frac{\Delta}{\Gamma} = \frac{ik-q}{ik+q}e^{-ikL}} \tag{4.95}$$

* For $x = \frac{L}{2}$, we have

$$\left.\begin{aligned}\Psi_{\mathrm{III}}\left(\frac{L}{2}\right) &= Ae^{-q\frac{L}{2}}\\ \Psi_{\mathrm{II}}\left(\frac{L}{2}\right) &= \Gamma e^{ik\frac{L}{2}} + \Delta e^{-ik\frac{L}{2}}\end{aligned}\right\} \Rightarrow Ae^{-q\frac{L}{2}} = \Gamma e^{ik\frac{L}{2}} + \Delta e^{-ik\frac{L}{2}} \tag{4.96}$$

and

$$\left.\begin{aligned}\Psi'_{\mathrm{III}}\left(\frac{L}{2}\right) &= -Aqe^{-q\frac{L}{2}}\\ \Psi'_{\mathrm{II}}\left(\frac{L}{2}\right) &= \Gamma ike^{ik\frac{L}{2}} - \Delta ike^{-ik\frac{L}{2}}\end{aligned}\right\} \Rightarrow -Aqe^{-q\frac{L}{2}} = \Gamma ike^{ik\frac{L}{2}} - \Delta ike^{-ik\frac{L}{2}} \tag{4.97}$$

Dividing the above relations by parts, it occurs that

$$\begin{aligned}-q = \frac{\Gamma ike^{ik\frac{L}{2}} - \Delta ike^{-ik\frac{L}{2}}}{\Gamma e^{ik\frac{L}{2}} + \Delta e^{-ik\frac{L}{2}}} &\Rightarrow\\ -\Gamma qe^{ik\frac{L}{2}} - \Delta qe^{-ik\frac{L}{2}} = \Gamma ike^{ik\frac{L}{2}} - \Delta ike^{-ik\frac{L}{2}} &\Rightarrow\\ \Delta(ik-q)e^{-ik\frac{L}{2}} = \Gamma(ik+q)e^{ik\frac{L}{2}} &\Rightarrow\end{aligned}$$

$$\boxed{\frac{\Delta}{\Gamma} = \frac{ik+q}{ik-q}e^{ikL}} \tag{4.98}$$

Combining Eqs. 4.95 and 4.98, we conclude that

$$\boxed{e^{2ikL} = \frac{(ik-q)^2}{(ik+q)^2} = \frac{-k^2+q^2-2ikq}{-k^2+q^2+2ikq}} \tag{4.99}$$

At this point, it would be useful to introduce the dimensionless quantities

$$\boxed{\xi = \frac{kL}{2}} \quad \text{and} \quad \boxed{\eta = \frac{qL}{2}} \tag{4.100}$$

as well as the quantity

$$\boxed{\alpha^2 \overset{\text{def}}{=} \xi^2 + \eta^2} \tag{4.101}$$

Therefore,

$$\alpha^2 = \frac{L^2}{4}(k^2 + q^2) = \frac{L^2}{4}\left[\frac{2m}{\hbar^2}(E + U_b) - \frac{2m}{\hbar^2}E\right] \Rightarrow$$

$$\boxed{\alpha^2 = \frac{mU_bL^2}{2\hbar^2}} \tag{4.102}$$

Hence, α is constant, independent of E, and expresses the efficiency of the quantum well. It is proportional to the mass m or the effective mass m^* of the particle, the depth of the well U_b and the squared width of the well L^2. In other words, the quantity α^2 expresses the lack of freedom of the particle, since when its mass or the depth of the well or the width of the well increase, the particle becomes more bound.

Additionally, if we define the quantity

$$\boxed{\beta^2 \overset{\text{def}}{=} -\xi^2 + \eta^2} \tag{4.103}$$

Eq. 4.99 becomes

$$e^{i4\xi} = \frac{-\xi^2 + \eta^2 - 2i\xi\eta}{-\xi^2 + \eta^2 + 2i\xi\eta} = \frac{\beta^2 - 2i\xi\eta}{\beta^2 + 2i\xi\eta} = \frac{(\beta^2 - 2i\xi\eta)^2}{(\beta^2 + 2i\xi\eta)(\beta^2 - 2i\xi\eta)} = \frac{\beta^4 - 4i\xi\eta\beta^2 - 4\xi^2\eta^2}{\beta^4 + 4\xi^2\eta^2} \Rightarrow$$

$$e^{i4\xi}(\beta^4 + 4\xi^2\eta^2) = \beta^4 - 4i\xi\eta\beta^2 - 4\xi^2\eta^2. \tag{4.104}$$

However, from the definitions of β^2 and α^2, we have

$$\beta^4 + 4\xi^2\eta^2 = \xi^4 + \eta^4 - 2\xi^2\eta^2 + 4\xi^2\eta^2 = (\xi^2 + \eta^2)^2 = \alpha^4 \tag{4.105}$$

and

$$\beta^4 - 4\xi^2\eta^2 = \beta^4 + 4\xi^2\eta^2 - 8\xi^2\eta^2 = \alpha^4 - 8\xi^2\eta^2. \tag{4.106}$$

Thus, Eq. 4.104 becomes

$$\alpha^4 e^{i4\xi} = \alpha^4 - 8\xi^2\eta^2 - 4i\xi\eta\beta^2 \Rightarrow$$

$$\alpha^4\cos(4\xi) + i\alpha^4\sin(4\xi) = (\alpha^4 - 8\xi^2\eta^2) + i(-4\xi\eta\beta^2) \Rightarrow$$

$$\left.\begin{aligned}\alpha^4\cos(4\xi) &= \alpha^4 - 8\xi^2\eta^2\\ \alpha^4\sin(4\xi) &= -4\xi\eta\beta^2\end{aligned}\right\} \Rightarrow \tan(4\xi) = \frac{-4\xi\eta\beta^2}{\alpha^4 - 8\xi^2\eta^2}, \tag{4.107}$$

which seems rather complex. However, it could be somewhat simplified if we notice that, by adding Eqs. 4.105 and 4.106, it occurs that

$$2\beta^2 = 2\alpha^4 - 8\xi^2\eta^2 \Rightarrow \xi^2\eta^2 = \frac{\alpha^4 - \beta^4}{4} \Rightarrow \xi\eta = \frac{\sqrt{\alpha^4 - \beta^4}}{2}. \tag{4.108}$$

The condition $\alpha^4 - \beta^4 > 0$ is true, since, performing the relevant substitutions, it is reduced to the condition $E + U_b > 0$, which is true, given that we are in energy region m. Substituting the above relation to Eq. 4.107, we conclude that the bound states in region m are given by the condition

$$\boxed{\tan(4\xi) = \frac{2\sqrt{\alpha^4 - \beta^4}\beta^2}{\alpha^4 - 2\beta^4}} \tag{4.109}$$

Let us examine if we can derive alternative, simpler forms than the one of Eq.4.109, by equating this time Eqs. 4.68, 4.69 and 4.85 (i.e., the alternative forms of the solutions in spatial region II) in energy region m, for $x = \pm\frac{L}{2}$. We will exploit the fact that we know that since **the potential energy** of the system is **even**, its **eigenfunctions** will be **alternately even and odd**.

- For **even** wavefunctions, $[\Psi(-x) = \Psi(x)]$:
  - In spatial regions I and III we have

$$\Psi_{\text{I}}(x) = \Psi_{\text{III}}(-x) \Rightarrow Be^{qx} = Ae^{qx} \Rightarrow B = A \tag{4.110}$$

  - In spatial region II we have

$$\Psi_{\text{II}}(x) = \Psi_{\text{II}}(-x) \Rightarrow \Gamma\cos(kx) + \Delta\sin(kx) = \Gamma\cos(kx) - \Delta\sin(kx) \Rightarrow \Delta = 0 \tag{4.111}$$

Hence, to sum up,

$$\Psi_{\text{I}}(x) = Ae^{qx} \qquad \Psi'_{\text{I}}(x) = Aqe^{qx} \tag{4.112}$$
$$\Psi_{\text{II}}(x) = \Gamma\cos(kx) \qquad \Psi'_{\text{II}}(x) = -\Gamma k\sin(kx) \tag{4.113}$$
$$\Psi_{\text{III}}(x) = Ae^{-qx} \qquad \Psi'_{\text{III}}(x) = -Aqe^{-qx}. \tag{4.114}$$

By demanding the continuity of $\Psi(x)$ and $\Psi'(x)$ at $x = -\frac{L}{2}$, it occurs that

$$\Psi_{\text{I}}(-\tfrac{L}{2}) = \Psi_{\text{II}}(-\tfrac{L}{2}) \Rightarrow Ae^{-q\frac{L}{2}} = \Gamma\cos\left(\frac{kL}{2}\right), \tag{4.115}$$

$$\Psi'_{\text{I}}(-\tfrac{L}{2}) = \Psi'_{\text{II}}(-\tfrac{L}{2}) \Rightarrow Aqe^{-q\frac{L}{2}} = \Gamma k\sin\left(\frac{kL}{2}\right) \tag{4.116}$$

Dividing the above equations by parts, we conclude that

$$\boxed{\tan\left(\frac{kL}{2}\right)} = \frac{q}{k} \tag{4.117}$$

or, alternatively,

$$\tan(\xi) = \frac{\eta}{\xi} \Rightarrow \boxed{\tan(\xi) = \frac{\sqrt{\alpha^2 - \xi^2}}{\xi}}. \tag{4.118}$$

It can be easily be shown that demanding the continuity of $\Psi(x)$ and $\Psi'(x)$ at $x = \frac{L}{2}$ leads to the exact same expression.

- For **odd** wavefunctions, $[\Psi(-x) = -\Psi(x)]$:
  - In spatial regions I and III we have

$$-\Psi_{\text{I}}(x) = \Psi_{\text{III}}(-x) \Rightarrow -Be^{qx} = Ae^{qx} \Rightarrow B = -A \tag{4.119}$$

  - Spatial region II we have

$$-\Psi_{\text{II}}(x) = \Psi_{\text{II}}(-x) \Rightarrow -\Gamma\cos(kx) - \Delta\sin(kx) = \Gamma\cos(kx) - \Delta\sin(kx) \Rightarrow \Gamma = 0 \tag{4.120}$$

Hence, to sum up,

$$\Psi_{\text{I}}(x) = -Ae^{qx} \qquad \Psi'_{\text{I}}(x) = -Aqe^{qx} \tag{4.121}$$
$$\Psi_{\text{II}}(x) = \Delta\sin(kx) \qquad \Psi'_{\text{II}}(x) = \Delta k\cos(kx) \tag{4.122}$$
$$\Psi_{\text{III}}(x) = Ae^{-qx} \qquad \Psi'_{\text{III}}(x) = -Aqe^{-qx}. \tag{4.123}$$

By demanding the continuity of $\Psi(x)$ and $\Psi'(x)$ at $x = -\frac{L}{2}$, it occurs that

$$\Psi_{\text{I}}(-\tfrac{L}{2}) = \Psi_{\text{II}}(-\tfrac{L}{2}) \Rightarrow -Ae^{-\frac{qL}{2}} = -\Delta \sin\left(\frac{kL}{2}\right), \tag{4.124}$$

$$\Psi'_{\text{I}}(-\tfrac{L}{2}) = \Psi'_{\text{II}}(-\tfrac{L}{2}) \Rightarrow -Aqe^{-\frac{qL}{2}} = \Delta k \cos\left(\frac{kL}{2}\right) \tag{4.125}$$

Dividing the above equations by parts, we conclude that

$$\boxed{\tan\left(\frac{kL}{2}\right)} = -\frac{k}{q} \tag{4.126}$$

or, alternatively,

$$\tan(\xi) = -\frac{\xi}{\eta} \Rightarrow \boxed{\tan(\xi) = -\frac{\xi}{\sqrt{\alpha^2 - \xi^2}}}. \tag{4.127}$$

It can be easily be shown that demanding the continuity of $\Psi(x)$ and $\Psi'(x)$ at $x = \frac{L}{2}$ leads to the exact same expression.

To wrap this up, using Eqs. 4.68, 4.69 and 4.85, and imposing the boundary conditions (the continuity of the wavefunction and its first derivative on the borders of the well), we conclude that in energy region m there are bound states which are given by the pair of solutions

$$\boxed{\tan(\xi) = \frac{\sqrt{\alpha^2 - \xi^2}}{\xi}} \quad \textbf{even} \quad \text{and} \quad \boxed{\tan(\xi) = -\frac{\xi}{\sqrt{\alpha^2 - \xi^2}}} \quad \textbf{odd} \tag{4.128}$$

We remind the reader that $k > 0 \iff \xi > 0$, while the function $\tan(\xi)$ is not defined for $\xi = (2\ell + 1)\frac{\pi}{2}, \forall\, \ell \in \mathbb{N}^*$. Eqs. 4.128 can be solved graphically. To this end, we define the function

$$f(\xi) := \frac{\sqrt{\alpha^2 - \xi^2}}{\xi}, \tag{4.129}$$

the field of definition of which is the interval $(0, \alpha]$, and for which $f(\alpha) = 0$, $\lim_{\xi \to 0^+} f(\xi) = +\infty$, as well as the function

$$g(\xi) := -\frac{\xi}{\sqrt{\alpha^2 - \xi^2}}, \tag{4.130}$$

the field of definition of which is the interval $[0, \alpha)$, and for which $g(0) = 0$, $\lim_{\xi \to \alpha^-} g(\xi) = -\infty$. The graphical solution to Eq. 4.128 is presented in Figure 4.12, for several values of the parameter α. From Figure 4.12 we notice that

- for $\alpha \in (0, \pi/2)$ $\quad$ $\exists$ 1 intersection of $\tan(\xi)$ and $f(\xi)$, and
  $\nexists$ any intersection of $\tan(\xi)$ and $g(\xi)$
- for $\alpha \in [\pi/2, \pi)$ $\quad$ $\exists$ 1 intersection of $\tan(\xi)$ and $f(\xi)$, and
  $\exists$ 1 intersection of $\tan(\xi)$ and $g(\xi)$
- for $\alpha \in [\pi, 3\pi/2)$ $\quad$ $\exists$ 2 intersections of $\tan(\xi)$ and $f(\xi)$, and
  $\exists$ 1 intersection of $\tan(\xi)$ and $g(\xi)$
- for $\alpha \in [3\pi/2, 2\pi)$ $\quad$ $\exists$ 2 intersections of $\tan(\xi)$ and $f(\xi)$, and
  $\exists$ 2 intersections of $\tan(\xi)$ and $g(\xi)$
- for $\alpha \in [2\pi, 5\pi/2)$ $\quad$ $\exists$ 3 intersections of $\tan(\xi)$ and $f(\xi)$, and
  $\exists$ 2 intersections of $\tan(\xi)$ and $g(\xi)$
- etc.

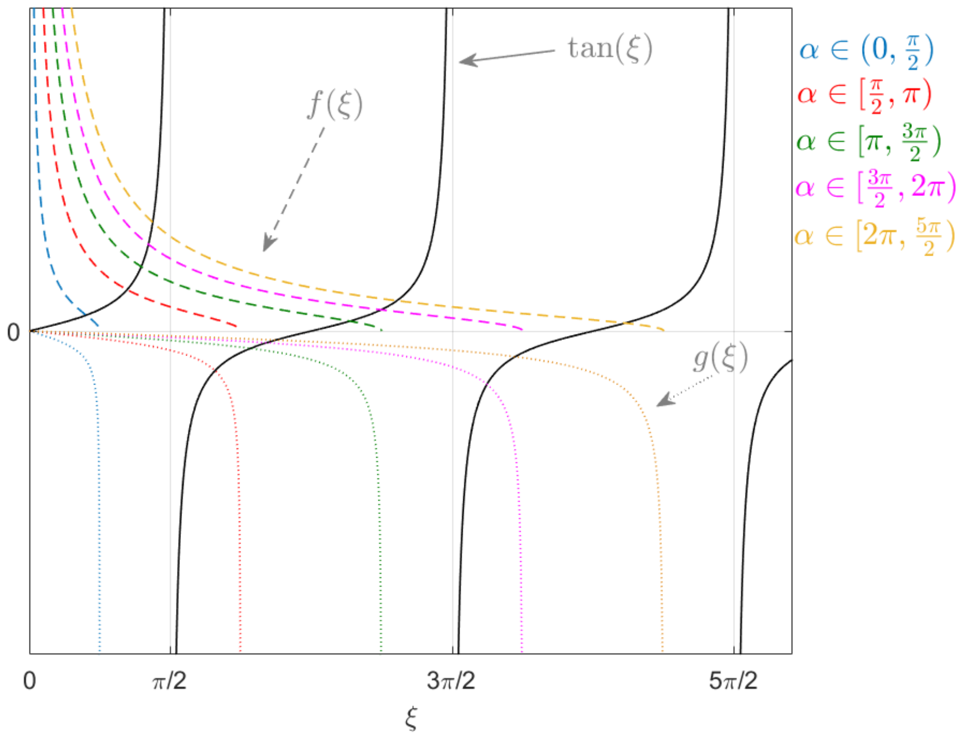

Figure 4.12: Graphical solution of the equations $\tan(\xi) = f(\xi)$ (cf. Eq. 4.129, dashed lines) and $\tan(\xi) = g(\xi)$ (cf. Eq. 4.130, dotted lines), for several values of the parameter α, which expresses the efficiency of the quantum well, within the intervals mentioned in the right side.

Thus, there is always **at least** one solution, while every time the parameter α is increased by $\frac{\pi}{2}$ one more solution is added. Hence, the number of solutions (bound states) is

$$n = 1 + \mathrm{Int}\left[\frac{\alpha}{\frac{\pi}{2}}\right] = 1 + \mathrm{Int}\left[\frac{\sqrt{\frac{mU_bL^2}{2\hbar^2}}}{\frac{\pi}{2}}\right] \Rightarrow$$

$$\boxed{n = 1 + \mathrm{Int}\left[\sqrt{\frac{2m^* U_b L^2}{\pi^2 \hbar^2}}\right]} \tag{4.131}$$

which is –the now proven– Eq. 4.60.

4.4 From isolated one-level systems to a two-level, three-level, and four-level system.

We will now narrate in detail how a 2LS is obtained from two isolated 1LS, when the latter approach each other. We follow the approach described in the textbook [9]. Relative to the Tight Binding method, the readers can also consult the textbooks [10, 11, 12]. We will define all the relevant integrals: normalization, on-site energies, potential energies of interaction of one 1LS with the other, overlap integrals, transfer or interaction integrals. We will address and solve the problem at three different approximation levels. We will also discuss the bonding and antibonding orbital of the 2LS, in terms of its eigenvalues and eigenvectors. Finally, we will also discuss, in a similar manner, how a 3LS is formed by three isolated 1LS, and how a 4LS is formed by four isolated 1LS.

4.4.1 Two-level system (2LS).

Let us report how a 2LS is formed by two 1LSs which get close to each other, within the tight-binding approximation. Let us assume that the isolated 1LSs have eigenenergies ϵ_{L} (the left one) and ϵ_{R} (the right one). This holds as long as they are isolated. However, when they are brought closer to each other and the unified system (i.e., the 2LS) is formed, the latter will have different eigenenergies; let us call them E_1 and E_2. This is narrated in a way in Figure 4.13.

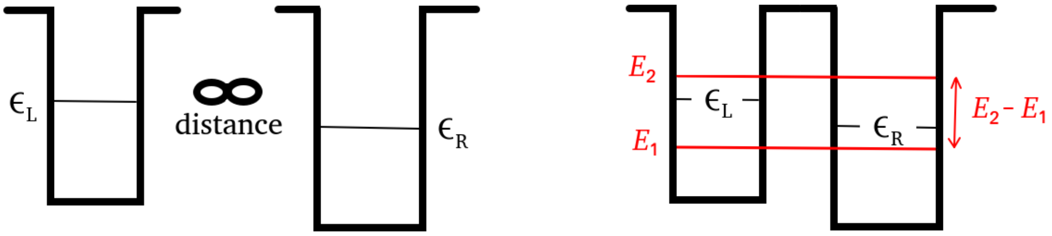

Figure 4.13: From two one-level systems (1LSs), one on the left (L) and one on the right (R), which have eigenenergies ϵ_{L} and ϵ_{R}, respectively, and are placed at infinite distance, to the unified two-level system (2LS), which has eigenenergies E_1 and E_2, different from ϵ_{L} and ϵ_{R}.

So, let the distance between the two isolated 1LSs be infinite. The Hamiltonian of the left (L) is $\hat{H}_{\mathrm{L}} = \hat{T} + \hat{U}_{\mathrm{L}}$, where $\hat{T}$ is the kinetic term and $\hat{U}_{\mathrm{L}}$ is the potential energy term. If its eigenstate is $\left|\psi_{\mathrm{L}}\right\rangle$ and its eigenenergy is $\epsilon_{\mathrm{L}} = \left\langle\psi_{\mathrm{L}}\right| \hat{H}_{\mathrm{L}} \left|\psi_{\mathrm{L}}\right\rangle$, then

$$\hat{H}_{\mathrm{L}} \left|\psi_{\mathrm{L}}\right\rangle = \epsilon_{\mathrm{L}} \left|\psi_{\mathrm{L}}\right\rangle . \tag{4.132}$$

The right (R) isolated system is at infinite distance from L, with Hamiltonian $\hat{H}_{\mathrm{R}} = \hat{T} + \hat{U}_{\mathrm{R}}$, eigenstate $\left|\psi_{\mathrm{R}}\right\rangle$, and eigenenergy $\epsilon_{\mathrm{R}} = \left\langle\psi_{\mathrm{R}}\right| \hat{H}_{\mathrm{R}} \left|\psi_{\mathrm{R}}\right\rangle$. Thus,

$$\hat{H}_{\mathrm{R}} \left|\psi_{\mathrm{R}}\right\rangle = \epsilon_{\mathrm{R}} \left|\psi_{\mathrm{R}}\right\rangle . \tag{4.133}$$

If we further suppose that the two 1LSs come closer to each other so that they become coupled, then we will have a 2LS. Let us write the eigenstates of the 2LS as a linear combination of the eigenstates of the two isolated 1LSs, i.e.,

$$\left|\psi\right\rangle = c_{\mathrm{L}} \left|\psi_{\mathrm{L}}\right\rangle + c_{\mathrm{R}} \left|\psi_{\mathrm{R}}\right\rangle . \tag{4.134}$$

The Hamiltonian of the 2LS will be

$$\hat{H} = \hat{T} + \hat{U}_{\mathrm{L}} + \hat{U}_{\mathrm{R}}. \tag{4.135}$$

Thus, if we substitute Eqs. (4.134) and (4.135) into

$$\hat{H} \left|\psi\right\rangle = E \left|\psi\right\rangle , \tag{4.136}$$

we will obtain

$$(\hat{T} + \hat{U}_{\mathrm{L}} + \hat{U}_{\mathrm{R}})(c_{\mathrm{L}} \left|\psi_{\mathrm{L}}\right\rangle + c_{\mathrm{R}} \left|\psi_{\mathrm{R}}\right\rangle) = E(c_{\mathrm{L}} \left|\psi_{\mathrm{L}}\right\rangle + c_{\mathrm{R}} \left|\psi_{\mathrm{R}}\right\rangle). \tag{4.137}$$

Multiplying Eq. (4.137) by $\left\langle\psi_{\mathrm{L}}\right|$, we obtain

$$c_{\mathrm{L}} \left\langle\psi_{\mathrm{L}}\right| \hat{T} + \hat{U}_{\mathrm{L}} + \hat{U}_{\mathrm{R}} \left|\psi_{\mathrm{L}}\right\rangle + c_{\mathrm{R}} \left\langle\psi_{\mathrm{L}}\right| \hat{T} + \hat{U}_{\mathrm{L}} + \hat{U}_{\mathrm{R}} \left|\psi_{\mathrm{R}}\right\rangle = c_{\mathrm{L}} E \langle\psi_{\mathrm{L}}|\psi_{\mathrm{L}}\rangle + c_{\mathrm{R}} E \langle\psi_{\mathrm{L}}|\psi_{\mathrm{R}}\rangle. \tag{4.138}$$

We call **on-site energy** of the L 1LS the term

$$\epsilon_{\mathrm{A}} := \left\langle\psi_{\mathrm{A}}\right| \hat{T} + \hat{U}_{\mathrm{A}} \left|\psi_{\mathrm{A}}\right\rangle , \tag{4.139}$$

while, the integral of **the potential energy** of the R 1LS at the L 1LS is

$$U_{\mathrm{LRL}} := \left\langle \psi_{\mathrm{L}} \right| \hat{U}_{\mathrm{R}} \left| \psi_{\mathrm{L}} \right\rangle . \tag{4.140}$$

We call **transfer or interaction integral** between L and R the term

$$t_{\mathrm{LR}} := \left\langle \psi_{\mathrm{L}} \right| \hat{T} + \hat{U}_{\mathrm{L}} + \hat{U}_{\mathrm{R}} \left| \psi_{\mathrm{R}} \right\rangle . \tag{4.141}$$

Finally, we cal **overlap integral** between L and R the term

$$S_{\mathrm{LR}} := \langle \psi_{\mathrm{L}} | \psi_{\mathrm{R}} \rangle . \tag{4.142}$$

Given that the eigenfunctions are normalized,

$$\langle \psi_{\mathrm{L}} | \psi_{\mathrm{L}} \rangle = \langle \psi_{\mathrm{R}} | \psi_{\mathrm{R}} \rangle = 1. \tag{4.143}$$

Hence, Eq. (4.138) can be written as

$$\boxed{c_{\mathrm{L}} \epsilon_{\mathrm{L}} + c_{\mathrm{L}} U_{\mathrm{LRL}} + c_{\mathrm{R}} t_{\mathrm{LR}} = c_{\mathrm{L}} E + c_{\mathrm{R}} E S_{\mathrm{LR}}} \tag{4.144}$$

Given that the integral U_{LRL} is very small, if we ignore it, then Eq. (4.144) reaches the simpler form

$$\boxed{c_{\mathrm{L}} \epsilon_{\mathrm{L}} + c_{\mathrm{R}} t_{\mathrm{LR}} = c_{\mathrm{L}} E + c_{\mathrm{R}} E S_{\mathrm{LR}}} \tag{4.145}$$

The assumption that U_{LRL} is negligible is the essence of the method that is called *Tight Binding*. It means that we can approximately ignore the potential energy of the other sites near to a particular site, hence,

$$\left\langle \psi_{\mathrm{L}} \right| \hat{T} + \hat{U}_{\mathrm{L}} + \hat{U}_{\mathrm{R}} \left| \psi_{\mathrm{L}} \right\rangle \approx \left\langle \psi_{\mathrm{L}} \right| \hat{T} + \hat{U}_{\mathrm{L}} \left| \psi_{\mathrm{L}} \right\rangle = \epsilon_{\mathrm{L}} \tag{4.146}$$

or written alternatively,

$$\left\langle \psi_{\mathrm{L}} \right| \hat{H} \left| \psi_{\mathrm{L}} \right\rangle \approx \left\langle \psi_{\mathrm{L}} \right| \hat{H}_{\mathrm{L}} \left| \psi_{\mathrm{L}} \right\rangle = \epsilon_{\mathrm{L}} . \tag{4.147}$$

Additionally, given that the overlap integral S_{LR} is somewhat small, if we ignore it as well, then Eq. (4.145) reaches the even simpler form

$$\boxed{c_{\mathrm{L}} \epsilon_{\mathrm{L}} + c_{\mathrm{R}} t_{\mathrm{LR}} = c_{\mathrm{L}} E} \tag{4.148}$$

Similarly, multiplying Eq. (4.137), by $\langle \psi_{\mathrm{R}} |$, we have

$$c_{\mathrm{L}} \left\langle \psi_{\mathrm{R}} \right| \hat{T} + \hat{U}_{\mathrm{L}} + \hat{U}_{\mathrm{R}} \left| \psi_{\mathrm{L}} \right\rangle + c_{\mathrm{R}} \left\langle \psi_{\mathrm{R}} \right| \hat{T} + \hat{U}_{\mathrm{L}} + \hat{U}_{\mathrm{R}} \left| \psi_{\mathrm{R}} \right\rangle = c_{\mathrm{L}} E \langle \psi_{\mathrm{R}} | \psi_{\mathrm{L}} \rangle + c_{\mathrm{R}} E \langle \psi_{\mathrm{R}} | \psi_{\mathrm{R}} \rangle . \tag{4.149}$$

Defining the integrals in the same fashion, we have

$$\epsilon_{\mathrm{R}} := \left\langle \psi_{\mathrm{R}} \right| \hat{T} + \hat{U}_{\mathrm{R}} \left| \psi_{\mathrm{R}} \right\rangle , \tag{4.150}$$

$$U_{\mathrm{RLR}} := \left\langle \psi_{\mathrm{R}} \right| \hat{U}_{\mathrm{L}} \left| \psi_{\mathrm{R}} \right\rangle , \tag{4.151}$$

$$t_{\mathrm{RL}} := \left\langle \psi_{\mathrm{R}} \right| \hat{T} + \hat{U}_{\mathrm{L}} + \hat{U}_{\mathrm{R}} \left| \psi_{\mathrm{L}} \right\rangle , \tag{4.152}$$

$$S_{\mathrm{RL}} := \langle \psi_{\mathrm{R}} | \psi_{\mathrm{L}} \rangle . \tag{4.153}$$

Hence, Eq. (4.149) is written as

$$\boxed{c_{\mathrm{L}} t_{\mathrm{RL}} + c_{\mathrm{R}} \epsilon_{\mathrm{R}} + c_{\mathrm{R}} U_{\mathrm{RLR}} = c_{\mathrm{L}} E S_{\mathrm{RL}} + c_{\mathrm{R}} E} \tag{4.154}$$

If we ignore the integral U_{RLR}, applying *Tight Binding*, then Eq. (4.154) reaches the simpler form

$$\boxed{c_{\mathrm{L}} t_{\mathrm{RL}} + c_{\mathrm{R}} \epsilon_{\mathrm{R}} = c_{\mathrm{L}} E S_{\mathrm{RL}} + c_{\mathrm{R}} E} \tag{4.155}$$

while, if we also ignore the integral S_{RL}, then Eq. (4.155) reaches the even simpler form

$$\boxed{c_{\mathrm{L}} t_{\mathrm{RL}} + c_{\mathrm{R}} \epsilon_{\mathrm{R}} = c_{\mathrm{R}} E} \tag{4.156}$$

Hence, in respect with the level of approximation chosen, we have to solve the system of Eqs. (4.144) and (4.154) or of Eqs. (4.145) and (4.155) or of Eqs. (4.148) and (4.156).

4.4.1.1 First level of approximation.

If we do not ignore any of the integrals U_{LRL}, U_{RLR} and S_{LR}, S_{RL}, then we have to solve the system of Eqs. (4.144) and (4.154). Since all integrals are real and due to hermiticity, we can define

$$t = t_{\mathrm{LR}} = t^*_{\mathrm{LR}} = t_{\mathrm{RL}} \in \mathscr{R}, \tag{4.157}$$

$$S = S_{\mathrm{LR}} = S^*_{\mathrm{LR}} = S_{\mathrm{RL}} \in \mathscr{R}. \tag{4.158}$$

Moreover, let us suppose, for simplicity that

$$U = U_{\mathrm{LRL}} = U^*_{\mathrm{LRL}} = U_{\mathrm{RLR}} \in \mathscr{R}. \tag{4.159}$$

Thus, the system of equations can be written in matrix form as

$$\begin{bmatrix} \epsilon_{\mathrm{L}} + U & t \\ t & \epsilon_{\mathrm{R}} + U \end{bmatrix} \begin{bmatrix} c_{\mathrm{L}} \\ c_{\mathrm{R}} \end{bmatrix} = \begin{bmatrix} \mathrm{E} & \mathrm{ES} \\ \mathrm{ES} & E \end{bmatrix} \begin{bmatrix} c_{\mathrm{L}} \\ c_{\mathrm{R}} \end{bmatrix} \tag{4.160}$$

or

$$\begin{bmatrix} \epsilon_{\mathrm{L}} + U - E & t - ES \\ t - ES & \epsilon_{\mathrm{R}} + U - E \end{bmatrix} \begin{bmatrix} c_{\mathrm{L}} \\ c_{\mathrm{R}} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}. \tag{4.161}$$

The matrix eigenvalues occur by the roots of its determinant

$$\begin{aligned} (\epsilon_{\mathrm{L}} + U - E)(\epsilon_{\mathrm{R}} + U - E) - (t - ES)^2 = 0 \Rightarrow \\ E^2 - (\epsilon_{\mathrm{L}} + \epsilon_{\mathrm{R}} + 2U)E + (\epsilon_{\mathrm{L}} + U)(\epsilon_{\mathrm{R}} + U) - t^2 - E^2S^2 + 2StE = 0 \Rightarrow \\ (1 - S^2)E^2 - (\epsilon_{\mathrm{L}} + \epsilon_{\mathrm{R}} + 2U - 2St)E + (\epsilon_{\mathrm{L}} + U)(\epsilon_{\mathrm{R}} + U) - t^2 = 0. \end{aligned}$$

So, we arrive at a quadratic equation with respect to the energy E. Its discriminant is

$$\Delta = (\epsilon_{\mathrm{L}} + \epsilon_{\mathrm{R}} + 2U - 2St)^2 - 4(1 - S^2)[(\epsilon_{\mathrm{L}} + U)(\epsilon_{\mathrm{R}} + U) - t^2].$$

Hence, the eigenvalues are

$$E_{1,2} = \frac{(\epsilon_{\mathrm{L}} + \epsilon_{\mathrm{R}} + 2U - 2St) \pm \sqrt{(\epsilon_{\mathrm{L}} + \epsilon_{\mathrm{R}} + 2U - 2St)^2 - 4(1 - S^2)[(\epsilon_{\mathrm{L}} + U)(\epsilon_{\mathrm{R}} + U) - t^2]}}{2(1 - S^2)}. \tag{4.162}$$

If we suppose that the two 1LS are **identical**, then $\epsilon_{\mathrm{L}} = \epsilon_{\mathrm{R}} := \epsilon$ and the calculations are simpler. Indeed, the matrix becomes

$$\begin{bmatrix} \epsilon + U - E & t - ES \\ t - ES & \epsilon + U - E \end{bmatrix} \begin{bmatrix} c_{\mathrm{L}} \\ c_{\mathrm{R}} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{4.163}$$

and, from the condition that the determinant becomes zero, we have

$$\begin{aligned} (\epsilon + U - E)^2 - (t - ES)^2 = 0 \Rightarrow \\ (\epsilon + U - E + t - ES)(\epsilon + U - E - t + ES) = 0 \Rightarrow \end{aligned}$$

$$E = \frac{\epsilon + U \pm t}{1 \pm S} \tag{4.164}$$

Let us assume that $\epsilon + U > 0$, taking the reference level appropriately. Also, usually $|t|$ is small relative to $|\epsilon + U|$. If we assume that $t < 0$ (attraction of the two 1LSs) and $S > 0$ (overlap integral of the eigenfunctions of the two ground states of the two 1LSs), then $E_1 = \frac{\epsilon+U+t}{1+S} < E_2 = \frac{\epsilon+U-t}{1-S}$. This can be shown by the nodes of the eigenvectors, as we will realize immediately below. According to the node theorem the number of nodes (roots) increases by 1 as we move from the ground state (no nodes) to higher states. Hence, the first excited state is the one which has one node. To calculate the eigenvectors, we use the relations

$$\left.\begin{aligned}(\epsilon+U-E)c_{\mathrm{L}}+(t-ES)c_{\mathrm{R}}&=0\\(t-ES)c_{\mathrm{L}}+(\epsilon+U-E)c_{\mathrm{R}}&=0\end{aligned}\right\}. \tag{4.165}$$

For the eigenvector that corresponds to the eigenvalue $E_1=\frac{\epsilon+U+t}{1+S}$, if we replace the eigenvalue E_1 in Eq. (4.165), we have

$$\left.\begin{aligned}\left(\epsilon+U-\frac{\epsilon+U+t}{1+S}\right)c_{\mathrm{L}}+\left(t-\frac{\epsilon+U+t}{1+S}S\right)c_{\mathrm{R}}&=0\\\left(t-\frac{\epsilon+U+t}{1+S}S\right)c_{\mathrm{L}}+\left(\epsilon+U-\frac{\epsilon+U+t}{1+S}\right)c_{\mathrm{R}}&=0\end{aligned}\right\}\Rightarrow$$

$$\left.\begin{aligned}\left(\frac{\epsilon+U+\epsilon S+US-\epsilon-U-t}{1+S}\right)c_{\mathrm{L}}+\left(\frac{t+tS-\epsilon S-US-tS}{1+S}\right)c_{\mathrm{R}}&=0\\\left(\frac{t+tS-\epsilon S-US-tS}{1+S}\right)c_{\mathrm{L}}+\left(\frac{\epsilon+U+\epsilon S+US-\epsilon-U-t}{1+S}\right)c_{\mathrm{R}}&=0\end{aligned}\right\}\Rightarrow$$

$$\left.\begin{aligned}(\epsilon S+US-t)c_{\mathrm{L}}+(t-\epsilon S-US)c_{\mathrm{R}}&=0\\(t-\epsilon S-US)c_{\mathrm{L}}+(\epsilon S+US-t)c_{\mathrm{R}}&=0\end{aligned}\right\}$$

Thus,

$$c_{\mathrm{L}}=c_{\mathrm{R}}=c. \tag{4.166}$$

Hence, the eigenvector that corresponds to the eigenvalue E_1 has the form

$$\vec{v}_1=\begin{bmatrix}c\\c\end{bmatrix}.$$

For it to be normalized, it must hold that

$$|\vec{v}_1|^2=1\Rightarrow 2|c|^2=1\Rightarrow |c|=1/\sqrt{2}.$$

Thus, a convenient choice would be

$$\vec{v}_1=\frac{1}{\sqrt{2}}\begin{bmatrix}1\\1\end{bmatrix}. \tag{4.167}$$

For the eigenvector that corresponds to the eigenvalue $E_2=\frac{\epsilon+U-t}{1-S}$, if we replace the eigenvalue E_2 in Eq. (4.165), we have

$$\left.\begin{aligned}\left(\epsilon+U-\frac{\epsilon+U-t}{1-S}\right)c_{\mathrm{L}}+\left(t-\frac{\epsilon+U-t}{1-S}S\right)c_{\mathrm{R}}&=0\\\left(t-\frac{\epsilon+U-t}{1-S}S\right)c_{\mathrm{L}}+\left(\epsilon+U-\frac{\epsilon+U-t}{1-S}\right)c_{\mathrm{R}}&=0\end{aligned}\right\}\Rightarrow$$

$$\left.\begin{aligned}\left(\frac{\epsilon+U-\epsilon S-US-\epsilon-U+t}{1-S}\right)c_{\mathrm{L}}+\left(\frac{t-tS-\epsilon S-US+tS}{1-S}\right)c_{\mathrm{R}}&=0\\\left(\frac{t-tS-\epsilon S-US+tS}{1-S}\right)c_{\mathrm{L}}+\left(\frac{\epsilon+U-\epsilon S-US-\epsilon-U+t}{1-S}\right)c_{\mathrm{R}}&=0\end{aligned}\right\}\Rightarrow$$

$$\left.\begin{aligned}(t-\epsilon S-US)c_{\mathrm{L}}+(t-\epsilon S-US)c_{\mathrm{R}}&=0\\(t-\epsilon S-US)c_{\mathrm{L}}+(t-\epsilon S-US)c_{\mathrm{R}}&=0\end{aligned}\right\}$$

Thus,

$$c_L = -c_R = c. \tag{4.168}$$

Hence, the eigenvector that corresponds to the eigenvalue E_2 has the form

$$\vec{v}_2 = \begin{bmatrix} c \\ -c \end{bmatrix}.$$

For it to be normalized, it must hold that

$$|\vec{v}_2|^2 = 1 \Rightarrow 2|c|^2 = 1 \Rightarrow |c| = 1/\sqrt{2}.$$

Thus, a convenient choice would be

$$\vec{v}_2 = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}. \tag{4.169}$$

As we can see, the eigenvector $\vec{v}_1$ of the level E_1 has no nodes, while the eigenvector $\vec{v}_2$ of the level E_2 has one node. Hence, the level $E_1 = \frac{\epsilon+U+t}{1+S}$ with eigenvector $\vec{v}_1$ is the ground level, while the level $E_2 = \frac{\epsilon+U-t}{1-S}$ with eigenvector $\vec{v}_2$ is the first excited level. For the condition $E_1 = \frac{\epsilon+U+t}{1+S} < E_2 = \frac{\epsilon+U-t}{1-S}$ to hold, it must also hold that $S > 0$ and $t < 0$ and the numerators have to be positive. The wavefunctions of the ground and first excited state of the unified quantum well (i.e., of the 2LS) are shown in Figure 4.14.

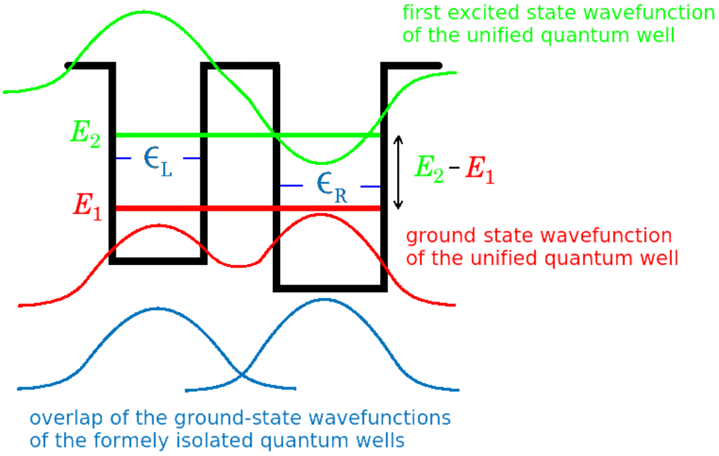

Figure 4.14: The wavefunctions of the ground and first excited state of the unified quantum well (i.e., of the 2LS), which are produced by the normalized addition (as obtained by the eigenvector $\vec{v}_1$) and by the normalized subtraction (as obtained by the eigenvector $\vec{v}_2$) of the ground state wavefunctions of the previously isolated quantum wells (i.e., of the two 1LSs).

4.4.1.2 Second level of approximation.

If we ignore the integrals $U_{LRL} = U_{RLR} = U$, but we do not ignore the integrals $S_{LR} = S_{RL} = S$, then the system of Equations to solve is the one of Eqs. (4.145) and (4.155), which can be written in matrix form as

$$\begin{bmatrix} \epsilon_L & t \\ t & \epsilon_R \end{bmatrix} \begin{bmatrix} c_L \\ c_R \end{bmatrix} = \begin{bmatrix} E & ES \\ ES & E \end{bmatrix} \begin{bmatrix} c_L \\ c_R \end{bmatrix} \tag{4.170}$$

or

$$\begin{bmatrix} \epsilon_L - E & t - ES \\ t - ES & \epsilon_R - E \end{bmatrix} \begin{bmatrix} c_L \\ c_R \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{4.171}$$

The matrix eigenvalues occur by the roots of its determinant, i.e.,

$$\begin{aligned}(\epsilon_\mathrm{L}-E)(\epsilon_\mathrm{R}-E)-(t-ES)^2&=0\Rightarrow\\ E^2-(\epsilon_\mathrm{L}+\epsilon_\mathrm{R})E+\epsilon_\mathrm{L}\epsilon_\mathrm{R}-t^2-E^2S^2+2StE&=0\Rightarrow\\ (1-S^2)E^2-(\epsilon_\mathrm{L}+\epsilon_\mathrm{R}-2St)E+\epsilon_\mathrm{L}\epsilon_\mathrm{R}-t^2&=0.\end{aligned}$$

So, we arrive at a quadratic equation with respect to the energy E. Its discriminant is

$$\Delta=(\epsilon_\mathrm{L}+\epsilon_\mathrm{R}-2St)^2-4(1-S^2)(\epsilon_\mathrm{L}\epsilon_\mathrm{R}-t^2) \tag{4.172}$$

Hence, the eigenvalues are

$$E_{1,2}=\frac{(\epsilon_\mathrm{L}+\epsilon_\mathrm{R}-2St)\pm\sqrt{(\epsilon_\mathrm{L}+\epsilon_\mathrm{R}-2St)^2-4(1-S^2)(\epsilon_\mathrm{L}\epsilon_\mathrm{R}-t^2)}}{2(1-S^2)}. \tag{4.173}$$

If we suppose that the two 1LSs are **identical**, then $\epsilon_\mathrm{L}=\epsilon_\mathrm{R}:=\epsilon$ and the calculations are simpler. Indeed, the system of equations in matrix form becomes

$$\begin{bmatrix}\epsilon-E & t-ES\\ t-ES & \epsilon-E\end{bmatrix}\begin{bmatrix}c_\mathrm{L}\\ c_\mathrm{R}\end{bmatrix}=\begin{bmatrix}0\\0\end{bmatrix} \tag{4.174}$$

and, from the condition that the determinant should be zero, we have

$$\begin{aligned}(\epsilon-E)^2-(t-ES)^2&=0\Rightarrow\\ (\epsilon-E+t-ES)(\epsilon-E-t+ES)&=0\Rightarrow\end{aligned}$$

$$E=\frac{\epsilon\pm t}{1\pm S}. \tag{4.175}$$

Let us assume $\epsilon>0$, taking taking the reference level appropriately. Also, usually $|t|$ is small relative to $|\epsilon|$. If we assume that $t<0$ (as attraction of the two 1LSs) and $S>0$ (as overlap integral of the eigenfunctions of the two 1LSs ground states), then $E_1=\frac{\epsilon+t}{1+S}<E_2=\frac{\epsilon-t}{1-S}$. This can be shown by the nodes of the eigenvectors, as we will realize immediately below. According to the node theorem the number of nodes (roots) increases by 1 as we move from the ground state (no nodes) to higher states. Hence, the first excited state is the one which has one node. To calculate the eigenvectors, we use the relations

$$\left.\begin{aligned}(\epsilon-E)c_\mathrm{L}+(t-ES)c_\mathrm{R}&=0\\ (t-ES)c_\mathrm{L}+(\epsilon-E)c_\mathrm{R}&=0\end{aligned}\right\} \tag{4.176}$$

For the eigenvector that corresponds to the eigenvalue $E_1=\frac{\epsilon+t}{1+S}$, if we replace the eigenvalue E_1 in Eq. (4.176), we have

$$\left.\begin{aligned}\left(\epsilon-\frac{\epsilon+t}{1+S}\right)c_\mathrm{L}+\left(t-\frac{\epsilon+t}{1+S}S\right)c_\mathrm{R}&=0\\ \left(t-\frac{\epsilon+t}{1+S}S\right)c_\mathrm{L}+\left(\epsilon-\frac{\epsilon+t}{1+S}\right)c_\mathrm{R}&=0\end{aligned}\right\}\Rightarrow$$

$$\left.\begin{aligned}\left(\frac{\epsilon+\epsilon S-\epsilon-t}{1+S}\right)c_\mathrm{L}+\left(\frac{t+tS-\epsilon S-tS}{1+S}\right)c_\mathrm{R}&=0\\ \left(\frac{t+tS-\epsilon S-tS}{1+S}\right)c_\mathrm{L}+\left(\frac{\epsilon+\epsilon S-\epsilon-t}{1+S}\right)c_\mathrm{R}&=0\end{aligned}\right\}\Rightarrow$$

$$\left.\begin{aligned}(\epsilon S-t)c_\mathrm{L}+(t-\epsilon S)c_\mathrm{R}&=0\\ (t-\epsilon S)c_\mathrm{L}+(\epsilon S-t)c_\mathrm{R}&=0\end{aligned}\right\}$$

Thus,

$$c_{\mathrm{L}} = c_{\mathrm{R}} = c. \tag{4.177}$$

Hence, the eigenvector that corresponds to the eigenvalue E_1 has the form

$$\vec{v}_1 = \begin{bmatrix} c \\ c \end{bmatrix}.$$

For it to be normalized, it must hold that

$$|\vec{v}_1|^2 = 1 \Rightarrow 2|c|^2 = 1 \Rightarrow |c| = 1/\sqrt{2}.$$

Thus, a convenient choice is

$$\vec{v}_1 = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}. \tag{4.178}$$

For the eigenvector that corresponds to the eigenvalue $E_2 = \frac{\epsilon - t}{1-S}$, if we replace the eigenvalue E_2 in Eq. (4.176), we have

$$\left.\begin{aligned} \left(\epsilon - \frac{\epsilon - t}{1-S}\right) c_{\mathrm{L}} + \left(t - \frac{\epsilon - t}{1-S} S\right) c_{\mathrm{R}} = 0 \\ \left(t - \frac{\epsilon - t}{1-S} S\right) c_{\mathrm{L}} + \left(\epsilon - \frac{\epsilon - t}{1-S}\right) c_{\mathrm{R}} = 0 \end{aligned}\right\} \Rightarrow$$

$$\left.\begin{aligned} \left(\frac{\epsilon - \epsilon S - \epsilon + t}{1-S}\right) c_{\mathrm{L}} + \left(\frac{t - tS - \epsilon S + tS}{1-S}\right) c_{\mathrm{R}} = 0 \\ \left(\frac{t - tS - \epsilon S + tS}{1-S}\right) c_{\mathrm{L}} + \left(\frac{\epsilon - \epsilon S - \epsilon + t}{1-S}\right) c_{\mathrm{R}} = 0 \end{aligned}\right\} \Rightarrow$$

$$\left.\begin{aligned} (t - \epsilon S) c_{\mathrm{L}} + (t - \epsilon S) c_{\mathrm{R}} = 0 \\ (t - \epsilon S) c_{\mathrm{L}} + (t - \epsilon S) c_{\mathrm{R}} = 0 \end{aligned}\right\}$$

Thus,

$$c_{\mathrm{L}} = -c_{\mathrm{R}} = c. \tag{4.179}$$

Hence, the eigenvector that corresponds to the eigenvalue E_2 has the form

$$\vec{v}_2 = \begin{bmatrix} c \\ -c \end{bmatrix}.$$

For it to be normalized, it must hold that

$$|\vec{v}_2|^2 = 1 \Rightarrow 2|c|^2 = 1 \Rightarrow |c| = 1/\sqrt{2}.$$

Thus, a convenient choice is

$$\vec{v}_2 = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}. \tag{4.180}$$

We observe that the eigenvector $\vec{v}_1$ of the level with eigenenergy E_1 has no nodes, while the eigenvector $\vec{v}_2$ of the level with eigenenergy E_2 has one node. Hence, the level with eigenenergy $E_1 = \frac{\epsilon + t}{1+S}$ and eigenvector $\vec{v}_1$ is the ground level, while the level with eigenenergy $E_2 = \frac{\epsilon - t}{1-S}$ and eigenvector $\vec{v}_2$ is the first excited level. For the condition $E_1 = \frac{\epsilon + t}{1+S} < E_2 = \frac{\epsilon - t}{1-S}$ to hold, the conditions $S > 0$ and $t < 0$ must be obeyed and the numerators have to be positive.

4.4.1.3 Third level of approximation.

If we ignore the integrals $U_{\mathrm{LRL}} = U_{\mathrm{RLR}} = U$ as well as the integrals $S_{\mathrm{LR}} = S_{\mathrm{RL}} = S$, then the system of equations to solve is the one of Eqs. (4.148) and (4.156), which can be written in matrix form as

$$\begin{bmatrix} \epsilon_{\mathrm{L}} & t \\ t & \epsilon_{\mathrm{R}} \end{bmatrix} \begin{bmatrix} c_{\mathrm{L}} \\ c_{\mathrm{R}} \end{bmatrix} = E \begin{bmatrix} c_{\mathrm{L}} \\ c_{\mathrm{R}} \end{bmatrix} \tag{4.181}$$

or

$$\begin{bmatrix} \epsilon_{\mathrm{L}} - E & t \\ t & \epsilon_{\mathrm{R}} - E \end{bmatrix} \begin{bmatrix} c_{\mathrm{L}} \\ c_{\mathrm{R}} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{4.182}$$

The matrix eigenvalues occur by the roots of its determinant, i.e.,

$$(\epsilon_{\mathrm{L}} - E)(\epsilon_{\mathrm{R}} - E) - t^2 = 0 \Rightarrow$$
$$E^2 - (\epsilon_{\mathrm{L}} + \epsilon_{\mathrm{R}})E + \epsilon_{\mathrm{L}}\epsilon_{\mathrm{R}} - t^2 = 0$$

Hence, we arrive at a quadratic equation with respect to the energy E. Its discriminant is

$$\Delta = (\epsilon_{\mathrm{L}} + \epsilon_{\mathrm{R}})^2 - 4(\epsilon_{\mathrm{L}}\epsilon_{\mathrm{R}} - t^2) = (\epsilon_{\mathrm{L}} - \epsilon_{\mathrm{R}})^2 + 4t^2 \tag{4.183}$$

Hence, the eigenvalues are

$$E_{1,2} = \frac{\epsilon_{\mathrm{L}} + \epsilon_{\mathrm{R}} \pm \sqrt{(\epsilon_{\mathrm{L}} - \epsilon_{\mathrm{R}})^2 + 4t^2}}{2} = \frac{\epsilon_{\mathrm{L}} + \epsilon_{\mathrm{R}}}{2} \pm \sqrt{\left(\frac{\epsilon_{\mathrm{L}} - \epsilon_{\mathrm{R}}}{2}\right)^2 + t^2}. \tag{4.184}$$

If we define the half-sum and half-difference of the on-site energies as

$$\Sigma = \frac{\epsilon_{\mathrm{L}} + \epsilon_{\mathrm{R}}}{2}, \quad \Delta = \frac{\epsilon_{\mathrm{L}} - \epsilon_{\mathrm{R}}}{2}, \tag{4.185}$$

then the eigenvalues take the form

$$E_{1,2} = \Sigma \pm \sqrt{\Delta^2 + t^2} \tag{4.186}$$

we observe that the two eigenvalues are separated by $\sqrt{\Delta^2 + t^2}$ from the half-sum, Σ, of the on-site energies. The gap between the two levels is $|E_2 - E_1| = 2\sqrt{\Delta^2 + t^2}$. If each of the two 1LSs with on-site energies ϵ_{L} and ϵ_{R} were fully occupied (with two electrons), then, when the 1LSs approach each other, their four electrons will be placed so that they will first occupy the lower level with eigenenergy $E_1 = \Sigma - \sqrt{\Delta^2 + t^2}$, and then the upper level with eigenenergy $E_2 = \Sigma + \sqrt{\Delta^2 + t^2}$ (cf. upper panel of Figure 4.15). If each of the two 1LSs was half-occupied (with one electron), then, when the 1LSs approach each other, their two electrons will be placed so that they will occupy the lower level, $E_1 = \Sigma - \sqrt{\Delta^2 + t^2}$, while the upper one will remain empty (cf. medium panel of Figure 4.15). Finally, if the 1LSs were both empty, the situation would be like the lower panel of Figure 4.15.

If we suppose that the two 1LSs are **identical**, then $\epsilon_{\mathrm{L}} = \epsilon_{\mathrm{R}} := \epsilon$. Therefore, $\Sigma = \epsilon$ and $\Delta = 0$. Calculations are simpler. The eigenvalues take the simple form

$$E_{1,2} = \epsilon \mp |t|. \tag{4.187}$$

Then, the energy width of the system will be

$$E_2 - E_1 = 2\,|t|. \tag{4.188}$$

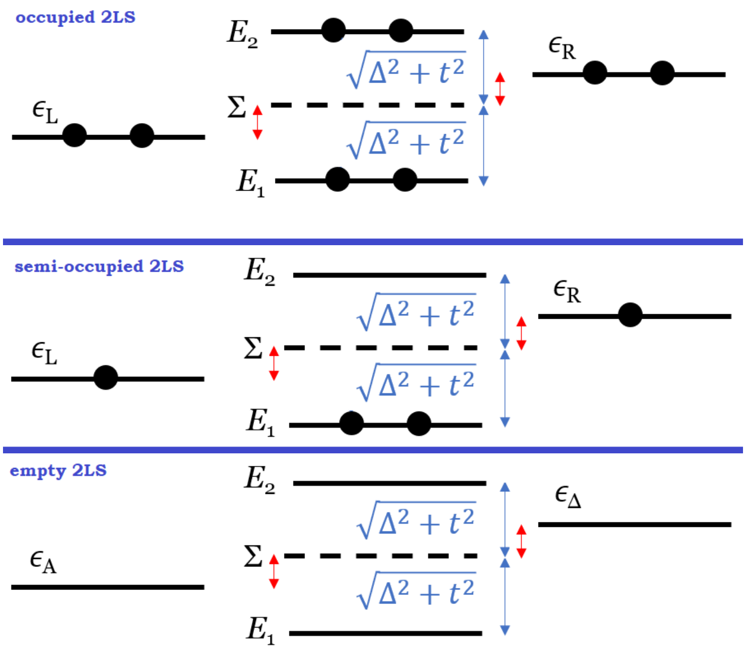

Figure 4.15: Occupied, semi-occupied and empty two-level system.

To calculate the eigenvectors, we use the relations

$$(\epsilon - E)c_L + tc_R = 0 \tag{4.189}$$

$$tc_L + (\epsilon - E)c_R = 0 \tag{4.190}$$

For the eigenvector that corresponds to the eigenvalue $E_1 = \epsilon - |t|$, that is for the lower level, if we replace the eigenvalue E_1 in Eq. (4.189), we obtain

$$\left.\begin{aligned} |t|c_L + tc_R &= 0 \\ tc_L + |t|c_R &= 0 \end{aligned}\right\} \Rightarrow c_R = -\frac{|t|}{t}c_L$$

Hence, the eigenvector that corresponds to the eigenvalue E_1 has the form

$$\vec{v}_1 = c_L \begin{bmatrix} 1 \\ -\frac{|t|}{t} \end{bmatrix}.$$

For it to be normalized, it must hold that

$$|c_L|^2 + |c_R|^2 = 1 \Rightarrow |c_L|^2 = 1/2 \Rightarrow |c_L| = 1/\sqrt{2}.$$

Thus, a convenient choice would be

$$\vec{v}_1 = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -\frac{|t|}{t} \end{bmatrix} \Rightarrow \vec{v}_1 = \begin{bmatrix} 1 \\ \pm 1 \end{bmatrix} \text{for } t \lessgtr 0. \tag{4.191}$$

In brief, the eigenvalue $E_1 = \epsilon - |t|$ corresponds to the ground level of the system and since $t < 0$ there are no nodes. This is reasonable, since the transfer integral t expresses the attraction between the two 1LSs that form the 2LS.

For the eigenvector that corresponds to the eigenvalue $E_2 = \epsilon + |t|$, that is for the upper level, if we replace the eigenvalue E_2 in Eq. (4.189), we obtain

$$\left.\begin{aligned} -|t|c_L + tc_R &= 0 \\ tc_L - |t|c_R &= 0 \end{aligned}\right\} \Rightarrow c_R = \frac{|t|}{t}c_L$$

Hence, the eigenvector that corresponds to the eigenvalue E_2 has the form

$$\vec{v}_2 = c_{\mathrm{L}} \begin{bmatrix} 1 \\ \frac{|t|}{t} \end{bmatrix}.$$

For it to be normalized, it must hold that

$$|c_{\mathrm{L}}|^2 + |c_{\mathrm{R}}|^2 = 1 \Rightarrow |c_{\mathrm{L}}|^2 = 1/2 \Rightarrow |c_{\mathrm{L}}| = 1/\sqrt{2}.$$

Therefore, a convenient choice would be

$$\vec{v}_2 = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ \frac{|t|}{t} \end{bmatrix} \Rightarrow \vec{v}_1 = \begin{bmatrix} 1 \\ \mp 1 \end{bmatrix} \text{for } t \lessgtr 0. \tag{4.192}$$

In brief, the eigenvalue $E_2 = \epsilon + |t|$ corresponds to the first excited level of the system and since $t < 0$ there is one node.

4.4.2 Three-level system (3LS).

Let us hypothesize we deal with a three-level system (3LS) composed of three 1LSs. Moving in a completely analogous manner as we did for the case of the 2LS in Subsection 4.4.1, if we ignore the integrals U and S (third level of approximation) and assume that the three 1LSs are identical (so that we have equal on-site energies $\epsilon_1 = \epsilon_2 = \epsilon_3 = \epsilon$ and hopping integrals t), then the system of equations to be solved is

$$\begin{bmatrix} \epsilon & t & 0 \\ t & \epsilon & t \\ 0 & t & \epsilon \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} \tag{4.193}$$

or

$$\begin{bmatrix} \epsilon - E & t & 0 \\ t & \epsilon - E & t \\ 0 & t & \epsilon - E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}. \tag{4.194}$$

The matrix eigenvalues occur by the roots of its determinant

$$\begin{aligned} (\epsilon - E)[(\epsilon - E)^2 - t^2] - t^2(\epsilon - E) = 0 \Rightarrow \\ (\epsilon - E)^3 - 2t^2(\epsilon - E) = 0 \Rightarrow \\ (E - \epsilon)[(\epsilon - E)^2 - 2t^2] = 0 \Rightarrow \end{aligned}$$

$$E = \epsilon \ \text{ or } \ E = \epsilon \pm \sqrt{2}|t|. \tag{4.195}$$

Hence, for $t < 0$, the eigenvalues of the 3LS are

$$E_1 = \epsilon + \sqrt{2}t, \quad E_2 = \epsilon, \quad E_3 = \epsilon - \sqrt{2}t. \tag{4.196}$$

The energy width of the system is

$$E_3 - E_1 = 2\sqrt{2}|t| \approx 2.83\ |t|. \tag{4.197}$$

Substituting the eigenvalues E_1, E_2 and E_3 to the system of equations

$$\left.\begin{aligned} (\epsilon - E)c_1 + tc_2 = 0 \\ tc_1 + (\epsilon - E)c_2 + tc_3 = 0 \\ tc_2 + (\epsilon - E)c_3 = 0 \end{aligned}\right\}, \tag{4.198}$$

we obtain the eigenvectors of the system.

For the eigenvalue $E_1 = \epsilon + \sqrt{2}t$, we have

$$\left.\begin{aligned} -\sqrt{2}c_1 + c_2 = 0 \\ c_1 - \sqrt{2}c_2 + c_3 = 0 \\ c_2 - \sqrt{2}c_3 = 0 \end{aligned}\right\} \Rightarrow c_1 = c_3 = \frac{c_2}{\sqrt{2}} := c. \tag{4.199}$$

The normalization condition yields

$$|c|^2 + |\sqrt{2}c|^2 + |c|^2 = 1 \Rightarrow 4|c|^2 = 1 \Rightarrow |c| = 1/2.$$

Thus, the eigenvector that corresponds to the eigenvalue E_1 is, e.g.,

$$\vec{v}_1 = \frac{1}{2}\begin{bmatrix} 1 \\ \sqrt{2} \\ 1 \end{bmatrix}. \tag{4.200}$$

For the eigenvalue $E_2 = \epsilon$, we have

$$\left.\begin{aligned} tc_2 = 0 \\ tc_1 + tc_3 = 0 \\ tc_2 = 0 \end{aligned}\right\} \Rightarrow c_2 = 0, c_1 = -c_3 := c. \tag{4.201}$$

The normalization condition yields

$$|c|^2 + 0 + |c|^2 = 1 \Rightarrow 2|c|^2 = 1 \Rightarrow |c| = 1/\sqrt{2}.$$

Thus, the eigenvector that corresponds to the eigenvalue E_2 is, e.g.,

$$\vec{v}_2 = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix}. \tag{4.202}$$

For the eigenvalue $E_3 = \epsilon - \sqrt{2}t$, we have

$$\left.\begin{aligned} \sqrt{2}c_1 + c_2 = 0 \\ c_1 + \sqrt{2}c_2 + c_3 = 0 \\ c_2 + \sqrt{2}c_3 = 0 \end{aligned}\right\} \Rightarrow c_1 = c_3 = -\frac{c_2}{\sqrt{2}} \overset{\text{def}}{=} c \tag{4.203}$$

The normalization condition yields

$$|c|^2 + |\sqrt{2}c|^2 + |c|^2 = 1 \Rightarrow 4|c|^2 = 1 \Rightarrow |c| = 1/2.$$

Thus, the eigenvector that corresponds to the eigenvalue E_3 is, e.g.,

$$\vec{v}_3 = \frac{1}{2}\begin{bmatrix} 1 \\ -\sqrt{2} \\ 1 \end{bmatrix} \tag{4.204}$$

4.4.3 Four-level system (4LS).

Suppose a four-level system (4LS) composed of four 1LSs. In a completely analogous manner to what we did in Subsection 4.4.1 for the 2LS, if we ignore the integrals U and S (third level of approximation) and assume that the four 1LSs are identical (so that they have equal on-site energies $\epsilon_1 = \epsilon_2 = \epsilon_3 = \epsilon_4 = \epsilon$ and hopping integrals t), then the system of equations to be solved is

$$\begin{bmatrix} \epsilon & t & 0 & 0 \\ t & \epsilon & t & 0 \\ 0 & t & \epsilon & t \\ 0 & 0 & t & \epsilon \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} \tag{4.205}$$

or

$$\begin{bmatrix} \epsilon - E & t & 0 & 0 \\ t & \epsilon - E & t & 0 \\ 0 & t & \epsilon - E & t \\ 0 & 0 & t & \epsilon - E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}. \tag{4.206}$$

The matrix eigenvalues occur by the roots of its determinant

$$\begin{aligned} (\epsilon - E)^2[(\epsilon - E)^2 - t^2] - (\epsilon - E)^2 t^2 - t^2[(\epsilon - E)^2 - t^2] = 0 \Rightarrow \\ (\epsilon - E)^2[(\epsilon - E)^2 - t^2] - (\epsilon - E)^2 t^2 - (\epsilon - E)^2 t^2 + t^4 = 0 \Rightarrow \\ (\epsilon - E)^4 - 3(\epsilon - E)^2 t^2 + t^4 = 0 \end{aligned}$$

Setting $y = (\epsilon - E)^2$ yields the quadratic equation

$$y^2 - 3yt^2 + t^4 = 0$$

with discriminant $\Delta = 9t^4 - 4t^4 = 5t^4$. Thus,

$$\begin{aligned} y &= \frac{3 \pm \sqrt{5}}{2} t^2 \Rightarrow \\ E &= \epsilon \pm \sqrt{\frac{3 \pm \sqrt{5}}{2}} |t| \end{aligned} \tag{4.207}$$

Hence, for $t < 0$, the eigenvalues of the 4LS are

$$E_1 = \epsilon + \sqrt{\frac{3 + \sqrt{5}}{2}}\, t, \quad E_2 = \epsilon + \sqrt{\frac{3 - \sqrt{5}}{2}}\, t, \quad E_3 = \epsilon - \sqrt{\frac{3 - \sqrt{5}}{2}}\, t, \quad E_4 = \epsilon - \sqrt{\frac{3 + \sqrt{5}}{2}}\, t. \tag{4.208}$$

The energy width of the system is

$$E_4 - E_1 = 2\sqrt{\frac{3 + \sqrt{5}}{2}}\, |t| \approx 3.24\, |t|. \tag{4.209}$$

Substituting the eigenvalues E_1, E_2, E_3 and E_4 to the system of equations

$$\left. \begin{aligned} (\epsilon - E)c_1 + tc_2 = 0, \\ tc_1 + (\epsilon - E)c_2 + tc_3 = 0, \\ tc_2 + (\epsilon - E)c_3 + tc_4 = 0, \\ tc_3 + (\epsilon - E)c_4 = 0, \end{aligned} \right\} \tag{4.210}$$

we obtain the eigenvectors of the system.

For the eigenvalue $E_1 = \epsilon + \sqrt{\frac{3+\sqrt{5}}{2}}\, t$, if we denote

$$\Gamma := \sqrt{\frac{3+\sqrt{5}}{2}} = \frac{\sqrt{5}+1}{2}, \tag{4.211}$$

we obtain

$$\left.\begin{aligned} &c_2 = \Gamma c_1, \\ &c_1 - \Gamma c_2 + c_3 = 0, \\ &c_2 - \Gamma c_3 + c_4 = 0, \\ &c_3 = \Gamma c_4. \end{aligned}\right\} \tag{4.212}$$

Using the first and fourth equation into the second and third, we obtain

$$\left.\begin{aligned} c_1 - \Gamma^2 c_1 + \Gamma c_4 = 0, \\ \Gamma c_1 - \Gamma^2 c_4 + c_4 = 0. \end{aligned}\right\} \Rightarrow \qquad \left.\begin{aligned} (1-\Gamma^2)c_1 + \Gamma c_4 = 0, \\ \Gamma c_1 + (1-\Gamma^2)c_4 = 0. \end{aligned}\right\} \tag{4.213}$$

From there it follows

$$\left.\begin{aligned} c_4 = \tfrac{\Gamma^2-1}{\Gamma} c_1, \\ c_4 = \tfrac{\Gamma}{\Gamma^2-1} c_1. \end{aligned}\right\} \tag{4.214}$$

It is apparent from Eq. (4.214), which is OK if $\Gamma \neq 0, \pm 1$, that $\frac{\Gamma^2-1}{\Gamma} = \pm 1$. If we perform detailed calculations, we obtain

$$\frac{\Gamma^2-1}{\Gamma} = \frac{\Gamma}{\Gamma^2-1} = 1. \tag{4.215}$$

Therefore it will hold that

$$c_1 = c_4 := c, \quad c_2 = c_3 = \Gamma c. \tag{4.216}$$

Consequently,

$$\vec{v}_1 = c \begin{bmatrix} 1 \\ \Gamma \\ \Gamma \\ 1 \end{bmatrix}. \tag{4.217}$$

Normalizing, we obtain $|c|^2(2+2\Gamma^2) = 1 \Rightarrow |c|^2 = \frac{1}{2(1+\Gamma^2)}$, that is

$$|c|^2 = \frac{1}{5+\sqrt{5}}. \tag{4.218}$$

Hence, we can make the convenient choice

$$c = \frac{1}{\sqrt{5+\sqrt{5}}}. \tag{4.219}$$

Therefore, the eigenvector corresponding to the eigenvalue E_1 has the form

$$\vec{v}_1 = \frac{1}{\sqrt{5+\sqrt{5}}}\begin{bmatrix} 1 \\ \frac{\sqrt{5}+1}{2} \\ \frac{\sqrt{5}+1}{2} \\ 1 \end{bmatrix}. \tag{4.220}$$

For the eigenvalue $E_2 = \epsilon + \sqrt{\frac{3-\sqrt{5}}{2}}\, t$, if we denote

$$\Gamma := \sqrt{\frac{3-\sqrt{5}}{2}} = \frac{\sqrt{5}-1}{2}, \tag{4.221}$$

we obtain

$$\left.\begin{aligned} & c_2 = \Gamma c_1, \\ & c_1 - \Gamma c_2 + c_3 = 0, \\ & c_2 - \Gamma c_3 + c_4 = 0, \\ & c_3 = \Gamma c_4. \end{aligned}\right\} \tag{4.222}$$

Using the first and fourth equation into the second and third, we obtain

$$\left.\begin{aligned} & c_1 - \Gamma^2 c_1 + \Gamma c_4 = 0, \\ & \Gamma c_1 - \Gamma^2 c_4 + c_4 = 0. \end{aligned}\right\} \Rightarrow \qquad \left.\begin{aligned} & (1-\Gamma^2)c_1 + \Gamma c_4 = 0, \\ & \Gamma c_1 + (1-\Gamma^2)c_4 = 0. \end{aligned}\right\} \tag{4.223}$$

From there it follows that

$$\left.\begin{aligned} & c_4 = \tfrac{\Gamma^2-1}{\Gamma} c_1, \\ & c_4 = \tfrac{\Gamma}{\Gamma^2-1} c_1. \end{aligned}\right\} \tag{4.224}$$

It is apparent from Eq. (4.224), which is OK if $\Gamma \neq 0, \pm 1$, that $\frac{\Gamma^2-1}{\Gamma} = \pm 1$. If we perform detailed calculations, we obtain

$$\frac{\Gamma^2-1}{\Gamma} = \frac{\Gamma}{\Gamma^2-1} = -1. \tag{4.225}$$

Therefore, it will hold

$$c_1 := c, \quad c_2 = \Gamma c, \quad c_3 = -\Gamma c, \quad c_4 = -c. \tag{4.226}$$

Consequently,

$$\vec{v}_2 = c\begin{bmatrix} 1 \\ \Gamma \\ -\Gamma \\ -1 \end{bmatrix}. \tag{4.227}$$

Normalizing, we obtain $|c|^2(2+2\Gamma^2) = 1 \Rightarrow |c|^2 = \frac{1}{2(1+\Gamma^2)}$, that is

$$|c|^2 = \frac{1}{5-\sqrt{5}}. \tag{4.228}$$

Hence, a convenient choice would be

$$c = \frac{1}{\sqrt{5-\sqrt{5}}}. \tag{4.229}$$

Therefore, the eigenvector corresponding to the eigenvalue E_2 has the form

$$\vec{v}_2 = \frac{1}{\sqrt{5-\sqrt{5}}}\begin{bmatrix} 1 \\ \frac{\sqrt{5}-1}{2} \\ -\frac{\sqrt{5}-1}{2} \\ -1 \end{bmatrix}. \tag{4.230}$$

For the eigenvalue $E_3 = \epsilon - \sqrt{\frac{3-\sqrt{5}}{2}}\,t$, if we denote

$$\Gamma := \sqrt{\frac{3-\sqrt{5}}{2}} = \frac{\sqrt{5}-1}{2}, \tag{4.231}$$

we obtain

$$\left.\begin{aligned} c_2 &= -\Gamma c_1, \\ c_1 + \Gamma c_2 + c_3 &= 0, \\ c_2 + \Gamma c_3 + c_4 &= 0, \\ c_3 &= -\Gamma c_4. \end{aligned}\right\} \tag{4.232}$$

Using the first and the fourth equation into the second and third, we obtain

$$\left.\begin{aligned} c_1 - \Gamma^2 c_1 - \Gamma c_4 = 0, \\ -\Gamma c_1 - \Gamma^2 c_4 + c_4 = 0. \end{aligned}\right\} \Rightarrow \qquad \left.\begin{aligned} (1-\Gamma^2)c_1 - \Gamma c_4 = 0, \\ -\Gamma c_1 + (1-\Gamma^2)c_4 = 0. \end{aligned}\right\} \tag{4.233}$$

From there it follows that

$$\left.\begin{aligned} c_4 &= \tfrac{1-\Gamma^2}{\Gamma} c_1, \\ c_4 &= \tfrac{\Gamma}{1-\Gamma^2} c_1. \end{aligned}\right\} \tag{4.234}$$

It is evident from Eq. (4.234), which is OK if $\Gamma \neq 0, \pm 1$, that $\frac{1-\Gamma^2}{\Gamma} = \pm 1$. If we perform detailed calculations we obtain

$$\frac{1-\Gamma^2}{\Gamma} = \frac{\Gamma}{1-\Gamma^2} = 1. \tag{4.235}$$

Consequently, it will hold that

$$c_4 = c_1 := c, \quad c_2 = -\Gamma c, \quad c_3 = -\Gamma c. \tag{4.236}$$

Therefore,

$$\vec{v}_3 = c\begin{bmatrix} 1 \\ -\Gamma \\ -\Gamma \\ 1 \end{bmatrix}. \tag{4.237}$$

Normalizing, we obtain $|c|^2(2+2\Gamma^2)=1 \Rightarrow |c|^2 = \frac{1}{2(1+\Gamma^2)}$, that is

$$|c|^2 = \frac{1}{5-\sqrt{5}}. \tag{4.238}$$

Hence, a convenient choice would be

$$c = \frac{1}{\sqrt{5-\sqrt{5}}}. \tag{4.239}$$

Therefore, the eigenvector corresponding to eigenvalue E_3 has the form

$$\vec{v}_3 = \frac{1}{\sqrt{5-\sqrt{5}}} \begin{bmatrix} 1 \\ -\frac{\sqrt{5}-1}{2} \\ -\frac{\sqrt{5}-1}{2} \\ 1 \end{bmatrix}. \tag{4.240}$$

For the eigenvalue $E_4 = \epsilon - \sqrt{\frac{3+\sqrt{5}}{2}}\, t$, if we denote

$$\Gamma := \sqrt{\frac{3+\sqrt{5}}{2}} = \frac{\sqrt{5}+1}{2}, \tag{4.241}$$

we obtain

$$\left.\begin{aligned} c_2 &= -\Gamma c_1, \\ c_1 + \Gamma c_2 + c_3 &= 0, \\ c_2 + \Gamma c_3 + c_4 &= 0, \\ c_3 &= -\Gamma c_4. \end{aligned}\right\} \tag{4.242}$$

using the first and fourth equation into the second and third, we obtain

$$\left.\begin{aligned} c_1 - \Gamma^2 c_1 - \Gamma c_4 &= 0, \\ -\Gamma c_1 - \Gamma^2 c_4 + c_4 &= 0. \end{aligned}\right\} \Rightarrow \quad \left.\begin{aligned} (1-\Gamma^2)c_1 - \Gamma c_4 &= 0, \\ -\Gamma c_1 + (1-\Gamma^2)c_4 &= 0. \end{aligned}\right\} \tag{4.243}$$

From there is follows that

$$\left.\begin{aligned} c_4 &= \frac{1-\Gamma^2}{\Gamma} c_1, \\ c_4 &= \frac{\Gamma}{1-\Gamma^2} c_1. \end{aligned}\right\} \tag{4.244}$$

It is evident from Eq. (4.244), which is OK if $\Gamma \neq 0, \pm 1$, that $\frac{1-\Gamma^2}{\Gamma} = \pm 1$. If we perform detailed calculations, we obtain

$$\frac{1-\Gamma^2}{\Gamma} = \frac{\Gamma}{1-\Gamma^2} = -1. \tag{4.245}$$

Therefore, it will hold that

$$c_1 := c, \quad c_2 = -\Gamma c, \quad c_3 = \Gamma c, \quad c_4 = -c. \tag{4.246}$$

Consequently,

$$\vec{v}_4 = c\begin{bmatrix} 1 \\ -\Gamma \\ \Gamma \\ -1 \end{bmatrix}. \tag{4.247}$$

Normalizing, we obtain $|c|^2(2+2\Gamma^2) = 1 \Rightarrow |c|^2 = \frac{1}{2(1+\Gamma^2)}$, that is

$$|c|^2 = \frac{1}{5+\sqrt{5}}. \tag{4.248}$$

Therefore, a convenient choice would be

$$c = \frac{1}{\sqrt{5+\sqrt{5}}}. \tag{4.249}$$

Hence, the eigenvector corresponding to the eigenvalue E_4 has the form

$$\vec{v}_4 = \frac{1}{\sqrt{5+\sqrt{5}}}\begin{bmatrix} 1 \\ -\frac{1+\sqrt{5}}{2} \\ \frac{1+\sqrt{5}}{2} \\ -1 \end{bmatrix}. \tag{4.250}$$

4.5 Discrete-continuous energy spectrum, subbands.

There are cases in which we have free motion in 2 (or 1) dimensions and bound states in 1 (or 2) dimensions, respectively; we call these quantum wells (or quantum wires). In such a scenario, the free motion leads to a continuous energy spectrum (i.e., bands, although since they correspond to less than 3 dimensions are called *subbands*), while the bound states we have a discrete energy spectrum, i.e. levels. Our below description is based on the Slater theorem [13], the Envelope Function Approximation, and the Effective Mass Approximation.

4.6 Slater theorem and consequences.

Using the Slater theorem [13], we can reduce the problem of electron motion in a crystal lattice plus perturbing potentials to a problem similar to electron motion solely in perturbing potentials; in other words, we simplify the solving process significantly. The papers by Bloch [14] and Wannier [15] are prerequisites. The theory of papers [14, 15] is extensively described, e.g. in book [16].

4.6.1 Unperturbed problem.

The Hamiltonian of the unperturbed problem is

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e}\nabla^2 + U_{\mathrm{L}}(\vec{r}). \tag{4.251}$$

The first term is the kinetic energy and the second term is the potential energy of a perfect periodic crystal. The solution of the unperturbed problem

$$\hat{H}_0\ \psi_0(\vec{p},\vec{r}) = E_0(\vec{p})\ \psi_0(\vec{p},\vec{r}), \tag{4.252}$$

where $E_0(\vec{p})$ or $E_0(\vec{k})$ are the energy band diagrams, which are commonly represented graphically, is the crystal momentum. This solution was provided by Wannier [15], who improved Bloch's theory [14].

Assume a monoatomic basis in our periodic crystal. Thus, let us suppose that the following hold: (a) The lattice points are described by the position vectors $\vec{R} = m_1\vec{a}_1 + m_2\vec{a}_2 + m_3\vec{a}_3 := \vec{R}_m$, where $m = \{m_1, m_2, m_3\},\ m_i \in \mathscr{Z}$ is a collective index for the lattice points and $\{\vec{a}_1, \vec{a}_2, \vec{a}_3\}$ are the primitive translation vectors (PTV), and (b) the axes origin coincides with some lattice point. Then [15],

$$\boxed{\psi_0(\vec{p},\vec{r}) = \sum_m \frac{1}{\sqrt{N}} e^{\frac{i}{\hbar}\vec{p}\cdot\vec{R}_m}\ \alpha(\vec{r}-\vec{R}_m)} \tag{4.253}$$

Alternatively, we can use $\vec{k}$, i.e.,

$$\hat{H}_0\ \psi_0(\vec{k},\vec{r}) = E_0(\vec{k})\ \psi_0(\vec{k},\vec{r}), \tag{4.254}$$

$$\psi_0(\vec{k},\vec{r}) = \sum_m \frac{1}{\sqrt{N}} e^{i\vec{k}\cdot\vec{R}_m}\ \alpha(\vec{r}-\vec{R}_m). \tag{4.255}$$

Of course, in our periodic crystalline lattice, the potential energy, $U_{\mathrm{L}}(\vec{r})$, is also periodic, i.e.,

$$U_{\mathrm{L}}(\vec{r}+\vec{R}_m) = U_{\mathrm{L}}(\vec{r}). \tag{4.256}$$

L stands for lattice. The Wannier functions are defined as

$$\boxed{\alpha(\vec{r}-\vec{R}_m) = \frac{1}{\sqrt{N}} \sum_{\vec{p}} e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{R}_m} \psi_0(\vec{p},\vec{r})} \tag{4.257}$$

Given the property

$$\sum_m e^{\frac{i}{\hbar}(\vec{p}\,'-\vec{p})\cdot\vec{R}_m} = \begin{cases} 0, & \vec{p}\,' \neq \vec{p} \\ N, & \vec{p}\,' = \vec{p} \end{cases} = \quad N\delta(\vec{p}\,'-\vec{p}), \tag{4.258}$$

where N is the total (very large...) number of lattice points in the crystal, it follows that

$$\sum_m e^{\frac{i}{\hbar}\vec{p}\,'\cdot\vec{R}_m} \alpha(\vec{r}-\vec{R}_m) = \sum_m \frac{1}{\sqrt{N}} \sum_{\vec{p}} e^{\frac{i}{\hbar}(\vec{p}\,'-\vec{p})\cdot\vec{R}_m} \psi_0(\vec{p},\vec{r}) = \tag{4.259}$$

$$\sum_{\vec{p}} \frac{1}{\sqrt{N}} \psi_0(\vec{p},\vec{r}) \sum_m e^{\frac{i}{\hbar}(\vec{p}\,'-\vec{p})\cdot\vec{R}_m} = \sum_{\vec{p}} \frac{1}{\sqrt{N}} \psi_0(\vec{p},\vec{r}) N\delta(\vec{p}\,'-\vec{p}) \tag{4.260}$$

$$= \sqrt{N}\psi_0(\vec{p}\,',\vec{r}). \tag{4.261}$$

Therefore, changing the symbol $\vec{p}\,'$ with $\vec{p}$, we have

$$\boxed{\psi_0(\vec{p},\vec{r}) = \sum_m \frac{1}{\sqrt{N}} e^{\frac{i}{\hbar}\vec{p}\cdot\vec{R}_m}\ \alpha(\vec{r}-\vec{R}_m)} \tag{4.262}$$

which is Eq. (4.253).

4.6.2 Perturbed problem.

Now, we want to find the functions $\psi_i(\vec{r})$ which satisfy the equation

$$\hat{H}\ \psi_i(\vec{r}) = E_i\ \psi_i(\vec{r}), \qquad \hat{H} = \hat{H}_0 + \hat{H}_1, \tag{4.263}$$

where i is some collective quantum number and $\hat{H}_1$ is the Hamiltonian which contains all the perturbing potential energies. We assume that $\hat{H}_1$ changes slowly as a function of $\vec{r}$. We are trying to express $\psi_i(\vec{r})$ in the form

$$\boxed{\psi_i(\vec{r}) = \sum_m \varphi_i(\vec{R}_m)\ \alpha(\vec{r} - \vec{R}_m)} \tag{4.264}$$

In other words, we are trying to find functions $\varphi_i(\vec{R}_m)$ that modify the atomic Wannier functions, $\alpha(\vec{r} - \vec{R}_m)$, in order to express the solution of the perturbed problem by substituting the exponential functions, $\frac{1}{\sqrt{N}}e^{\frac{i}{\hbar}\vec{p}\cdot\vec{R}_m}$, which modify the atomic Wannier functions, $\alpha(\vec{r} - \vec{R}_m)$, within the unperturbed problem. The *Slater theorem* states that the envelope functions, $\varphi_i(\vec{r})$, satisfy the differential equation

$$\boxed{[E_0(-i\hbar\nabla) + \hat{H}_1(\vec{r})]\ \varphi_i(\vec{r}) = E_i\ \varphi_i(\vec{r})} \tag{4.265}$$

In Eq. (4.265), we have changed $\vec{R}_m$ to $\vec{r}$, which is now a coarse grained $\vec{r}$. Eq. (4.265) is called the *Envelope Function Equation* (EFE). However, for the Slater theorem to hold, we have to assume that $\hat{H}_1(\vec{r})$ is a slowly changing function of the coarse grained position $\vec{r}$. Eq. (4.265) is a Schrödinger-type equation for $\varphi_i(\vec{r})$, in which the perturbing potential energy $\hat{H}_1$ appears as the potential energy, while $E_0(\vec{p})$ of the unperturbed problem (with $\vec{p}$ being substituted by the differential operator $-i\hbar\nabla$) appears as the kinetic energy operator.

4.7 From the Schrödinger Equation to the Effective Mass Equation, using the Envelope Function Approximation and the Effective Mass Approximation.

In the single-electron Schrödinger equation

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \tag{4.266}$$

the Hamiltonian is written as

$$\hat{H} = \frac{\vec{p}^2}{2m_e} + U(\vec{r}) \qquad \text{without external magnetic field,} \tag{4.267}$$

$$\hat{H} = \frac{(\hat{\vec{p}} - q\vec{A})^2}{2m_e} + U(\vec{r}) \qquad \text{with external magnetic field, where } \vec{A} \text{ is the vector potential,} \tag{4.268}$$

where $U(\vec{r})$ is the total potential energy, analyzed, say, as

$$U(\vec{r}) = U_{\mathrm{L}}(\vec{r}) + U_{\mathrm{S}}(\vec{r}) + U_{\mathrm{E}}(\vec{r}) + U_{\mathrm{xc}}(\vec{r}) + U_{\mathrm{M}}(\vec{r}). \tag{4.269}$$

$U_{\mathrm{L}}(\vec{r})$, where L stands for Lattice, is the potential energy of the perfect periodic crystalline lattice. $U_{\mathrm{S}}(\vec{r})$, where S stands for Scattering, is the scattering potential energy due to defects, impurities, phonons, etc.. $U_{\mathrm{E}}(\vec{r})$, where E stands for External, is the potential energy due to externally applied fields and macroscopic space charges. $U_{\mathrm{xc}}(\vec{r})$, where xc stands for exchange and correlation, is the exchange and correlation potential energy, which describes the effect of the rest electrons. The last term, $U_{\mathrm{M}}(\vec{r})$, where M stands for magnetic, is the magnetic potential energy, e.g., $-\vec{\mu}\cdot\vec{B}$ or $-\sum_i \vec{\mu}_i\cdot\vec{B}$, where i runs over the magnetic building blocks of the system.

Applying the Slater theorem [13], Eq. (4.265), see Section 4.6, we arrive at the Envelope Function Equation (EFE)

$$E_0(-i\hbar\nabla)\varphi(\vec{r}) + [U_{\mathrm{S}}(\vec{r}) + U_{\mathrm{E}}(\vec{r}) + U_{\mathrm{xc}}(\vec{r}) + U_{\mathrm{M}}(\vec{r})]\varphi(\vec{r}) = E\varphi(\vec{r}). \tag{4.270}$$

Here, $\varphi(\vec{r})$ is the envelope function, which crudely describes the wavefunction's configuration from lattice point to lattice point, see Section 4.6. The operator $-i\hbar\nabla$ replaces the crystal momentum $\vec{p} = \hbar\vec{k}$ in the energy band diagrams $\mathrm{E}_0(\vec{p})$, i.e., $-i\nabla$ replaces $\vec{k}$,

$$\vec{k} = (k_x, k_y, k_z) \leftrightarrow -i\vec{\nabla} = -i(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}). \tag{4.271}$$

The dispersion relation of a free electron is parabolic, with coefficient $\alpha = \frac{\hbar^2}{2m_e}$, i.e.,

$$\mathrm{E}_0(\vec{k}) = \frac{\vec{p}^2}{2m_e} = \frac{\hbar^2\vec{k}^2}{2m_e} = -\frac{\hbar^2\nabla^2}{2m_e}. \tag{4.272}$$

Close to the minimum of a specific band (e.g. the conduction band) we can analogously write

$$\mathrm{E}_0(\vec{k}) = E_{\mathrm{c}0} + \frac{\vec{p}^2}{2m^*} = E_{\mathrm{c}0} + \frac{\hbar^2\vec{k}^2}{2m^*} = E_{\mathrm{c}0} - \frac{\hbar^2\nabla^2}{2m^*}, \tag{4.273}$$

where m^* is the effective mass and it is generally a tensor. In more symmetric cases, we can write

$$\mathrm{E}_0(\vec{k}) = E_{\mathrm{c}0} + \frac{\hbar^2 k_x^2}{2m_x^*} + \frac{\hbar^2 k_y^2}{2m_y^*} + \frac{\hbar^2 k_z^2}{2m_z^*} \tag{4.274}$$

and in the simplest case

$$\mathrm{E}_0(\vec{k}) = E_{\mathrm{c}0} + \frac{\hbar^2 k^2}{2m^*} = E_{\mathrm{c}0} - \frac{\hbar^2\nabla^2}{2m^*}. \tag{4.275}$$

In other words, the effective mass determines the coefficient $\alpha = \frac{\hbar^2}{2m^*}$ of the parabola, just like in the case of the free electron, where the coefficient is $\alpha = \frac{\hbar^2}{2m_e}$. This means that the effective mass m^* expresses the steepness of the curvature close to the band minimum. See Figure 4.16, in which the case $m^* < m_e$ is presented. Popular semiconductors have small effective masses. For example, in GaAs, $m^* \approx 0.067m_e$.

If we restrict ourselves to the latter, simplest, case, then Eq. (4.270) becomes the so-called Effective Mass Equation (EME).

$$-\frac{\hbar^2\nabla^2}{2m^*}\varphi(\vec{r}) + [E_{\mathrm{c}0} + U_{\mathrm{E}}(\vec{r}) + U_{\mathrm{xc}}(\vec{r}) + U_{\mathrm{M}}(\vec{r})]\varphi(\vec{r}) + U_{\mathrm{S}}(\vec{r})\varphi(\vec{r}) = E\varphi(\vec{r}). \tag{4.276}$$

Let us focus on cases without $U_{\mathrm{M}}(\vec{r})$. The quantity $E_{\mathrm{c}0} + U_{\mathrm{E}}(\vec{r}) + U_{\mathrm{xc}}(\vec{r})$ is the one we draw when we create band diagrams for heterostructures. Commonly, we solve Eq. (4.276) assuming that $U_{\mathrm{S}}(\vec{r}) = 0$ and estimate the effect of $U_{\mathrm{S}}(\vec{r})$ using the scattering and transport theory (e.g. by solving the Boltzmann transport equation) [17].

Let us now consider a junction of two different materials, e.g. GaAs and $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$. In this case, the conduction band minimum, $E_{\mathrm{c}0}$, is higher in the trimer than in the dimer (see Figure 4.17). A well is

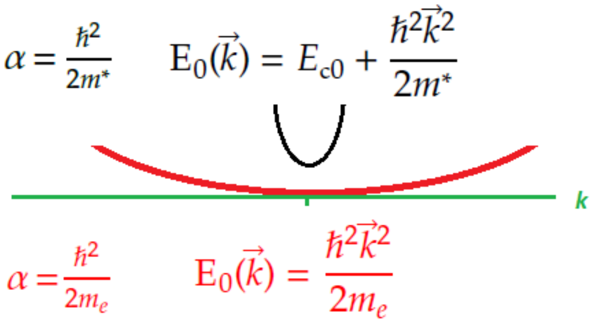

Figure 4.16: The steepness of the curvature close to the band minimum is expressed by the effective mass, m^*. Here, the case $m^* < m_e$ is presented.

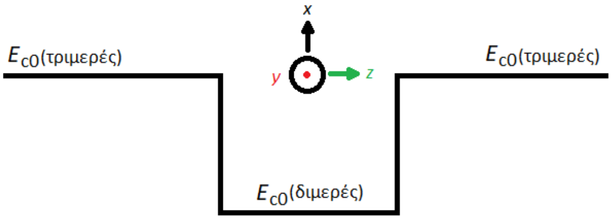

Figure 4.17: A junction of two different materials, e.g. GaAs and $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$, so that the conduction band minimum, E_{c0}, is higher in the trimer than in the dimer. A well is formed.

formed. If the well width, i.e. the thickness of the medium layer, is smaller than the electron mean free path, then a quantum description is needed. Therefore, we have a quantum well.

If m^* is a constant scalar for each material but has different value for each material, then

$$\mathrm{E}_0(\vec{k}) = E_{c0}(z) + \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m^*(z)} \tag{4.277}$$

and if we further assume that $U_S(\vec{r}) = 0$, it follows that

$$-\frac{\hbar^2}{2m^*(z)}\frac{\partial^2\varphi(\vec{r})}{\partial z^2} + \frac{\hbar^2 \vec{k}_{xy}^{\,2}}{2m^*(z)}\varphi(\vec{r}) + [E_{c0} + U_{\mathrm{E}}(\vec{r}) + U_{\mathrm{xc}}(\vec{r})]\varphi(\vec{r}) = E\varphi(\vec{r}), \tag{4.278}$$

$$-\frac{\hbar^2}{2m^*(z)}\frac{\partial^2\varphi(\vec{r})}{\partial z^2} + -\frac{\hbar^2}{2m^*(z)}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\varphi(\vec{r}) + [E_{c0} + U_{\mathrm{E}}(\vec{r}) + U_{\mathrm{xc}}(\vec{r})]\varphi(\vec{r}) = E\varphi(\vec{r}), \tag{4.279}$$

and the variables are not separable, due to the presence of $m^*(z)$ in the second term, even if $U_{\mathrm{E}}(\vec{r}) = U_{\mathrm{E}}(\vec{z})$ and $U_{\mathrm{xc}}(\vec{r}) = U_{\mathrm{xc}}(\vec{z})$. On the other hand, if m^* is constant and scalar, then the variables can be separated. Such an assumption is not that unreasonable, since electrons are mainly in GaAs. However, it becomes less realistic as the well width decreases, since this leads to an increased envelope function surpassing of the $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ barrier [17].

4.8 Electron eigenstates in a quantum well with constant effective mass.

For $U_{\mathrm{S}}(\vec{r}) = 0$, Eq. (4.276) can be written as

$$-\frac{\hbar^2}{2m^*}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\varphi(\vec{r}) + \underbrace{\left[E_{c0} + U_{\mathrm{E}}(\vec{r}) + U_{\mathrm{xc}}(\vec{r})\right]}_{U(\vec{r})}\varphi(\vec{r}) = E\varphi(\vec{r}). \tag{4.280}$$

We have defined $U(\vec{r}) := E_{c0} + U_{\mathrm{E}}(\vec{r}) + U_{\mathrm{xc}}(\vec{r})$. Let m^* be constant and scalar and $U(\vec{r}) = U(z)$ as it is qualitatively shown in Figure 4.18. The presence of three different layers, i.e., of three different E_{c0}, leads in itself to a square well without curvature. However, the term $U_{\mathrm{E}}(\vec{r})$ of the Hamiltonian -specifically, its part that corresponds to space charges (and occurs by solving the Poisson equation)- and, secondarily, the term $U_{\mathrm{xc}}(\vec{r})$, lead to a deformation of the bands which is called band bending [17].

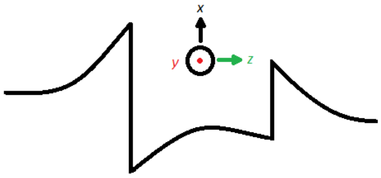

Figure 4.18: A quantum well between three layers of materials with band bending.

We can try a solution of separate variables to Eq. (4.280), i.e. of the form

$$\varphi(\vec{r}) = X(x)\;Y(y)\;Z(z). \tag{4.281}$$

Then,

$$-\frac{\hbar^2}{2m^*}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\varphi(\vec{r}) + U(\vec{r})\varphi(\vec{r}) = E\varphi(\vec{r}), \tag{4.282}$$

$$-\frac{\hbar^2}{2m^*}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)XYZ + U(\vec{r})XYZ = EXYZ, \tag{4.283}$$

$$-\frac{\hbar^2}{2m^*}YZ\frac{\partial^2 X}{\partial x^2} - \frac{\hbar^2}{2m^*}XZ\frac{\partial^2 Y}{\partial y^2} - \frac{\hbar^2}{2m^*}XY\frac{\partial^2 Z}{\partial z^2} + U(z)XYZ = EXYZ, \tag{4.284}$$

$$\underbrace{-\frac{\hbar^2}{2m^*}\frac{1}{X}\frac{\partial^2 X}{\partial x^2}}_{f_1(x)}\underbrace{-\frac{\hbar^2}{2m^*}\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}}_{f_2(y)}\underbrace{-\frac{\hbar^2}{2m^*}\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} + U(z)}_{f_3(z)} = E. \tag{4.285}$$

There are three terms on the left-hand side of Eq. (4.285); the first $f_1(x)$, depends only on x, the second, $f_2(y)$, depends only on y, and the third, $f_3(z)$, depends only on z. On the right-hand side there is E and the equation must hold $\forall\, x, y, z$. Hence, E does not depend on x, y, z and the equation can be divided into three parts, i.e.,

$$E = E_x + E_y + E_z. \tag{4.286}$$

$$-\frac{\hbar^2}{2m^*}\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = E_x, \tag{4.287}$$

$$-\frac{\hbar^2}{2m^*}\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = E_y, \tag{4.288}$$

$$-\frac{\hbar^2}{2m^*}\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} + U(z) = E_z. \tag{4.289}$$

- For the first equation,

$$-\frac{\hbar^2}{2m^*}\frac{\partial^2 X(x)}{\partial x^2} = E_x\, X(x), \tag{4.290}$$

we try solutions of the form

$$X(x) = Ae^{ik_x x} \quad \text{(eigenfunctions)} \tag{4.291}$$

and it follows that

$$\frac{\hbar^2 k_x^2}{2m^*}\, X(x) = E_x\, X(x), \tag{4.292}$$

$$E_x = \frac{\hbar^2 k_x^2}{2m^*} \quad \text{(eigenenergies)}. \tag{4.293}$$

We observe that the eigenenergies and eigenfunctions are the characteristic ones of a free particle moving in the x dimension. We normalize over the whole length of the heterostructure along the x-axis, i.e.

$$\int_{-L_x/2}^{+L_x/2} dx|X(x)|^2 = 1 \Rightarrow |A|^2 L_x = 1, \quad \text{hence, a convenient choice is} \quad A = \frac{1}{\sqrt{L_x}}. \tag{4.294}$$

- For the second equation,

$$-\frac{\hbar^2}{2m^*}\frac{\partial^2 Y(y)}{\partial y^2} = E_y\, Y(y), \tag{4.295}$$

we try solutions of the form

$$Y(y) = Be^{ik_y y} \quad \text{(eigenfunctions)} \tag{4.296}$$

and it follows that

$$\frac{\hbar^2 k_y^2}{2m^*}\, Y(y) = E_y\, Y(y), \tag{4.297}$$

$$E_y = \frac{\hbar^2 k_y^2}{2m^*} \quad \text{(eigenenergies)}. \tag{4.298}$$

We observe that the eigenenergies and eigenfunctions are the characteristic ones of a free particle moving in the y dimension. We normalize over the whole length of the heterostructure along the y-axis, i.e.

$$\int_{-L_y/2}^{+L_y/2} dy\big|Y(y)\big|^2 = 1 \Rightarrow |B|^2 L_y = 1, \quad \text{hence, a convenient choice is} \quad B = \frac{1}{\sqrt{L_y}}. \tag{4.299}$$

- For the third, equation,

$$-\frac{\hbar^2}{2m^*}\frac{\partial^2 Z(z)}{\partial z^2} + U(z)\, Z(z) = E_z\, Z(z), \tag{4.300}$$

we will generally have some eigenenergies E_i and eigenfunctions $\zeta_i(z)$ which correspond to *bound* states. (We will not focus on energies larger than the top of the well.) Let us assumed that the eigenfunctions are normalized, so that

$$\int_{-L_z/2}^{+L_z/2} dz|\zeta_i(z)|^2 = 1. \tag{4.301}$$

Hence, in summary, we obtain the eigenenergies

$$E_i(k_x, k_y) = E_i + \frac{\hbar^2 k_x^2}{2m^*} + \frac{\hbar^2 k_y^2}{2m^*} \tag{4.302}$$

and the (envelope) eigenfunctions

$$\varphi_{i,k_x,k_y}(\vec{r}) = \frac{1}{\sqrt{S}} \zeta_i(z) e^{ik_x x} e^{ik_y y}, \tag{4.303}$$

where $S = L_x L_y$ is the cross section of the heterostructure on the xy-plane. In other words, the electron is free along the x- and y-axes, while it is bound along the z-axis (at least for energies smaller than the top of the well). The index i is discrete and the indices k_x, k_y are "continuous". These two elements constitute the quasi two-dimensional character of such electrons.

4.9 Density of eigenstates of a quasi two-dimensional electron gas.

The density of eigenstates is defined as

$$g(\varepsilon) := \sum_{\mu} \delta(\varepsilon - E_\mu) = 2 \sum_{\lambda} \delta(\varepsilon - E_\lambda), \tag{4.304}$$

where the first (second) summation over μ (λ) denotes all the eigenstates (energy eigenstates), i.e. the factor 2 is due to spin. Summation is carried out over all "continuous" and discrete indices. In our case, it is carried out over the "continuous" quantum numbers k_x, k_y and the discrete quantum number i. In other words,

$$g(\varepsilon) = 2 \sum_{i,k_x,k_y} \delta\left(\varepsilon - E_i - \frac{\hbar^2 (k_x^2 + k_y^2)}{2m^*}\right). \tag{4.305}$$

Let us impose periodic boundary conditions along the x- and y-directions, i.e.,

$$e^{ik_x\left(-\frac{L_x}{2}\right)} = e^{ik_x\left(\frac{L_x}{2}\right)} \Rightarrow e^{ik_x L_x} = 1 = e^{i2\pi n_x}, n_x \in \mathscr{Z} \Rightarrow k_x = \frac{2\pi n_x}{L_x}. \tag{4.306}$$

$$e^{ik_y\left(-\frac{L_y}{2}\right)} = e^{ik_y\left(\frac{L_y}{2}\right)} \Rightarrow e^{ik_y L_y} = 1 = e^{i2\pi n_y}, n_y \in \mathscr{Z} \Rightarrow k_y = \frac{2\pi n_y}{L_y}. \tag{4.307}$$

Therefore,

$$k_x = \frac{2\pi n_x}{L_x} \Rightarrow \Delta k_x = \frac{2\pi}{L_x} \Delta n_x, \quad k_y = \frac{2\pi n_y}{L_y} \Rightarrow \Delta k_y = \frac{2\pi}{L_y} \Delta n_y. \tag{4.308}$$

$$g(\varepsilon) = 2 \sum_{i,k_x,k_y} \delta\left(\varepsilon - E_i - \frac{\hbar^2 (k_x^2 + k_y^2)}{2m^*}\right) \Delta n_x \Delta n_y, \quad \text{where } \Delta n_x = \Delta n_y = 1. \tag{4.309}$$

Using Eq. (4.308), it follows that

$$g(\varepsilon) = 2 \sum_{i,k_x,k_y} \delta\left(\varepsilon - E_i - \frac{\hbar^2 (k_x^2 + k_y^2)}{2m^*}\right) \frac{L_x}{2\pi} \Delta k_x \frac{L_y}{2\pi} \Delta k_y. \tag{4.310}$$

And, since $S = L_x L_y$ is the cross section of the heterostructure on the xy-plane, we can write

$$g(\varepsilon) = 2\frac{S}{(2\pi)^2} \sum_{i,k_x,k_y} \delta\left(\varepsilon - E_i - \frac{\hbar^2(k_x^2 + k_y^2)}{2m^*}\right) \Delta k_x \Delta k_y \tag{4.311}$$

Now, let us suppose that

$$\Delta k_x \to dk_x \quad \text{assuming} \quad L_x \to \infty \text{ or, better, } >> L_z, \tag{4.312}$$

$$\Delta k_y \to dk_y \quad \text{assuming} \quad L_y \to \infty \text{ or, better, } >> L_z. \tag{4.313}$$

In this “qualitative” fashion, we conclude that

$$g(\varepsilon) = 2\frac{S}{(2\pi)^2} \int_{k_x} dk_x \int_{k_y} dk_y \sum_i \delta\left(\varepsilon - E_i - \frac{\hbar^2(k_x^2 + k_y^2)}{2m^*}\right) \tag{4.314}$$

which, of course, can also be implied by a known theorem.

Now, let us change the coordinates in the plane $k_x k_y$ from Cartesian to polar. As we can see in Figure 4.19, the norm, $|\vec{k}|$, of the two-dimensional vector $\vec{k} = (k_x, k_y)$ in the plane $k_x k_y$, is $\left|\vec{k}\right| := k_{\|} = \sqrt{k_x^2 + k_y^2}$, where the infinitesimal change in the radial direction is denoted by $dk_{\|}$ and the infinitesimal change in the polar direction, i.e., normal to the radial direction, is denoted by $dk_{\perp} = k_{\|} d\phi$. ϕ is the polar angle in the plane $k_x k_y$. Therefore, we can write

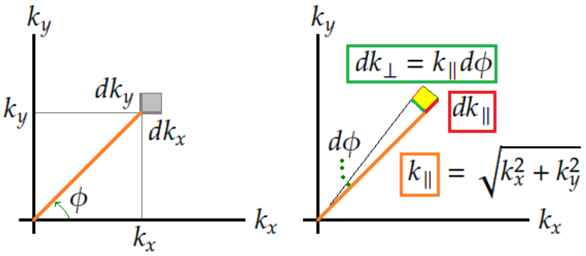

Figure 4.19: From Cartesian to polar coordinates in the plane $k_x k_y$.

$$g(\varepsilon) = 2\frac{S}{(2\pi)^2} \int_0^{\infty} \int_0^{2\pi} dk_{\|} k_{\|} d\phi \sum_i \delta\left(\varepsilon - E_i - \frac{\hbar^2 k_{\|}^2}{2m^*}\right), \tag{4.315}$$

$$g(\varepsilon) = \frac{S}{\pi} \sum_i \int_0^{\infty} dk_{\|} k_{\|} \delta\left(\varepsilon - E_i - \frac{\hbar^2 k_{\|}^2}{2m^*}\right). \tag{4.316}$$

Now, performing the variable change

$$\chi = \frac{\hbar^2 k_{\|}^2}{2m^*} \quad \Rightarrow \quad d\chi = \frac{\hbar^2}{m^*} k_{\|} dk_{\|}, \tag{4.317}$$

it occurs that

$$g(\varepsilon) = \frac{Sm^*}{\pi\hbar^2} \sum_i \int_0^{\infty} d\chi \delta(\varepsilon - E_i - \chi). \tag{4.318}$$

As it can be seen in Figure 4.20, when $\varepsilon - E_i$ lies within the interval $(0, \infty)$, i.e., when $\varepsilon > E_i$, the integral is equal to 1, otherwise it is 0. This can be expressed as

$$\boxed{g(\varepsilon) = \frac{m^* S}{\pi\hbar^2} \sum_i \Theta(\varepsilon - E_i)} \tag{4.319}$$

The density of (eigen)states, with its characteristic step-like form, is presented in Figure 4.21.

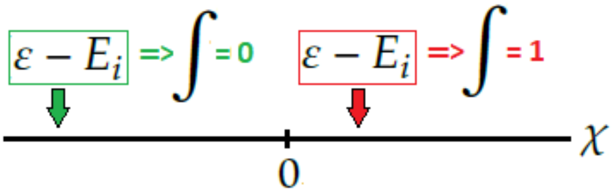

Figure 4.20: $\varepsilon - E_i$ lies within the interval $(0, \infty)$, i.e., when $\varepsilon > E_i$, the integral is equal to 1, otherwise it is 0.

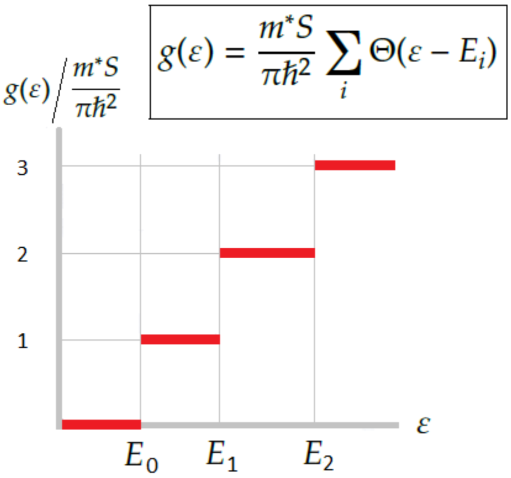

Figure 4.21: Density of (eigen)states of a quasi two-dimensional electron gas.

4.10 Spatial density of occupied states, i.e. electron density.

The spatial density of occupied states, i.e. the electron density or spatial electron density is

$$n(\vec{r}) := \int_{-\infty}^{+\infty} d\varepsilon\; g(\varepsilon)\; f_0(\varepsilon)\; \left|\varphi_{i,k_x,k_y}(\vec{r})\right|^2, \tag{4.320}$$

where $g(\varepsilon)$ is the density of states, $f_0(\varepsilon)$ is the Fermi-Dirac distribution, and $\varphi_{i,k_x,k_y}(\vec{r})$ is the normalized envelope function of level i. Caution: there is already a summation over i inside $g(\varepsilon)$. Substituting Eqs. (4.319), (4.303) and the definition of the Fermi-Dirac distribution function, we obtain

$$n(\vec{r}) = \int_{-\infty}^{+\infty} d\varepsilon\; \frac{m^* S}{\pi\hbar^2}\sum_i \Theta(\varepsilon - E_i)\; \frac{1}{1 + \exp\left(\frac{\varepsilon - \mu(T)}{k_B T}\right)}\; \frac{1}{S}|\zeta_i(z)|^2 \tag{4.321}$$

$$n(\vec{r}) = \frac{m^*}{\pi\hbar^2}\sum_i |\zeta_i(z)|^2 \int_{-\infty}^{+\infty} d\varepsilon\; \Theta(\varepsilon - E_i)\; \frac{1}{1 + \exp\left(\frac{\varepsilon - \mu(T)}{k_B T}\right)} \tag{4.322}$$

$$n(\vec{r}) = \frac{m^*}{\pi\hbar^2}\sum_i |\zeta_i(z)|^2 \int_{E_i}^{+\infty} d\varepsilon\; \frac{1}{1 + \exp\left(\frac{\varepsilon - \mu(T)}{k_B T}\right)} \tag{4.323}$$

We now perform the variable change $\chi(T) := \frac{\varepsilon}{k_B T}$, and denote $\kappa(T) := \frac{\mu(T)}{k_B T}$ [below we write them as χ and κ, for simplicity]. Thus, it follows that

$$n(\vec{r}) = \frac{m^* k_B T}{\pi\hbar^2}\sum_i |\zeta_i(z)|^2 \int_{\frac{E_i}{k_B T}}^{+\infty} d\chi\; \frac{1}{1 + \exp(\chi - \kappa)}, \tag{4.324}$$

and since $(\ln(1+e^{-x}))' = \frac{-e^{-x}}{1+e^{-x}} = \frac{-1}{1+e^{x}}$, we can write

$$n(\vec{r}) = \frac{m^* k_{\mathrm{B}} T}{\pi \hbar^2} \sum_i |\zeta_i(z)|^2 \Big[-\ln\Big(1+\exp(\kappa-\chi)\Big)\Big]_{\frac{E_i}{k_{\mathrm{B}}T}}^{+\infty} . \tag{4.325}$$

However,

$$\Big[-\ln\Big(1+\exp(\kappa-\chi)\Big)\Big]_{\frac{E_i}{k_{\mathrm{B}}T}}^{+\infty} = 0 + \ln\left(1+\exp\left(\kappa - \frac{E_i}{k_{\mathrm{B}}T}\right)\right), \tag{4.326}$$

thus,

$$\boxed{n(\vec{r}) = \frac{m^* k_{\mathrm{B}} T}{\pi \hbar^2} \sum_i |\zeta_i(z)|^2 \ln\left(1+\exp\left(\frac{\mu(T)-E_i}{k_{\mathrm{B}}T}\right)\right) = n(z)} \tag{4.327}$$

For $T = 0$,

$$f_0(\varepsilon) = \begin{cases} 1, & \varepsilon \leq E_{\mathrm{F}} \\ 0, & \varepsilon > E_{\mathrm{F}} \end{cases} = \Theta(E_{\mathrm{F}} - \varepsilon), \tag{4.328}$$

where E_{F} is the so-called Fermi energy, i.e., the chemical potential at temperature $T = 0$ $[\, E_{\mathrm{F}} := \mu(0)]$. Substituting to the definition (4.320), we obtain

$$n(\vec{r}) = \int_{-\infty}^{E_{\mathrm{F}}} d\varepsilon \; \frac{m^* S}{\pi \hbar^2} \sum_i \Theta(\varepsilon - E_i) \, 1 \, \frac{1}{S} |\zeta_i(z)|^2, \tag{4.329}$$

$$n(\vec{r}) = \frac{m^*}{\pi \hbar^2} \sum_i |\zeta_i(z)|^2 \int_{-\infty}^{E_{\mathrm{F}}} d\varepsilon \; \Theta(\varepsilon - E_i), \tag{4.330}$$

$$n(\vec{r}) = \frac{m^*}{\pi \hbar^2} \sum_{\substack{i \\ \text{occupied}}} |\zeta_i(z)|^2 \int_{E_i}^{E_{\mathrm{F}}} d\varepsilon . \tag{4.331}$$

Only the occupied levels contribute now. In conclusion, we obtain the formula

$$\boxed{n(\vec{r}) = \frac{m^*}{\pi \hbar^2} \sum_{\substack{i \\ \text{occupied}}} |\zeta_i(z)|^2 \, (E_{\mathrm{F}} - E_i) = n(z)} \tag{4.332}$$

4.11 Spatial electron density, electron energy density, total number of electrons.

As seen in Eq. (4.320) of the previous Section 4.10, the spatial electron density is defined as

$$n(\vec{r}) := \int_{-\infty}^{+\infty} d\varepsilon \; g(\varepsilon) \; f_0(\varepsilon) \; \left| \varphi_{i,k_x,k_y}(\vec{r}) \right|^2 . \tag{4.333}$$

Similarly, the electron energy density is defined as

$$n(\varepsilon) := \int_{\text{everywhere}} d^3 r \; g(\varepsilon) \; f_0(\varepsilon) \; \left| \varphi_{i,k_x,k_y}(\vec{r}) \right|^2 , \tag{4.334}$$

while the total number of electrons is

$$N := \int_{-\infty}^{+\infty} d\varepsilon \int_{\text{everywhere}} d^3 r \; g(\varepsilon) \; f_0(\varepsilon) \; \left| \varphi_{i,k_x,k_y}(\vec{r}) \right|^2 , \tag{4.335}$$

since

$$N := \int_{\text{everywhere}} d^3r \, n(\vec{r}). \tag{4.336}$$

In the context of electronic devices, the sheet (or surface) electron density

$$N_{\text{s}} := \frac{N}{S}. \tag{4.337}$$

is used. Using Eq. 4.327, which holds for all temperatures T, we obtain

$$N := \int_{\text{everywhere}} d^3r \, \frac{m^* k_{\text{B}} T}{\pi \hbar^2} \sum_i |\zeta_i(z)|^2 \ln\left(1 + \exp\left(\frac{\mu(T) - E_i}{k_{\text{B}} T}\right)\right) \Rightarrow \tag{4.338}$$

$$N = \frac{m^* S k_{\text{B}} T}{\pi \hbar^2} \sum_i \ln\left(1 + \exp\left(\frac{\mu(T) - E_i}{k_{\text{B}} T}\right)\right), \tag{4.339}$$

while, using Eq. 4.332, which holds for $T = 0$, we obtain

$$N := \int_{\text{everywhere}} d^3r \, \frac{m^*}{\pi \hbar^2} \sum_{\substack{i \\ \text{occupied}}} |\zeta_i(z)|^2 \, (E_{\text{F}} - E_i) \Rightarrow \tag{4.340}$$

$$N = \frac{m^* S}{\pi \hbar^2} \sum_{\substack{i \\ \text{occupied}}} (E_{\text{F}} - E_i). \tag{4.341}$$

Let us provide an example, to obtain a better understanding of the orders of magnitude we are discussing. Suppose $S = 1\ \text{cm}^2$, $m^* = 0.067\, m_e$ (GaAs), and a single occupied state with $E_{\text{F}} - E_i = 30$ meV. Then $N \approx \frac{0.067\ 9.1\ 10^{-31}\ 10^{-4}}{\pi\ 1.054^2\ 10^{-68}}\ 30\ 10^{-3}\ 1.602\ 10^{-19} \approx 0.9\ 10^{12}$, hence the surface electron density is $N_{\text{s}} \approx 0.9\ 10^{12}\ \text{cm}^{-2}$.

4.12 Density of eigenstates of a quasi one-dimensional electron gas.

It is left as an exercise to prove that, in the case of a quasi one-dimensional electron gas, with free states along the x-direction and bound states along the y-, z-directions, the envelope eigenfunctions are given by the expression

$$\varphi_{i,j,k_x}(\vec{r}) = \frac{1}{\sqrt{L_x}} e^{ik_x x} v_j(y) \zeta_i(z) \tag{4.342}$$

and the corresponding eigenenergies by the expression

$$E_{i,j,k_x} = E_i + E_j + \frac{\hbar^2 k_x^2}{2m^*}, \tag{4.343}$$

where k_x is “continuous” and i, j are discrete.

From the definition of the density of eigenstates [Eq. (4.304)], using Eq. (4.343), we sum over all the “continuous” and discrete indices. Here, k_x is “continuous” and i, j are discrete. In other words,

$$g(\varepsilon) = 2 \sum_{i,j,k_x} \delta\left(\varepsilon - E_i - E_j - \frac{\hbar^2 k_x^2}{2m^*}\right). \tag{4.344}$$

Imposing periodic boundary conditions along the x-axis, we have

$$e^{ik_x\left(-\frac{L_x}{2}\right)} = e^{ik_x\left(\frac{L_x}{2}\right)} \Rightarrow e^{ik_xL_x} = 1 = e^{i2\pi n_x}, n_x \in \mathscr{Z} \Rightarrow k_x = \frac{2\pi n_x}{L_x} \Rightarrow \Delta k_x = \frac{2\pi}{L_x}\Delta n_x, \tag{4.345}$$

where $\Delta n_x = 1$. Hence, Eq. (4.344) becomes

$$g(\varepsilon) = 2\sum_{i,j,k_x} \delta\left(\varepsilon - E_i - E_j - \frac{\hbar^2 k_x^2}{2m^*}\right)\Delta n_x = 2\frac{L_x}{2\pi}\sum_{i,j,k_x} \delta\left(\varepsilon - E_i - E_j - \frac{\hbar^2 k_x^2}{2m^*}\right)\Delta k_x. \tag{4.346}$$

Now, let us suppose that

$$\Delta k_x \to dk_x \quad \text{assuming} \quad L_x \to \infty \text{ or, better, } >> L_y, L_z. \tag{4.347}$$

Therefore,

$$g(\varepsilon) = \frac{L_x}{\pi}\sum_{i,j}\int_{-\infty}^{\infty} dk_x \delta\left(\varepsilon - E_i - E_j - \frac{\hbar^2 k_x^2}{2m^*}\right) = 2\frac{L_x}{\pi}\sum_{i,j}\int_{0}^{\infty} dk_x \delta\left(\varepsilon - E_i - E_j - \frac{\hbar^2 k_x^2}{2m^*}\right). \tag{4.348}$$

We now perform the variable change

$$\chi = \frac{\hbar^2 k_x^2}{2m^*} \quad \Rightarrow \quad d\chi = \frac{\hbar^2}{m^*}k_x dk_x \quad \Rightarrow \quad dk_x = \frac{\sqrt{m^*}}{\hbar\sqrt{2}}\frac{d\chi}{\sqrt{\chi}}. \tag{4.349}$$

Hence,

$$g(\varepsilon) = 2\frac{L_x}{\pi}\frac{\sqrt{m^*}}{\hbar\sqrt{2}}\sum_{i,j}\int_0^{\infty} d\chi \frac{1}{\sqrt{\chi}}\delta\left(\varepsilon - E_i - E_j - \chi\right). \tag{4.350}$$

Thus,

$$\boxed{g(\varepsilon) = \frac{L_x\sqrt{2m^*}}{\pi\hbar}\sum_{i,j}\frac{1}{\sqrt{\varepsilon - E_i - E_j}}\Theta(\varepsilon - E_i - E_j)} \tag{4.351}$$

The density of (eigen)states, with its characteristic saw-tooth form and the so-called van Hove singularities, where the DOS gets infinite approaching from above, is presented in Figure 4.22.

4.13 Density of eigenstates of a three-dimensional electron gas.

It is left as an exercise to prove that, in the case of a three-dimensional electron gas, with free states along all the x, y, z-directions, the envelope eigenfunctions are given by the expression

$$\varphi_{i,j,k_x}(\vec{r}) = \frac{1}{\sqrt{V}}\, e^{ik_x x}e^{ik_y y}e^{ik_z z}, \tag{4.352}$$

where $V = L_xL_yL_z$, and the corresponding eigenenergies by the expression

$$E_{k_x,k_y,k_z} = \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m^*} = \frac{\hbar^2 k^2}{2m^*}, \tag{4.353}$$

where k_x, k_y, k_z are “continuous” indices.

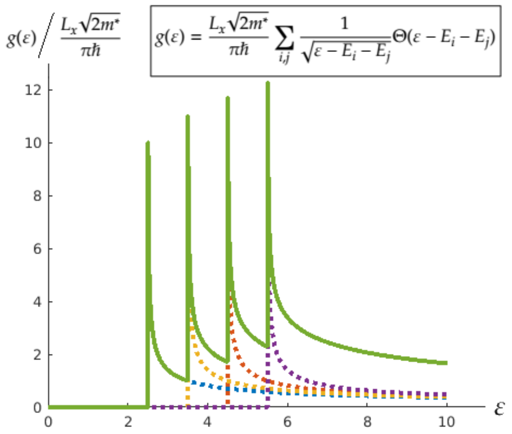

Figure 4.22: Density of (eigen)states of a quasi one-dimensional electron gas with its characteristic saw-tooth form and the so-called van Hove singularities. In this specific example, we have put $E_{i=0} = 0.5$, $E_{i=1} = 1.5$, $E_{j=0} = 2$, $E_{j=1} = 4$, in arbitrary units, just to make the figure.

From the definition of the density of eigenstates [Eq. (4.304)], using Eq. (4.353), we sum over all the "continuous" indices. In other words,

$$g(\varepsilon) = 2\sum_{k_x,k_y,k_z}\delta\left(\varepsilon - \frac{\hbar^2k^2}{2m^*}\right). \tag{4.354}$$

Imposing periodic boundary conditions along the x-axis, we have

$$e^{ik_x\left(-\frac{L_x}{2}\right)} = e^{ik_x\left(\frac{L_x}{2}\right)} \Rightarrow e^{ik_xL_x} = 1 = e^{i2\pi n_x}, n_x \in \mathscr{Z} \Rightarrow k_x = \frac{2\pi n_x}{L_x} \Rightarrow \Delta k_x = \frac{2\pi}{L_x}\Delta n_x, \tag{4.355}$$

where $\Delta n_x = 1$. Similarly,

$$\Delta k_y = \frac{2\pi}{L_y}\Delta n_y, \quad \Delta k_z = \frac{2\pi}{L_z}\Delta n_z, \tag{4.356}$$

where $\Delta n_y = \Delta n_z = 1$. Therefore, Eq. (4.354) becomes

$$g(\varepsilon) = 2\sum_{k_x,k_y,k_z}\delta\left(\varepsilon - \frac{\hbar^2k^2}{2m^*}\right)\Delta n_x\Delta n_y\Delta n_z = \frac{2V}{(2\pi)^3}\sum_{k_x,k_y,k_z}\delta\left(\varepsilon - \frac{\hbar^2k^2}{2m^*}\right)\Delta k_x\Delta k_y\Delta k_z. \tag{4.357}$$

Now, let us suppose that

$$\Delta k_x \to dk_x \quad \text{assuming} \quad L_x \to \infty \tag{4.358}$$
$$\Delta k_y \to dk_y \quad \text{assuming} \quad L_y \to \infty \tag{4.359}$$
$$\Delta k_z \to dk_z \quad \text{assuming} \quad L_z \to \infty. \tag{4.360}$$

In this "qualitative" fashion, we conclude that

$$g(\varepsilon) = \frac{2V}{(8\pi)^3}\int_{-\infty}^{\infty}dk_x\int_{-\infty}^{\infty}dk_y\int_{-\infty}^{\infty}dk_z\delta\left(\varepsilon - \frac{\hbar^2k^2}{2m^*}\right). \tag{4.361}$$

which, of course, can also be implied by a known theorem. Changing to spherical coordinates, the above relationship becomes

$$g(\varepsilon) = \frac{V}{4\pi^3}\int_0^{\infty}4\pi k^2dk\delta\left(\varepsilon - \frac{\hbar^2k^2}{2m^*}\right). \tag{4.362}$$

We now perform the variable change

$$\chi = \frac{\hbar^2 k^2}{2m^*} \quad \Rightarrow \quad d\chi = \frac{\hbar^2}{m^*} k dk \quad \Rightarrow \quad dk = \frac{\sqrt{m^*}}{\hbar\sqrt{2}} \frac{d\chi}{\sqrt{\chi}}. \tag{4.363}$$

Hence,

$$g(\varepsilon) = \frac{V m^{*\frac{3}{2}} \sqrt{2}}{\pi^2 \hbar^3} \int_0^\infty d\chi \frac{\chi}{\sqrt{\chi}} \delta(\varepsilon - \chi) \, . \tag{4.364}$$

Thus,

$$\boxed{g(\varepsilon) = \frac{V m^{*\frac{3}{2}} \sqrt{2}}{\pi^2 \hbar^3} \sqrt{\varepsilon}\, \Theta(\varepsilon)}. \tag{4.365}$$

The density of (eigen)states, which, in contrast to the previous cases, is a continuous function of energy, is presented in Figure 4.23.

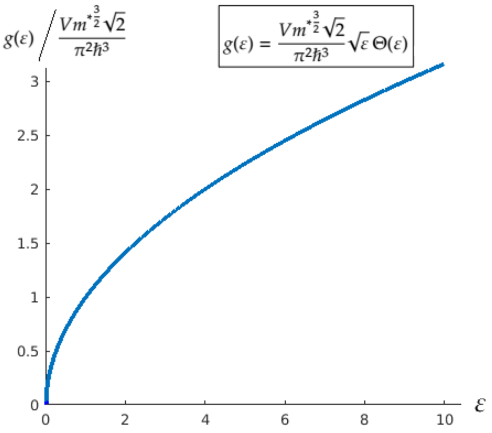

Figure 4.23: Density of (eigen)states of a three-dimensional electron gas.

More for continuous spectrum in solids, energy bands, and so on can be found in classical solid state physics books, for example in [16], [18], [19], [20].

4.14 Degrees of Freedom: translational, vibrational, rotational.

Simply, degrees of freedom of a physical system are the number of independent ways in which it may move. These are translational, vibrational or rotational. Alternatively, the minimum number of independent variables required to describe completely the state of the system. Classically, a molecule with N atoms has $3N$ degrees of freedom. Its center of mass can move in 3 directions, x, y, z, therefore, it has 3 translational degrees of freedom. Hence, there remain $3N - 3$ vibrational and rotational degrees of freedom.

We will give an example of a diatomic molecule, A-B. The molecule can vibrate along the line connecting the two atoms. [Let us suppose that this line lies along the x-axis.] Therefore, it has one vibrational degree of freedom. It can also rotate around the perpendicular directions at the line connecting the two atoms, i.e., here around the y- and the z-axis. Therefore it has 2 rotational degrees of freedom.

Generally, if a molecule is linear, it has 2 rotational degrees of freedom, hence, there remain $3\text{N} - 5$ vibrational degrees of freedom. If a molecule is non-linear, it has 3 rotational degrees of freedom, hence, there remain $3N - 6$ vibrational degrees of freedom. In the quantum world, these movements correspond to different quantum numbers. For more, see a Physical Chemistry book, e.g. [21].

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CHAPTER 5

SEMICLASSICAL APPROXIMATION I

In this Chapter:

We discuss the semiclassical approach of the electromagnetic (EM) field - two-level, three-level, multi-level system (2LS, 3LS, MLS) interaction. We manipulate the EM field classically, while 2LS, 3LS, MLS are treated quantum mechanically, that is, as a set of eigenstates. We introduce the dipole approximation, after having discussed briefly the electric dipole moment and its analogies with the magnetic dipole moment. Unperturbed is the system without EM field. The perturbed system, i.e., the system subjected to EM field, is manipulated with time-dependent perturbation theory. We arrive at a linear system of differential equations. We evaluate the perturbation potential energy matrix elements. We give analytical solutions for 2LS, 3LS, MLS within the rotating wave approximation (RWA). We encounter for the first time Rabi oscillations, i.e., time-dependent probabilities to find the electron at the levels. We introduce the Rabi frequency, which expresses the magnitude and the effectiveness of the perturbation, i.e., of the entanglement with the EM field. For the solution of the differential equations we use the eigenvalue method, which is more general, but also other alternatives. We calculate approximatively the Einstein coefficients. For the 3LS we use a viable, analytically solvable, variation, with equidistant levels in one dimension, an hypothesis that we keep for the MLS, which we solve finally. Relative helpful references are [1, 2, 3, 4, 5, 6].
Prerequisite knowledge: Basic knowledge of Electromagnetism, Quantum Physics, and Mathematics.

Let us recall some necessary abbreviations: 1LS = single-level system, 2LS = two-level system, 3LS = three-level system, MLS = multi-level system. For example, a 2LS may be two consecutive levels of an atom, molecule, quantum dot (or nanoparticle). This is schematically depicted in Figure 5.1, together with relevant quantities: the eigenenergies of the two levels E_2 and E_1, the angular frequency of the EM field, ω, the energy distance between the two levels, $\hbar\Omega$, the Rabi frequency, Ω_R, which shows how much the two levels are tangled by the EM field, and the detuning, $\Delta = \omega - \Omega$.

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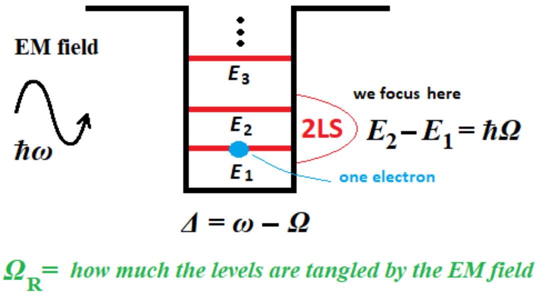

Figure 5.1: Schematically, a two-level system (2LS) and relevant quantities: eigenenergies of the two levels, E_2 and E_1, angular frequency of the EM field, ω, energy distance between the two levels, $\hbar\Omega$, Rabi frequency, Ω_R, which shows how much the two levels are tangled by the EM field, and detuning, $\Delta = \omega - \Omega$.

5.1 Semiclassical treatment. EM field: classically. Two-level system: quantum mechanically.

Semiclassical treatment means that while the two-level system (e.g., atom, quantum dot, nanoparticle, color center, etc.) is treated quantum mechanically as an eigenstate system, the EM field is treated classically. The EM field is considered as an external, time-dependent perturbation. Moreover, we consider that the EM field is so dense that photon absorption or emission by the two-level system of study cannot substantially affect the amplitudes of the electric and magnetic fields. If we are interested fluctuations of the EM field density, we need to abandon the semiclassical approximation. This is done in Chapter 8, where the 2LS - EM field complex is studied in its full quantum mechanical form; that is, in Chapter 8 we will treat the EM field quantum mechanically, as well.

5.2 Unperturbed system, i.e., without an EM field.

Let us consider the electronic Hamiltonian in the unperturbed two-level system,

$$\hat{H}_0 = \frac{\hat{\vec{p}}^{\,2}}{2m_e} + U(\vec{r}). \tag{5.1}$$

For example, in the hydrogen atom, the potential (Coulomb) energy is

$$U(\vec{r}) = (-e)\frac{1}{4\pi\varepsilon_0}\frac{e}{r} = \frac{-e^2}{4\pi\varepsilon_0 r}, \tag{5.2}$$

where e is the elementary charge. In a multi-electron system with atomic number Z the potential (Coulomb) energy is

$$U(\vec{r}) = \frac{-Ze^2}{4\pi\varepsilon_0 r}. \tag{5.3}$$

We can alternatively consider the screened form of the potential energy, i.e.,

$$U_S(\vec{r}) = \frac{-Ze^2}{4\pi\varepsilon_0 r}e^{-k_0 r}. \tag{5.4}$$

Generally, the Coulomb potential has the form

$$V(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{Ze}{r}, \tag{5.5}$$

while the screened Coulomb potential has the form

$$V_S(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{Ze}{r}e^{-k_0 r}, \tag{5.6}$$

where k_0 is the strength of the damping factor or Thomas-Fermi wave vector. The screened potential $V_S(\vec{r})$ is also called the Thomas-Fermi or Yukawa potential. The above potentials and potential energies are, in final analysis, dependent on r and not $\vec{r}$; that means that they are central potentials and central potential energies. The Yukawa potential drops faster than the Coulomb potential, due to the factor $e^{-k_0 r}$; this is depicted in Figure 5.2.

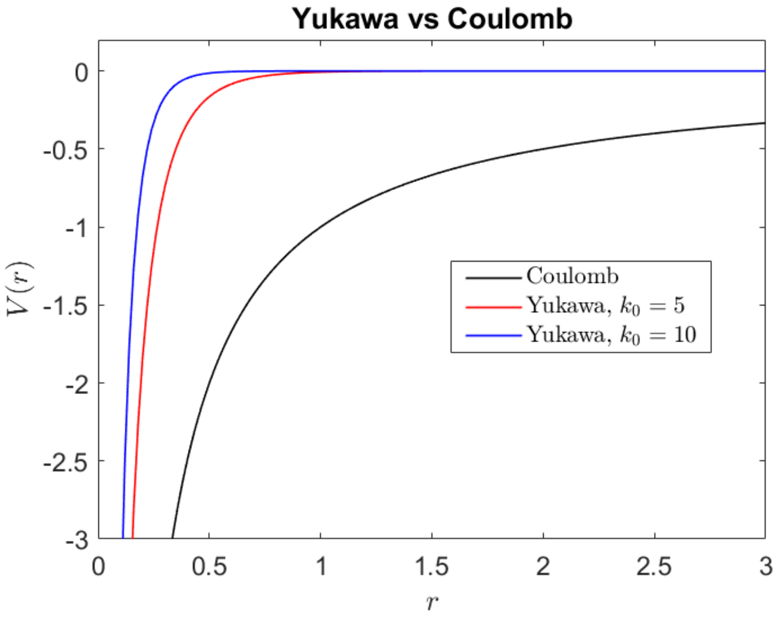

Figure 5.2: Comparison of the Yukawa and Coulomb potential energies, which are here simplified as $V_{\text{Yukawa}}(r) = -\frac{1}{r}e^{-k_0 r}$ and $V_{\text{Coulomb}}(r) = -\frac{1}{r}$. r, k_0 are dimensionless and positive. The Coulomb potential energy has an effect in larger distances, while the Yukawa potential energy drops more rapidly, due to the factor $e^{-k_0 r}$.

Let us consider the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} = \hat{H}_0\Psi(\vec{r},t) \tag{5.7}$$

where $\Psi(\vec{r},t)$ is the wavefunction of the unperturbed electron. Furthermore, let us assume the separation of variables

$$\Psi(\vec{r},t) = \Phi(\vec{r})\, T(t). \tag{5.8}$$

$\frac{(5.7)}{(5.8)} \Rightarrow \Phi(\vec{r})i\hbar\frac{dT(t)}{dt} = T(t)\hat{H}_0\Phi(\vec{r}) \Rightarrow \frac{i\hbar}{T(t)}\frac{dT(t)}{dt} = \frac{\hat{H}_0\Phi(\vec{r})}{\Phi(\vec{r})}$, for $T(t) \neq 0 \neq \Phi(\vec{r})$. [If $T(t) = 0$ or $\Phi(\vec{r}) = 0$, then Eq. 5.7 is trivially satisfied]. However, for the last equation to be satisfied $\forall\, t$ and $\forall\, \vec{r}$, it must hold that

$$\frac{i\hbar}{T(t)}\frac{dT(t)}{dt} = \frac{\hat{H}_0\Phi(\vec{r})}{\Phi(\vec{r})} = E\ (\text{CONSTANT}) \tag{5.9}$$

since the one part depends solely on t and the other part depends solely on $\vec{r}$. Thus,

1. $\hat{H}_0\Phi(\vec{r}) = E\Phi(\vec{r})$, hence E are the energy eigenvalues, generally distinct, which are characterized by some "collective number" k, i.e.,

$$\hat{H}_0\Phi_k(\vec{r}) = E_k\Phi_k(\vec{r}). \tag{5.10}$$

2. $\dfrac{dT}{T} = \dfrac{Edt}{i\hbar} \Rightarrow \ln T = -\dfrac{iEt}{\hbar} + c \Rightarrow T(t) = e^c e^{-\frac{iEt}{\hbar}} \Rightarrow$

$$T(t) = \mathscr{N} e^{-\frac{iEt}{\hbar}}. \tag{5.11}$$

Therefore, wrapping this up

$$\Psi_k(\vec{r}, t) = \mathscr{N} e^{-\frac{iE_k t}{\hbar}}\Phi_k(\vec{r}), \tag{5.12}$$

where $\mathscr{N}$ is a normalization constant. The eigenstates of the UNPERTURBED PROBLEM are described by

$$\hat{H}_0\Phi_k(\vec{r}) = E_k\Phi_k(\vec{r}), \tag{5.13}$$

where E_k are the eigenenergies and $\Phi_k(\vec{r})$ the orthonormal eigenfunctions. In addition, we define

$$E_k := \hbar\Omega_k. \tag{5.14}$$

Let us demand

$$\int \left|\Psi_k(\vec{r}, t)\right|^2 dV = 1 \Leftrightarrow |\ |\mathscr{N}|^2 \cancelto{1}{\int \left|\Phi_k(\vec{r})\right|^2 dV} = 1. \tag{5.15}$$

This is why we called $\mathscr{N}$ a normalization constant and assumed that $\Phi_k(\vec{r})$ are orthonormal. $dV = d^3r$ is the elementary volume and k a collective quantum number. For example, in the hydrogen atom, $k = \{n, \ell, m_\ell\}$. In the hydrogen atom, the eigenfunction $\Phi_k(r, \theta, \phi)$ corresponds to the eigenvalue

$$E_k = \frac{-R_E}{n^2} = E_n, \tag{5.16}$$

where

$$R_E = \frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2} \simeq 13.6 \text{ eV} \tag{5.17}$$

is the Rydberg energy. More details on the hydrogen atom can be found in Chapter 7.

5.3 Perturbed system. Time-dependent perturbation theory. Dipole moment. Dipole approximation.

5.3.1 Arriving at a Linear System of Differential Equations.

Let us consider the hydrogen Hamiltonian in the perturbed 2LS, i.e., subject to an EM field

$$\hat{H} = \hat{H}_0 + U_{\mathscr{E}}(\vec{r}, t) \tag{5.18}$$

and assume that the potential energy of the perturbation, $U_{\mathscr{E}}(\vec{r}, t)$, is adequately **small** compared to $\hat{H}_0$. We want to solve the problem

$$i\hbar\frac{\partial\Psi(\vec{r}, t)}{\partial t} = \hat{H}\Psi(\vec{r}, t) \tag{5.19}$$

under the initial condition

$$\Psi(\vec{r}, 0) = \Phi(\vec{r}) = \text{known}. \tag{5.20}$$

We assume that we can expand both $\Psi(\vec{r},0)=\Phi(\vec{r})$ and $\Psi(\vec{r},t)$ over the eigenfunctions of the unperturbed problem $\Phi_k(\vec{r})$. Therefore, we can write

$$\Phi(\vec{r}) = \sum_k f_k \Phi_k(\vec{r}), \tag{5.21}$$

$$\Psi(\vec{r},t) = \sum_k C_k(t) e^{-i\Omega_k t}\Phi_k(\vec{r}), \tag{5.22}$$

thus,

$$C_k(0) = f_k. \tag{5.23}$$

From Equations 5.18, 5.19, 5.22 it occurs that

$$i\hbar\frac{\partial}{\partial t}\Big[\sum_k C_k(t)e^{-i\Omega_k t}\Phi_k(\vec{r})\Big] = \Big[\hat{H}_0 + U_{\mathscr{E}}(\vec{r},t)\Big]\Big[\sum_k C_k(t)e^{-i\Omega_k t}\Phi_k(\vec{r})\Big]. \tag{5.24}$$

Let us calculate the two hand-sides of Eq. 5.24. For the left hand-side, which we call A′, we have:

$$A' = i\hbar\sum_k \dot{C}_k(t)e^{-i\Omega_k t}\Phi_k(\vec{r}) + i\hbar\sum_k C_k(t)(-i\Omega_k)e^{-i\Omega_k t}\Phi_k(\vec{r}).$$

Therefore, due to Eq. 5.14, it occurs that

$$A' = i\hbar\sum_k \dot{C}_k(t)e^{-i\Omega_k t}\Phi_k(\vec{r}) + \sum_k C_k(t)E_k e^{-i\Omega_k t}\Phi_k(\vec{r}).$$

For the right-hand side, which we call B′, we have:

$$B' = \sum_k C_k(t)e^{-i\Omega_k t}E_k\Phi_k(\vec{r}) + \sum_k C_k(t)e^{-i\Omega_k t}U_{\mathscr{E}}(\vec{r},t)\Phi_k(\vec{r}).$$

Thus, by eliminating the second term of A′ and the first term of B′, it occurs that

$$i\hbar\sum_k \dot{C}_k(t)e^{-i\Omega_k t}\Phi_k(\vec{r}) = \sum_k C_k(t)e^{-i\Omega_k t}U_{\mathscr{E}}(\vec{r},t)\Phi_k(\vec{r}). \tag{5.25}$$

Now, we exploit the fact that $\Phi_k(\vec{r})$ are orthonormal. We multiply Eq.(5.25) by $\Phi^*_{k'}(\vec{r})$ and integrate over space, i.e.,

$$i\hbar\sum_k \dot{C}_k(t)e^{-i\Omega_k t}\int \Phi^*_{k'}(\vec{r})\Phi_k(\vec{r})dV = \sum_k C_k(t)e^{-i\Omega_k t}\int \Phi^*_{k'}(\vec{r})U_{\mathscr{E}}(\vec{r},t)\Phi_k(\vec{r})dV \tag{5.26}$$

However, since $\Phi_k(\vec{r})$ are orthonormal,

$$\int \Phi^*_{k'}(\vec{r})\Phi_k(\vec{r})dV = \delta_{k'k},$$

the above equation becomes,

$$i\hbar\dot{C}_{k'}(t)e^{-i\Omega_{k'}t} = \sum_k C_k(t)e^{-i\Omega_k t}U_{\mathscr{E}k'k}(t), \tag{5.27}$$

where

$$U_{\mathscr{E}k'k}(t) = \int \Phi^*_{k'}(\vec{r})U_{\mathscr{E}}(\vec{r},t)\Phi_k(\vec{r})dV = \langle\Phi_{k'}|U_{\mathscr{E}}(\vec{r},t)|\Phi_k\rangle \tag{5.28}$$

are the matrix element of the potential energy of the perturbation. Generally, the matrix elements of any given physical quantity, M, are defined as

$$\boxed{M_{k'k} := \int dV \Phi^*_{k'}(\vec{r})\hat{M}(\vec{r}, -i\hbar\vec{\nabla})\Phi_k(\vec{r}) = \langle \Phi_{k'}|U_{\mathscr{E}}(\vec{r},t)|\Phi_k\rangle} \tag{5.29}$$

More on this subject can be found in Appendix B.6, where the two formalisms are discussed in more detail.

So, we finally arrive at

$$\boxed{\dot{C}_{k'}(t) = \frac{-i}{\hbar}\sum_k C_k(t)e^{i(\Omega_{k'}-\Omega_k)t}U_{\mathscr{E}k'k}(t)} \tag{5.30}$$

In other words, we arrive at a Linear System of First Order Differential Equations. Solving the problem of Eq. 5.30) is identical to solving the problem of Eqs. 5.18, 5.19.

The above procedure constitutes the so-called time-dependent perturbation theory. We will apply it to a two-level system subject to a monochromatic and polarized electric wave, i.e., our perturbation will have these features. Afterwards, we will apply it to a three-level system, as well.

We notice that since $\int |\Psi(\vec{r},t)|^2 dV = 1 \Leftrightarrow \int \Psi^*(\vec{r},t)\Psi(\vec{r},t)dV = 1$,

$$\Rightarrow \int dV \sum_{k'} C^*_{k'}(t)e^{i\Omega_{k'}t}\Phi^*_{k'}(\vec{r}) \sum_k C_k(t)e^{-i\Omega_k t}\Phi_k(\vec{r}) = 1 \Rightarrow$$

$$\Rightarrow \sum_{k'}\sum_k C^*_{k'}(t)C_k(t)e^{i(\Omega_{k'}-\Omega_k)t}\int dV\Phi^*_{k'}(\vec{r})\Phi_k(\vec{r}) = 1 \Rightarrow$$

$$\boxed{\sum_k |C_k(t)|^2 = 1} \Rightarrow \sum_k |C_k(0)|^2 = 1 \Rightarrow \boxed{\sum_k |f_k|^2 = 1} \tag{5.31}$$

5.3.2 Dipole moments.

Suppose an electric dipole PM (P: plus, M: minus) with charge $q > 0$ at P and $-q < 0$ at M. The electric dipole moment is defined as

$$\vec{\mathscr{P}} := q\vec{d} \tag{5.32}$$

where $\vec{d} = \overrightarrow{\mathrm{MP}}$. In Figure 5.3 we consider the hydrogen atom, so the electric charge on the nucleus N ≡ P is $q = e > 0$, while, on the position of the electron E ≡ M, it is $-q = -e < 0$. Additionally, $\vec{d} = \overrightarrow{\mathrm{MP}} = \overrightarrow{\mathrm{EN}}$. If the axes origin is O, we call $\vec{r}_E$ the position vector of the electron relative to O, $\vec{R}$ the position vector of the nucleus relative to O, while $\vec{r} = \overrightarrow{\mathrm{NE}} = \overrightarrow{\mathrm{PM}}$ is the position vector of the electron relative to the nucleus. Then, $\vec{d} = -\vec{r}$, hence

$$\vec{\mathscr{P}} = q\vec{d} = e(-\vec{r}) = -e\vec{r} \tag{5.33}$$

We now restrict ourselves to forces coming form the electric field traveling monochromatic and polarized EM wave

$$\boxed{\vec{\mathscr{E}} = \vec{\mathscr{E}}_a \exp\left[i(\vec{k}\cdot\vec{r}_H - \omega t + \phi)\right]}$$

where $\vec{\mathscr{E}}_a$ determined the polarization of the wave and $\omega = 2\pi\nu$ is the angular frequency (ν is the frequency). $\vec{k}$ is the wavevector with magnitude $k = 2\pi/\lambda$, where λ is the wavelength. ϕ is some arbitrary phase. However, we will assume that the position of the electron, $\vec{r}_H$, does not significantly differ from the position of the nucleus, $\vec{R}$, for the length scales that are of interest here. In other words, $\boxed{\vec{r}_H \simeq \vec{R}}$. The reason why we did so is that we consider optical wavelengths. If, e.g., $\lambda = 500$ nm, then, given that the

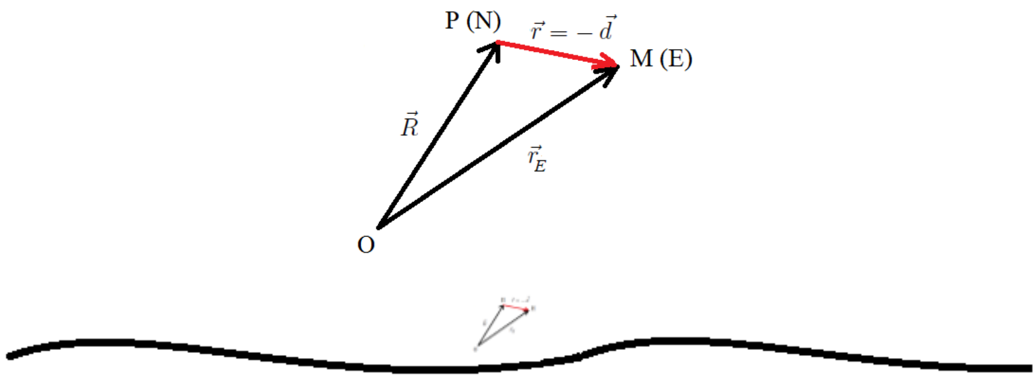

Figure 5.3: (Upper panel) The axes origin O, the positive charge P (plus), which can be represented by the nucleus N in an atom, the negative charge M (minus), which can be represented by one electron E moving around the nucleus. We define $\vec{d} := \overrightarrow{MP}$. Usually, when studying an atom, we consider the position vector of the electron relative to the nucleus $\overrightarrow{NE} = \vec{r} = -\vec{d}$. The electric dipole moment is defined as $\vec{\mathscr{P}} := q\vec{d}$ something that we can therefore write $\vec{\mathscr{P}} = -e\vec{r}$, if we refer to e.g. the hydrogen atom. For the latter case, we notice the vectors $\overrightarrow{OP} := \vec{R}$ and $\overrightarrow{OE} := \vec{r}_E$. (Lower panel) Very schematically: Under these conditions, the wave length is much larger than the spatial extent of the system, something like $\lambda >> \alpha$; thus, the electric field is practically homogeneous. For example, for optical wavelengths, $\lambda \sim 500$ nm, and for the hydrogen atom $\alpha \sim \alpha_0$ (Bohr radius), hence, $\lambda/a_0 \sim 10^4$. The triangle OPM (ONE), which is shown in the upper panel, is shown in the lower panel smaller than the wavelength, but in fact it is much ($\sim 10^4$ times) smaller.

size of the electron's' 'trajectory" is of the order of the Bohr radius, $a_0 \simeq 0.529$ Å $= 0.529 \cdot 10^{-10}$ m $\simeq 0.5 \cdot 10^{-1}$ nm, it occurs that

$$\frac{\lambda}{a_0} = \frac{500\,\text{nm}}{0.5 \cdot 10^{-1}\,\text{nm}} = \frac{5 \cdot 10^2}{5 \cdot 10^{-2}} = 10^4 \Rightarrow \lambda >> a_0 \sim |\vec{r}|$$

Thus, the electric field is practicaly homogeneous, it is practically not space-dependent. Therefore,

$$\vec{\mathscr{E}} \approx \vec{\mathscr{E}}_a \exp\left[i(\vec{k} \cdot \vec{R} - \omega t + \phi)\right] = \underbrace{\vec{\mathscr{E}}_a \exp\left[i(\vec{k} \cdot \vec{R} + \phi)\right]}_{\vec{\mathscr{E}}_0} \exp(-i\omega t),$$

hence,

$$\boxed{\vec{\mathscr{E}} = \vec{\mathscr{E}}_0 \exp(-i\omega t) = \vec{\mathscr{E}}(t)}. \tag{5.34}$$

In other words, we incorporated the factor $\exp\left[i(\vec{k} \cdot \vec{R} + \phi)\right]$ into the amplitude, assuming that the electric field has practically ONLY SPATIAL dependence.

Additionally, let us use the symbol V to denote potential and the symbol U to denote potential energy. We can write

$$\left.\begin{array}{l} \vec{\mathscr{E}} = -\vec{\nabla} V \\ dV = \dfrac{\partial V}{\partial x}dx + \dfrac{\partial V}{\partial y}dy + \dfrac{\partial V}{\partial z}dz = \vec{\nabla} V \cdot d\vec{r} \end{array}\right\} \Rightarrow dV = -\vec{\mathscr{E}} \cdot d\vec{r} \Rightarrow$$

$$V(\vec{r}, t) - \overset{\text{set to 0}}{\cancel{V(\vec{0}, t)}} = -\vec{\mathscr{E}} \cdot \vec{r}$$

It is implied that for this to happen during integration we assumed that $\vec{\mathscr{E}}$ is space-independent. If we multiply by $(-e)$, we find the potential energy of the electron due to the perturbation

$$U(\vec{r},t) - \overset{\text{we have set to 0}}{\cancel{U(\vec{0},t)}} = e\vec{\mathscr{E}}\cdot\vec{r}$$

hence, from Eq. 5.33 it occurs that

$$\boxed{U(\vec{r},t) = e\vec{\mathscr{E}}\cdot\vec{r} = -\vec{\mathscr{P}}\cdot\vec{\mathscr{E}}(t)} \tag{5.35}$$

The above set of assumptions, which led to the perturbation potential energy of Eq. 5.35, is called the **dipole approximation.**

Next, we remind the reader of some analogies between the electric and magnetic fields, as we list the electric dipole moment, magnetic dipole moment, potential energy of electric dipole, potential energy of magnetic dipole and the respective torques. $\vec{L}$ is the orbital momentum, $\vec{S}$ is the spin, and g a dimensionless factor.

Analogies Reminder

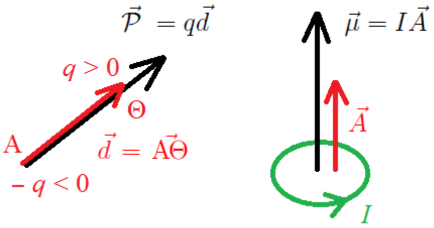

Figure 5.4: Electric and magnetic dipole.

$\vec{\mathscr{E}}$ (Electric Field)	$\vec{B}$ (Magnetic Field)
$\vec{\mathscr{P}} = q\vec{d}$ electric dipole moment	$\vec{\mu} = I\vec{A}$ magnetic dipole moment
	or $\vec{\mu} = (q/2m)(\vec{L} + g\vec{S})$
$U_{\mathscr{E}} = -\vec{\mathscr{P}}\cdot\vec{\mathscr{E}}$ potential energy	$U_B = -\vec{\mu}\cdot\vec{B}$ potential energy
$\vec{\tau} = \vec{\mathscr{P}}\times\vec{\mathscr{E}}$ torque	$\vec{\tau} = \vec{\mu}\times\vec{B}$ torque
$[\vec{\mathscr{P}}] = \mathrm{Cm}$	$[\vec{\mu}] = \mathrm{Am}^2$
$[U_{\mathscr{E}}] = \mathrm{Cm}\dfrac{\mathrm{N}}{\mathrm{C}} = \mathrm{Nm} = \mathrm{J}$	$[U_B] = \mathrm{Am}^2\dfrac{\mathrm{N}}{\mathrm{Am}} = \mathrm{Nm} = \mathrm{J}$
$[\vec{\tau}] = \mathrm{Cm}\dfrac{\mathrm{N}}{\mathrm{C}} = \mathrm{Nm}$	$[\vec{\tau}] = \mathrm{Am}^2\dfrac{\mathrm{N}}{\mathrm{Am}} = \mathrm{Nm}$

We have shown that, for optical wavelengths, we can write (Eq. 5.34)

$$\boxed{\vec{\mathscr{E}} = \vec{\mathscr{E}}_0 \exp(-i\omega t) = \vec{\mathscr{E}}(t)}$$

Considering that polarization occurs along the z-direction and taking the real part of Eq. 5.34, we obtain

$$\boxed{\vec{\mathscr{E}}(t) = \mathscr{E}_0\,\hat{z}\,\cos\omega t}$$

Hence,

$$U_{\mathscr{E}} = -\vec{\mathscr{P}}\cdot\vec{\mathscr{E}} = -(-e)\vec{r}\cdot\mathscr{E}_0\,\hat{z}\,\cos\omega t \Rightarrow$$

$$\boxed{U_{\mathscr{E}} = e\mathscr{E}_0\,z\,\cos\omega t} \tag{5.36}$$

5.3.3 Matrix elements of the perturbation potential energy.

Let us now focus on the matrix elements of the potential energy of the perturbation

$$U_{\mathscr{E}k'k}(t) = \int dV \Phi^*_{k'}(\vec{r}) U_{\mathscr{E}}(\vec{r},t) \Phi_k(\vec{r}) = \int dV \Phi^*_{k'}(\vec{r})\, z\, \Phi_k(\vec{r})\; e\mathscr{E}_0 \cos\omega t \Rightarrow$$

$$\boxed{U_{\mathscr{E}k'k}(t) = e\mathscr{E}_0 \cos\omega t \int dV \Phi^*_{k'}(\vec{r})\, z\, \Phi_k(\vec{r})} \tag{5.37}$$

Let us denote the matrix elements of the z coordinate as

$$z_{k'k} := \int dV \Phi^*_{k'}(\vec{r})\, z\, \Phi_k(\vec{r}). \tag{5.38}$$

These have the properties

$$\begin{aligned} z^*_{k'k} &= z_{kk'} \\ z_{kk} &= \int dV \underbrace{|\Phi_k(\vec{r})|^2}_{\text{even}} \; \underbrace{z}_{\text{odd}} = 0 \end{aligned} \tag{5.39}$$

Hence, the non-diagonal elements are symmetric, while the diagonal elements become zero. The latter property occurs due to the fact that in systems such as atoms, quantum wells, etc, the eigenfunctions are either even or odd. Therefore, their squared magnitude is an even function.

Finally, the matrix elements of the potential energy of the perturbation can be written as

$$\boxed{U_{\mathscr{E}k'k}(t) = e\mathscr{E}_0 \cos\omega t\; z_{k'k}} \tag{5.40}$$

In Figure 5.5 we present a two-level system. This can be composed of the two lowest levels of an atom, a quantum dot, etc. We commonly choose the photons of the EM field to closely match the energy difference between the two levels, i.e., $\hbar\omega = h\nu \sim E_2 - E_1$; however this doesn't mean that they have to be perfectly matching. This assumption will prove itself useful afterwards, when we introduce the Rotating Wave Approximation. For a two-level system ($k = 1$ or $k = 2$) we can write

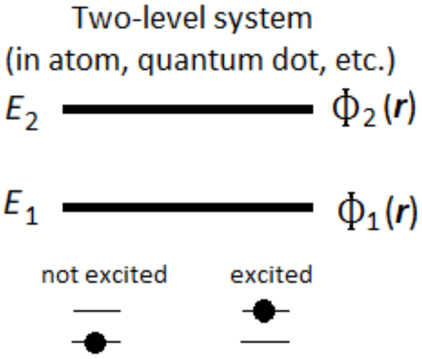

Figure 5.5: A two-level system. When the electron is at the lower level, E_1, the system is characterized as unexcited, while when it is at the upper level, E_2, the system is characterized as excited.

$$\begin{aligned} U_{\mathscr{E}12}(t) &= e\mathscr{E}_0 \cos\omega t\; z_{12} \\ U_{\mathscr{E}21}(t) &= e\mathscr{E}_0 \cos\omega t\; z_{21} \\ U_{\mathscr{E}kk}(t) &= e\mathscr{E}_0 \cos\omega t\; z_{kk} = 0 \end{aligned} \qquad \text{or} \qquad \begin{aligned} U_{\mathscr{E}12}(t) &= -\mathscr{P}_{z12}\,\mathscr{E}_0 \cos\omega t \\ U_{\mathscr{E}21}(t) &= -\mathscr{P}_{z21}\,\mathscr{E}_0 \cos\omega t \\ U_{\mathscr{E}kk}(t) &= 0 \end{aligned}$$

The second column is deduced by the first since $\vec{\mathscr{P}} = -e\vec{r} \Rightarrow \mathscr{P}_z = -ez$, hence the respective matrix elements are $\mathscr{P}_{zk'k} = -ez_{k'k}$. Thus, Eq. 5.40 becomes

$$\boxed{U_{\mathscr{E}k'k}(t) = -\mathscr{P}_{zk'k}\,\mathscr{E}_0 \cos\omega t} \tag{5.41}$$

If our eigenfunctions are real, then for our two-level system it holds that

$$\boxed{\mathscr{P}_{z12} = -ez_{12} = -ez_{21} = \mathscr{P}_{z21} := \mathscr{P}_z := \mathscr{P}} \tag{5.42}$$

and this $\mathscr{P}$ is used in the next section. Therefore

$$\begin{aligned} U_{\mathscr{E}12}(t) &= -\mathscr{P}\,\mathscr{E}_0 \cos\omega t \\ U_{\mathscr{E}21}(t) &= -\mathscr{P}\,\mathscr{E}_0 \cos\omega t \\ U_{\mathscr{E}kk}(t) &= 0,\ k = 1 \text{ ή } k = 2 \end{aligned}$$

Hence, Eq. 5.41 becomes

$$\boxed{\begin{array}{ll} U_{\mathscr{E}k'k}(t) = -\mathscr{P}\,\mathscr{E}_0 \cos\omega t & k \neq k' \\ U_{\mathscr{E}k'k}(t) = 0 & k = k' \end{array}} \tag{5.43}$$

which means that **the magnitude of the perturbation is proportional to** $\mathscr{P}\mathscr{E}_0$. This is expressed by the **Rabi frequency** $\Omega_R = \dfrac{\mathscr{P}\mathscr{E}_0}{\hbar}$. The detuning (see Eq. 5.49) and the Rabi frequency (see Eq. 5.50) determine the period and amplitude of the oscillations within the two-level system, as it will be shown below.

5.4 Equations describing the time-evolution of a two-level system. Rabi frequency. Rotating Wave Approximation (RWA).

We had arrived at a Linear System of First Order Differential Equations (Eq. 5.30) which, if solved, essentially solves the problem of Eqs. 5.18, 5.19. Eq. 5.30 was

$$\boxed{\dot{C}_{k'}(t) = \frac{-i}{\hbar} \sum_k C_k(t) e^{i(\Omega_{k'}-\Omega_k)t} U_{\mathscr{E}k'k}(t)}$$

We will now solve it for a two-level system. We define

$$\boxed{\Omega := \Omega_2 - \Omega_1 = \frac{E_2 - E_1}{\hbar}}, \tag{5.44}$$

where Eq. 5.14 was used. We will also use the identity $\cos\omega t = \dfrac{e^{i\omega t} + e^{-i\omega t}}{2}$.

$$\boxed{k' = 1} \qquad \dot{C}_1(t) = -\frac{i}{\hbar} C_1(t) \cancelto{1}{e^{i(\Omega_1-\Omega_1)t}} \cancelto{0}{U_{\mathscr{E}11}(t)} - \frac{i}{\hbar} C_2(t)\, e^{i(\Omega_1-\Omega_2)t}\, U_{\mathscr{E}12}(t)$$

$$\dot{C}_1(t) = -\frac{i}{\hbar} C_2(t)\, e^{-i\Omega t} \left(-\mathscr{E}_0\right) \mathscr{P} \cos\omega t = \frac{i\mathscr{E}_0\,\mathscr{P}}{\hbar} C_2(t)\, e^{-i\Omega t} \left\{\frac{e^{i\omega t} + e^{-i\omega t}}{2}\right\}$$

$$\boxed{\dot{C}_1(t) = \frac{i\mathscr{E}_0\,\mathscr{P}}{2\hbar} \left[e^{-i(\Omega-\omega)t} + e^{-i(\Omega+\omega)t}\right] C_2(t)} \tag{5.45}$$

$$\boxed{k' = 2} \qquad \dot{C}_2(t) = -\frac{i}{\hbar}\, C_1(t)\, e^{i(\Omega_2-\Omega_1)t}\, U_{\mathscr{E}21}(t) - \frac{i}{\hbar}\, C_2(t) \cancelto{1}{e^{i(\Omega_2-\Omega_2)t}} \cancelto{0}{U_{\mathscr{E}22}(t)}$$

$$\dot{C}_2(t) = -\frac{i}{\hbar}\, C_1(t)\, e^{i\Omega t}\, (-\mathscr{E}_0)\, \mathscr{P}\, \cos\omega t = \frac{i\mathscr{E}_0\, \mathscr{P}}{\hbar}\, C_1(t)\, e^{i\Omega t} \left\{ \frac{e^{i\omega t} + e^{-i\omega t}}{2} \right\}$$

$$\boxed{\dot{C}_2(t) = \frac{i\mathscr{E}_0\, \mathscr{P}}{2\hbar} \left[e^{i(\Omega+\omega)t} + e^{i(\Omega-\omega)t} \right] C_1(t)} \tag{5.46}$$

Therefore, we have the following two equations, which describe the time-evolution of the two-level system

$$\boxed{\begin{aligned} \dot{C}_1(t) &= C_2(t) \frac{i\mathscr{E}_0\, \mathscr{P}}{2\hbar} \left[e^{-i(\Omega-\omega)t} \quad + \quad \cancelto{(0\ \text{RWA})}{e^{-i(\Omega+\omega)t}} \right] \\ \dot{C}_2(t) &= C_1(t) \frac{i\mathscr{E}_0\, \mathscr{P}}{2\hbar} \left[\cancelto{(0\ \text{RWA})}{e^{i(\Omega+\omega)t}} \quad + \quad e^{i(\Omega-\omega)t} \right] \end{aligned}} \tag{5.47}$$

Given that the photons of the EM field adequately match the energy difference between the two levels, without this meaning that they match perfectly, i.e., assuming that $\hbar\omega \sim E_2 - E_1$, it follows that $\omega \sim \Omega_2 - \Omega_1 = \Omega$. Therefore, terms containing $(\Omega - \omega)$ are changing slowly, while terms containing $(\Omega + \omega)$ are changing rapidly. Hence, in any remarkable time scale, these rapid oscillations will have on average zero (or, let us say, close to zero) effect on the results. The rotating wave approximation, (RWA) is the assertion that these rapid terms can be ignored. Thus, subsequent to the RWA, Equations 5.47 become

$$\boxed{\begin{aligned} \dot{C}_1(t) &= C_2(t) \frac{i}{2} \overbrace{\boxed{\frac{\mathscr{E}_0\, \mathscr{P}}{\hbar}}}^{\Omega_R} e^{-i \underbrace{\boxed{(\Omega-\omega)}}_{-\Delta} t} \\ \dot{C}_2(t) &= C_1(t) \frac{i}{2} \underbrace{\boxed{\frac{\mathscr{E}_0\, \mathscr{P}}{\hbar}}}_{\Omega_R} e^{i \underbrace{\boxed{(\Omega-\omega)}}_{-\Delta} t} \end{aligned}} \tag{5.48}$$

We have defined detuning as

$$\boxed{\Delta := \omega - \Omega} \tag{5.49}$$

and the Rabi frequency[1] as

$$\boxed{\Omega_R := \frac{\mathscr{P}\mathscr{E}_0}{\hbar}} \tag{5.50}$$

Next, we will make a transformation to obtain a system of differential equations with time-independent coefficients. In other words,

$$\begin{aligned} C_1(t) &= \mathbb{C}_1(t)\, e^{\frac{-i(\Omega-\omega)t}{2}} \\ C_2(t) &= \mathbb{C}_2(t)\, e^{\frac{i(\Omega-\omega)t}{2}} \end{aligned} \tag{5.51}$$

$$\dot{C}_1(t) = \dot{\mathbb{C}}_1(t)\, e^{\frac{-i(\Omega-\omega)t}{2}} + \mathbb{C}_1(t) \left(\frac{-i(\Omega-\omega)}{2} \right) e^{\frac{-i(\Omega-\omega)t}{2}}$$

$$\dot{C}_2(t) = \dot{\mathbb{C}}_2(t)\, e^{\frac{i(\Omega-\omega)t}{2}} + \mathbb{C}_2(t) \left(\frac{i(\Omega-\omega)}{2} \right) e^{\frac{i(\Omega-\omega)t}{2}}$$

---

[1] After Isidor Isaak Rabi (1898-1988).

Hence, Eq. 5.48 becomes

$$\begin{cases} \dot{\mathbb{C}}_1(t)\, e^{\frac{-i(\Omega-\omega)t}{2}} + \mathbb{C}_1(t)\left(\frac{-i(\Omega-\omega)}{2}\right) e^{\frac{-i(\Omega-\omega)t}{2}} = \mathbb{C}_2(t)\, e^{\frac{i(\Omega-\omega)t}{2}}\ \frac{i\mathscr{E}_0\,\mathscr{P}}{2\hbar}\ e^{-i(\Omega-\omega)t} \\ \dot{\mathbb{C}}_2(t)\, e^{\frac{i(\Omega-\omega)t}{2}} + \mathbb{C}_2(t)\left(\frac{i(\Omega-\omega)}{2}\right) e^{\frac{i(\Omega-\omega)t}{2}} = \mathbb{C}_1(t)\, e^{\frac{-i(\Omega-\omega)t}{2}}\ \frac{i\mathscr{E}_0\,\mathscr{P}}{2\hbar}\ e^{i(\Omega-\omega)t} \end{cases}$$

$$\begin{cases} \dot{\mathbb{C}}_1(t) + \mathbb{C}_1(t)\left(\frac{-i(\Omega-\omega)}{2}\right) = \mathbb{C}_2(t)\, e^{\frac{i(\Omega-\omega)t}{2}}\ e^{\frac{i(\Omega-\omega)t}{2}}\ \frac{i\mathscr{E}_0\,\mathscr{P}}{2\hbar}\ e^{-i(\Omega-\omega)t} \\ \dot{\mathbb{C}}_2(t) + \mathbb{C}_2(t)\left(\frac{i(\Omega-\omega)}{2}\right) = \mathbb{C}_1(t)\, e^{-\frac{i(\Omega-\omega)t}{2}}\ e^{-\frac{i(\Omega-\omega)t}{2}}\ \frac{i\mathscr{E}_0\,\mathscr{P}}{2\hbar}\ e^{i(\Omega-\omega)t} \end{cases}$$

and, having defined $\Delta := \omega - \Omega$ (Eq. 5.49) and $\Omega_R := \frac{\mathscr{E}_0\,\mathscr{P}}{\hbar}$ (Eq. 5.50)

$$\begin{cases} \dot{\mathbb{C}}_1(t) = -\frac{i\Delta}{2}\,\mathbb{C}_1(t) + \frac{i\Omega_R}{2}\,\mathbb{C}_2(t) \\ \dot{\mathbb{C}}_2(t) = +\frac{i\Omega_R}{2}\,\mathbb{C}_1(t) + \frac{i\Delta}{2}\,\mathbb{C}_2(t) \end{cases}$$

Therefore, we arrive at a system of differential equations with time-independent coefficients:

$$\boxed{\begin{bmatrix} \dot{\mathbb{C}}_1(t) \\ \dot{\mathbb{C}}_2(t) \end{bmatrix} = \begin{bmatrix} -\frac{i\Delta}{2} & \frac{i\Omega_R}{2} \\ \frac{i\Omega_R}{2} & \frac{i\Delta}{2} \end{bmatrix} \begin{bmatrix} \mathbb{C}_1(t) \\ \mathbb{C}_2(t) \end{bmatrix}} \tag{5.52}$$

If our eigenfunctions were not real, then the upper-right matrix element would be $\frac{i\Omega_R^*}{2}$, thus, then we would define, e.g., $\mathscr{P}_{z21} = -ez_{21} := \mathscr{P}$, hence $\mathscr{P}_{z12} = -ez_{12} = \mathscr{P}_{z21}^* = \mathscr{P}^*$.

In order to solve the system of Eq. 5.52 we introduce the vector

$$\vec{x}(t) = \begin{bmatrix} \mathbb{C}_1(t) \\ \mathbb{C}_2(t) \end{bmatrix}. \tag{5.53}$$

Thus,

$$\dot{\vec{x}}(t) = \begin{bmatrix} \dot{\mathbb{C}}_1(t) \\ \dot{\mathbb{C}}_2(t) \end{bmatrix}, \tag{5.54}$$

and denoting

$$\tilde{A} = \begin{bmatrix} -\frac{i\Delta}{2} & \frac{i\Omega_R}{2} \\ \frac{i\Omega_R}{2} & \frac{i\Delta}{2} \end{bmatrix} := -i\mathrm{A} \Rightarrow \qquad \mathrm{A} = \begin{bmatrix} \frac{\Delta}{2} & -\frac{\Omega_R}{2} \\ -\frac{\Omega_R}{2} & -\frac{\Delta}{2} \end{bmatrix} \tag{5.55}$$

the system of Eq. 5.52 is written as

$$\boxed{\dot{\vec{x}}(t) = \tilde{A}\,\vec{x}(t)}. \tag{5.56}$$

Let us try solutions of the form

$$\vec{x}(t) = \vec{v}\, e^{\tilde{\lambda} t}, \tag{5.57}$$

hence,

$$\vec{v}\,\tilde{\lambda}\, e^{\tilde{\lambda} t} = \tilde{A}\,\vec{v}\, e^{\tilde{\lambda} t} \Rightarrow \left.\begin{matrix} \tilde{A}\vec{v} = \tilde{\lambda}\vec{v} \\ \tilde{\lambda} := -i\lambda \end{matrix}\right\} \Rightarrow -i\mathrm{A}\vec{v} = -i\lambda\vec{v} \Rightarrow \underbrace{\mathrm{A}\vec{v} = \lambda\vec{v}}_{\text{eigenvalue problem}}$$

Thus, the whole thing is essentially reduced to the eigenvalue problem

$$\boxed{\mathrm{A}\vec{v} = \lambda\vec{v}} \tag{5.58}$$

from which the normalized eigenvectors $\vec{v}_1, \vec{v}_2$, which correspond to the eigenvalues λ_1, λ_2, will occur. Having checked that the normalized eigenvectors $\vec{v}_1, \vec{v}_2$, which correspond to the eigenvalues λ_1, λ_2, are linearly independent, the solution to our problem is

$$\boxed{\vec{x}(t) = \sum_{k=1}^{2} c_k\, \vec{v}_k\, e^{-i\lambda_k t}}$$

where, of course, $\tilde{\lambda}_k = -i\lambda_k$. The initial conditions determine the coefficients c_k. But, first, let us obtain the eigenvalues.

$$\mathrm{A}\vec{v} = \lambda\vec{v} \Rightarrow \mathrm{A}\vec{v} - \lambda\mathrm{I}\vec{v} = 0 \Rightarrow (\mathrm{A} - \lambda\mathrm{I})\vec{v} = 0$$

where I is the 2×2 unit matrix. Thus,

$$\det(\mathrm{A} - \lambda\mathrm{I}) = 0 \Rightarrow \begin{bmatrix} \frac{\Delta}{2} - \lambda & -\frac{\Omega_R}{2} \\ -\frac{\Omega_R}{2} & -\frac{\Delta}{2} - \lambda \end{bmatrix} = 0 \Rightarrow$$

in the general case

$$\lambda_{2,1} = \pm\frac{\sqrt{\Omega_R^2 + \Delta^2}}{2}, \tag{5.59}$$

while, in the resonance case $(\Delta = 0)$

$$\lambda_{2,1} = \pm\frac{\Omega_R}{2}. \tag{5.60}$$

In the following pages, we will also find the eigenvectors, as well as the solution to the system of Eq. 5.52, imposing different initial conditions.

$\boxed{\text{SOLUTION for } \Delta = 0.}$

We present the analytical SOLUTION for $\Delta = 0$. If we assume that $\Delta := \omega - \Omega = 0$, then $\mathrm{A} = \begin{bmatrix} 0 & -\frac{\Omega_R}{2} \\ -\frac{\Omega_R}{2} & 0 \end{bmatrix}$ and $\lambda_{2,1} = \pm\frac{\Omega_R}{2}$

For $\boxed{\lambda_1 = -\frac{\Omega_R}{2}}$

$$\begin{bmatrix} 0 & -\frac{\Omega_R}{2} \\ -\frac{\Omega_R}{2} & 0 \end{bmatrix}\begin{bmatrix} v_{11} \\ v_{21} \end{bmatrix} = -\frac{\Omega_R}{2}\begin{bmatrix} v_{11} \\ v_{21} \end{bmatrix} \Rightarrow \left.\begin{matrix} -\frac{\Omega_R}{2}v_{21} = -\frac{\Omega_R}{2}v_{11} \\ -\frac{\Omega_R}{2}v_{11} = -\frac{\Omega_R}{2}v_{21} \end{matrix}\right\} \Rightarrow v_{21} = v_{11}$$

Thus, e.g., the normalized $\vec{v}_1 = \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix}$.

For $\boxed{\lambda_2 = \frac{\Omega_R}{2}}$

$$\begin{bmatrix} 0 & -\frac{\Omega_R}{2} \\ -\frac{\Omega_R}{2} & 0 \end{bmatrix}\begin{bmatrix} v_{12} \\ v_{22} \end{bmatrix} = \frac{\Omega_R}{2}\begin{bmatrix} v_{12} \\ v_{22} \end{bmatrix} \Rightarrow \left.\begin{matrix} -\dfrac{\Omega_R}{2}v_{22} = \dfrac{\Omega_R}{2}v_{12} \\ -\dfrac{\Omega_R}{2}v_{12} = \dfrac{\Omega_R}{2}v_{22} \end{matrix}\right\} \Rightarrow v_{22} = -v_{12}$$

Thus, e.g., the normalized $\vec{v}_2 = \begin{bmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{bmatrix}$.

Therefore,

$$\vec{x}(t) = \begin{bmatrix} \mathbb{C}_1(t) \\ \mathbb{C}_2(t) \end{bmatrix} = c_1\,\vec{v}_1\,e^{-i\lambda_1 t} + c_2\,\vec{v}_2\,e^{-i\lambda_2 t} = c_1\begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix} e^{i\frac{\Omega_R}{2}t} + c_2\begin{bmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{bmatrix} e^{-i\frac{\Omega_R}{2}t} \Rightarrow$$

$$\begin{bmatrix} C_1(t)\,e^{i\frac{(\Omega-\omega)}{2}t} \\ C_2(t)\,e^{-i\frac{(\Omega-\omega)}{2}t} \end{bmatrix} = \begin{bmatrix} \dfrac{c_1}{\sqrt{2}}e^{i\frac{\Omega_R}{2}t} + \dfrac{c_2}{\sqrt{2}}e^{-i\frac{\Omega_R}{2}t} \\ \dfrac{c_1}{\sqrt{2}}e^{i\frac{\Omega_R}{2}t} - \dfrac{c_2}{\sqrt{2}}e^{-i\frac{\Omega_R}{2}t} \end{bmatrix} \Rightarrow \text{(we assumed } \Delta = 0) \Rightarrow$$

$$\Rightarrow \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \begin{bmatrix} \dfrac{c_1}{\sqrt{2}}e^{i\frac{\Omega_R}{2}t} + \dfrac{c_2}{\sqrt{2}}e^{-i\frac{\Omega_R}{2}t} \\ \dfrac{c_1}{\sqrt{2}}e^{i\frac{\Omega_R}{2}t} - \dfrac{c_2}{\sqrt{2}}e^{-i\frac{\Omega_R}{2}t} \end{bmatrix} \tag{5.61}$$

Let the initial conditions be $C_1(0) = 1$ and $C_2(0) = 0$. Thus,

$$\left.\begin{matrix} 1 = \dfrac{c_1}{\sqrt{2}} + \dfrac{c_2}{\sqrt{2}} \Rightarrow c_1 + c_2 = \sqrt{2} \\ 0 = \dfrac{c_1}{\sqrt{2}} - \dfrac{c_2}{\sqrt{2}} \Rightarrow c_1 = c_2 \end{matrix}\right\} \Rightarrow c_1 = c_2 = \frac{\sqrt{2}}{2}$$

Therefore,

$$\begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \begin{bmatrix} \frac{1}{2}e^{i\frac{\Omega_R}{2}t} + \frac{1}{2}e^{-i\frac{\Omega_R}{2}t} \\ \frac{1}{2}e^{i\frac{\Omega_R}{2}t} - \frac{1}{2}e^{-i\frac{\Omega_R}{2}t} \end{bmatrix} = \begin{bmatrix} \cos\left(\dfrac{\Omega_R}{2}t\right) \\ i\sin\left(\dfrac{\Omega_R}{2}t\right) \end{bmatrix}$$

Hence,

$$\begin{aligned} C_1(t) &= \cos\left(\frac{\Omega_R}{2}t\right) \\ C_2(t) &= i\sin\left(\frac{\Omega_R}{2}t\right) \end{aligned} \tag{5.62}$$

and, thus,

$$\boxed{\begin{aligned} |C_1(t)|^2 &= \cos^2\left(\frac{\Omega_R}{2}t\right) \\ |C_2(t)|^2 &= \sin^2\left(\frac{\Omega_R}{2}t\right) \end{aligned}} \tag{5.63}$$

Of course, $|C_k(t)|^2 := P_k(t)$ is the probability that, at time t, the electron lies at level k. The period of the oscillations is

$$\boxed{T_R = \frac{2\pi}{\Omega_R}} \tag{5.64}$$

Let us denote $\mathscr{A}$ the maximum transfer percentage, i.e., the maximum probability to find it, e.g., at level 2, having placed it initially at level (the amplitude of the oscillation is $\mathscr{A}/2$.) Thus, in the case of resonance $(\omega = \Omega \Leftrightarrow \Delta = 0)$, we have

$$\boxed{\mathscr{A} = 1} \tag{5.65}$$

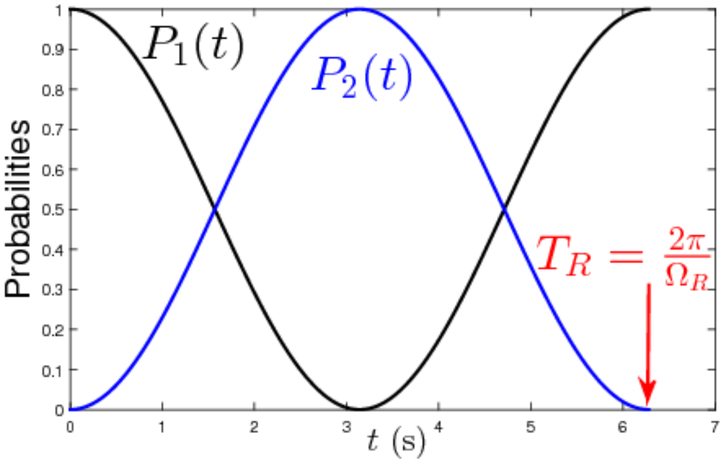

Figure 5.6: Oscillations of a two-level system at resonance, i.e., for $\omega = \Omega \Leftrightarrow \Delta = 0$. The period of the oscillations is $T_R = \frac{2\pi}{\Omega_R}$, while their maximum transfer percentage is $\mathscr{A} = 1$. We have assigned a typical value $\Omega_R = 1\ \mathrm{s}^{-1}$ without having in mind a particular system.

In the general case, the maximum transfer percentage depends on detuning, e.g. $\mathscr{A} = \frac{\Omega_R^2}{\Delta^2 + \Omega_R^2}$, as we will see in the following pages. In Figure 5.6, we present the oscillations of a two-level system at resonance.

We can also define the maximum transfer rate as the ratio between the maximum transfer percentage and the oscillation's period, i.e., as $\frac{\mathscr{A}}{T_R}$. For a two-level system at resonance, the maximum transfer rate is

$$\frac{\mathscr{A}}{T_R} = \frac{1}{\frac{2\pi}{\Omega_R}} = \frac{\Omega_R}{2\pi} \tag{5.66}$$

Finally, we can define the mean transfer rate as

$$\boxed{k = \frac{\langle |C_2(t)|^2 \rangle}{t_{2\mathrm{mean}}}}, \tag{5.67}$$

where $\langle |C_2(t)|^2 \rangle$ is the time-averaged probability to find the electron at the upper level and $t_{2\mathrm{mean}}$ is the time it takes so that the probability to find the electron to the upper level becomes equal to its average for the first time. For a two-level system at resonance, we have

$$\begin{aligned}\langle |C_2(t)|^2 \rangle &= \frac{1}{T_R}\int_0^{T_R} dt \cos^2\left(\frac{2\pi}{T_R}t\right) = \frac{1}{2T_R}\int_0^{T_R} dt \left(1 + \cos\left(\frac{4\pi}{T_R}t\right)\right) \\ &= \frac{1}{2T}\left(T + \frac{T_R}{4\pi}\sin\left(\frac{4\pi}{T_R}t\right)\Big|_0^{T_R}\right) = \frac{1}{2}\end{aligned} \tag{5.68}$$

and, for $t_{2\text{mean}}$, it holds that

$$\frac{1}{2} = \sin^2\left(\frac{\Omega_R}{2} t_{2\text{mean}}\right) = \frac{1}{2} - \frac{1}{2}\cos(\Omega_R t_{2\text{mean}}) \Rightarrow \cos(\Omega_R t_{2\text{mean}}) = 0 \Rightarrow \Omega_R t_{2\text{mean}} = \frac{\pi}{2} \Rightarrow$$

$$t_{2\text{mean}} = \frac{\pi}{2\Omega_R} \tag{5.69}$$

Therefore,

$$k = \frac{\Omega_R}{\pi}. \tag{5.70}$$

We observe that the ratio between the mean and the maximum transfer rate is, in our case, equal to 2, hence, the two rates are connected through the relationship

$$k = 2\frac{\mathscr{A}}{T_R}. \tag{5.71}$$

Let the initial conditions be $C_1(0) = \frac{1}{\sqrt{2}}e^{i\theta}$, $C_2(0) = \frac{1}{\sqrt{2}}e^{i\phi}$, with probability $|C_1(0)|^2 = |C_2(0)|^2 = \frac{1}{2}$. In other words, we assume that, at time 0, the electron is equally shared between the two levels, while we also assume an arbitrary phase difference. Thus,

$$\left.\begin{aligned} \frac{1}{\sqrt{2}}e^{i\theta} &= \frac{c_1}{\sqrt{2}} + \frac{c_2}{\sqrt{2}} \Rightarrow c_1 + c_2 = e^{i\theta} \\ \frac{1}{\sqrt{2}}e^{i\phi} &= \frac{c_1}{\sqrt{2}} - \frac{c_2}{\sqrt{2}} \Rightarrow c_1 - c_2 = e^{i\phi} \end{aligned}\right\}.$$

If we add and subtract the above two equations by parts, we conclude that

$$\left.\begin{aligned} 2c_1 &= e^{i\theta} + e^{i\phi} \Rightarrow c_1 = \frac{e^{i\theta} + e^{i\phi}}{2} \\ 2c_2 &= e^{i\theta} - e^{i\phi} \Rightarrow c_2 = \frac{e^{i\theta} - e^{i\phi}}{2} \end{aligned}\right\}.$$

Therefore,

$$\begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \begin{bmatrix} \frac{e^{i\theta}+e^{i\phi}}{2\sqrt{2}} e^{i\frac{\Omega_R}{2}t} + \frac{e^{i\theta}-e^{i\phi}}{2\sqrt{2}} e^{-i\frac{\Omega_R}{2}t} \\ \frac{e^{i\theta}+e^{i\phi}}{2\sqrt{2}} e^{i\frac{\Omega_R}{2}t} - \frac{e^{i\theta}-e^{i\phi}}{2\sqrt{2}} e^{-i\frac{\Omega_R}{2}t} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} e^{i\theta}\cos\left(\frac{\Omega_R}{2}t\right) + e^{i\phi} i \sin\left(\frac{\Omega_R}{2}t\right) \\ e^{i\theta} i \sin\left(\frac{\Omega_R}{2}t\right) + e^{i\phi}\cos\left(\frac{\Omega_R}{2}t\right) \end{bmatrix} \Rightarrow$$

$$\begin{bmatrix} |C_1(t)|^2 \\ |C_2(t)|^2 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} \cos^2\left(\frac{\Omega_R}{2}t\right) + \sin^2\left(\frac{\Omega_R}{2}t\right) + e^{i\theta}\cos\left(\frac{\Omega_R}{2}t\right)e^{-i\phi}(-i)\sin\left(\frac{\Omega_R}{2}t\right) + e^{i\phi} i \sin\left(\frac{\Omega_R}{2}t\right)e^{-i\theta}\cos\left(\frac{\Omega_R}{2}t\right) \\ \cos^2\left(\frac{\Omega_R}{2}t\right) + \sin^2\left(\frac{\Omega_R}{2}t\right) + e^{i\theta} i \sin\left(\frac{\Omega_R}{2}t\right)e^{-i\phi}\cos\left(\frac{\Omega_R}{2}t\right) + e^{i\phi}\cos\left(\frac{\Omega_R}{2}t\right)e^{-i\theta}(-i)\sin\left(\frac{\Omega_R}{2}t\right) \end{bmatrix}$$

$$= \frac{1}{2} \begin{bmatrix} 1 + \frac{i}{2}\cos\left(\frac{\Omega_R}{2}t\right)\sin\left(\frac{\Omega_R}{2}t\right)\left(e^{i(\phi-\theta)} - e^{i(\theta-\phi)}\right) \\ 1 + \frac{i}{2}\cos\left(\frac{\Omega_R}{2}t\right)\sin\left(\frac{\Omega_R}{2}t\right)\left(e^{i(\theta-\phi)} - e^{i(\phi-\theta)}\right) \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 + i\sin(\Omega_R t)(e^{i(\phi-\theta)} - e^{i(\theta-\phi)}) \\ 1 - i\sin(\Omega_R t)(e^{i(\phi-\theta)} - e^{i(\theta-\phi)}) \end{bmatrix}$$

Thus, if we also exploit the identity $e^{i\psi} - e^{-i\psi} = 2i\sin\psi$, we arrive at the expressions

$$\boxed{\begin{aligned} P_1(t) = |C_1(t)|^2 &= \frac{1}{2} + \frac{1}{2}\sin(\Omega_R t)\sin\left(\theta - \phi\right) \\ P_2(t) = |C_2(t)|^2 &= \frac{1}{2} - \frac{1}{2}\sin(\Omega_R t)\sin\left(\theta - \phi\right) \end{aligned}} \tag{5.72}$$

From the form of the above equations, we observe that, in the general case, there is an oscillation around the value $\frac{1}{2}$, which was the probability imposed by the initial conditions. The period of oscillation is always the same, $\mathrm{T} = \frac{2\pi}{\Omega_R}$, but its amplitude depends on the phase difference. However, we also observe that, if the coefficients are **in-phase**, i.e., if $\theta - \phi = 0$, then the time-dependence of the probabilities vanishes and it holds that $P_1(t) = P_2(t) = \frac{1}{2}, \forall\, t$. In Figure 5.7, we present the oscillations of a two-level system for these initial conditions, for different values of the phase difference.

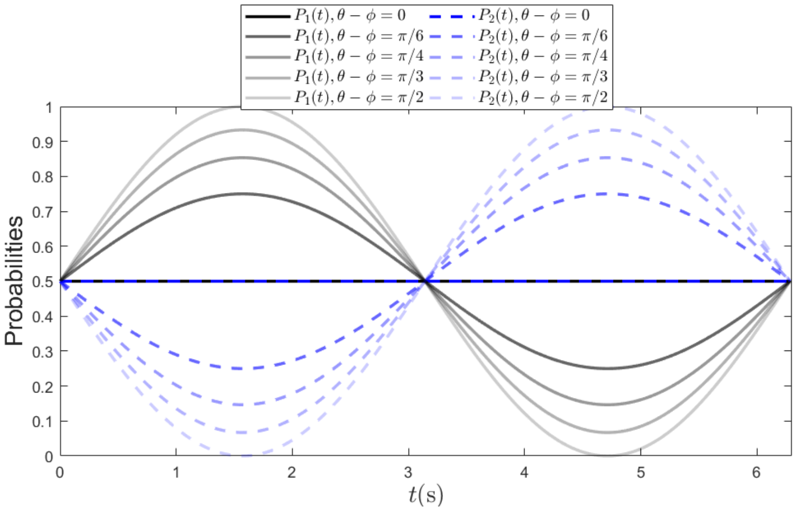

Figure 5.7: Oscillations of a two-level system at resonance, i.e., for $\omega = \Omega \Leftrightarrow \Delta = 0$, for the initial conditions $C_1(0) = \frac{1}{\sqrt{2}}e^{i\theta}, C_2(0) = \frac{1}{\sqrt{2}}e^{i\phi}$ and different values of the phase difference $\theta - \phi$. The period of the oscillations is $T_R = \frac{2\pi}{\Omega_R}$, while their maximum transfer percentage depends on the phase difference $\theta - \phi$. We have assigned a typical value $\Omega_R = 1\ \mathrm{s}^{-1}$ without having in mind a particular system.

Let the initial conditions be $C_1(0) = 0$ and $C_2(0) = 1$. Thus,

$$\left.\begin{aligned} 0 &= \frac{c_1}{\sqrt{2}} + \frac{c_2}{\sqrt{2}} \Rightarrow c_1 = -c_2 \\ 1 &= \frac{c_1}{\sqrt{2}} - \frac{c_2}{\sqrt{2}} \Rightarrow c_1 - c_2 = \sqrt{2} \end{aligned}\right\} \Rightarrow c_1 = -c_2 = \frac{\sqrt{2}}{2}$$

Therefore,

$$\begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \begin{bmatrix} \frac{1}{2}e^{i\frac{\Omega_R}{2}t} - \frac{1}{2}e^{-i\frac{\Omega_R}{2}t} \\ \frac{1}{2}e^{i\frac{\Omega_R}{2}t} + \frac{1}{2}e^{-i\frac{\Omega_R}{2}t} \end{bmatrix} = \begin{bmatrix} i\sin\left(\frac{\Omega_R}{2}t\right) \\ \cos\left(\frac{\Omega_R}{2}t\right) \end{bmatrix}$$

Hence,

$$C_1(t) = i\sin\left(\frac{\Omega_R}{2}t\right) C_2(t) \quad = \cos\left(\frac{\Omega_R}{2}t\right) \tag{5.73}$$

and, thus,

$$\boxed{\begin{aligned} |C_1(t)|^2 &= \sin^2\left(\frac{\Omega_R}{2}t\right) \\ |C_2(t)|^2 &= \cos^2\left(\frac{\Omega_R}{2}t\right) \end{aligned}} \tag{5.74}$$

Comparing to Equations 5.63, we observe that the situation is completely analogous to the case with initial conditions $C_1(0) = 0$ and $C_2(0) = 1$. Therefore, the period of the oscillation, the maximum transfer percentage, as well as the maximum and mean transfer rates will be the same, with the only difference that here they refer to the probability that the electron drops from the upper level to the lower one.

$\boxed{\text{SOLUTION for } \Delta \neq 0}$

$$A = \begin{bmatrix} \frac{\Delta}{2} & -\frac{\Omega_R}{2} \\ -\frac{\Omega_R}{2} & -\frac{\Delta}{2} \end{bmatrix} \text{ and } \lambda_{2,1} = \pm\frac{\sqrt{\Omega_R^2+\Delta^2}}{2}$$

$$\text{For } \boxed{\lambda_1 = -\frac{\sqrt{\Omega_R^2+\Delta^2}}{2} := -\lambda < 0}$$

$$\begin{bmatrix} \frac{\Delta}{2} & -\frac{\Omega_R}{2} \\ -\frac{\Omega_R}{2} & -\frac{\Delta}{2} \end{bmatrix}\begin{bmatrix} v_{11} \\ v_{21} \end{bmatrix} = -\frac{\sqrt{\Omega_R^2+\Delta^2}}{2}\begin{bmatrix} v_{11} \\ v_{21} \end{bmatrix} \Rightarrow$$

$$\frac{\Delta}{2}v_{11} - \frac{\Omega_R}{2}v_{21} = -\frac{\sqrt{\Omega_R^2+\Delta^2}}{2}v_{11} \Rightarrow \left(\frac{\Delta}{2} + \frac{\sqrt{\Omega_R^2+\Delta^2}}{2}\right)v_{11} = \frac{\Omega_R}{2}v_{21} \quad \text{(1st)}$$

$$-\frac{\Omega_R}{2}v_{11} - \frac{\Delta}{2}v_{21} = -\frac{\sqrt{\Omega_R^2+\Delta^2}}{2}v_{21} \Rightarrow -\frac{\Omega_R}{2}v_{11} = \left(\frac{\Delta}{2} - \frac{\sqrt{\Omega_R^2+\Delta^2}}{2}\right)v_{21} \quad \text{(2nd)}$$

$$\Rightarrow \left(\frac{\Delta}{2} + \frac{\sqrt{\Omega_R^2+\Delta^2}}{2}\right)v_{11} = \frac{\Omega_R}{2}\frac{-\frac{\Omega_R}{2}v_{11}}{\left(\frac{\Delta}{2} - \frac{\sqrt{\Omega_R^2+\Delta^2}}{2}\right)} \overset{*\,(\text{if } v_{11}\neq 0)}{\Longrightarrow}$$

$$\frac{\Delta^2}{4} - \frac{\Omega_R^2}{4} - \frac{\Delta^2}{4} = -\frac{\Omega_R^2}{4},$$

which holds. That is, it is sufficient that $\overset{*}{\boxed{v_{11} \neq 0}}$, thus, e.g., from (1st) it is implied that

$$\boxed{v_{21} = \frac{\frac{\Delta}{2} + \frac{\sqrt{\Omega_R^2+\Delta^2}}{2}}{\frac{\Omega_R}{2}}v_{11}} \quad \text{ή} \quad v_{21} = \alpha\, v_{11} \quad \text{thus} \quad \vec{v}_1 = \begin{bmatrix} \beta \\ \alpha\beta \end{bmatrix}$$

For it to be normalized, it must hold that $\beta^2 + \alpha^2\beta^2 = 1$, e.g., $\beta = \dfrac{1}{\sqrt{1+\alpha^2}} \Rightarrow \boxed{\vec{v}_1 = \begin{bmatrix} \frac{1}{\sqrt{1+\alpha^2}} \\ \frac{a}{\sqrt{1+\alpha^2}} \end{bmatrix}}$

For $\boxed{\lambda_2 = +\frac{\sqrt{\Omega_R^2+\Delta^2}}{2} := +\lambda > 0}$

$$\begin{bmatrix} \frac{\Delta}{2} & -\frac{\Omega_R}{2} \\ -\frac{\Omega_R}{2} & -\frac{\Delta}{2} \end{bmatrix}\begin{bmatrix} v_{12} \\ v_{22} \end{bmatrix} = \frac{\sqrt{\Omega_R^2+\Delta^2}}{2}\begin{bmatrix} v_{12} \\ v_{22} \end{bmatrix} \Rightarrow$$

$$\frac{\Delta}{2}v_{12} - \frac{\Omega_R}{2}v_{22} = \frac{\sqrt{\Omega_R^2+\Delta^2}}{2}v_{12} \Rightarrow \left(\frac{\Delta}{2} - \frac{\sqrt{\Omega_R^2+\Delta^2}}{2}\right)v_{12} = \frac{\Omega_R}{2}v_{22} \quad \text{(1st)}$$

$$-\frac{\Omega_R}{2}v_{12} - \frac{\Delta}{2}v_{22} = \frac{\sqrt{\Omega_R^2+\Delta^2}}{2}v_{22} \Rightarrow -\frac{\Omega_R}{2}v_{12} = \left(\frac{\Delta}{2} + \frac{\sqrt{\Omega_R^2+\Delta^2}}{2}\right)v_{22} \quad \text{(2nd)}$$

$$\Rightarrow \left(\frac{\Delta}{2} - \frac{\sqrt{\Omega_R^2+\Delta^2}}{2}\right)v_{12} = \frac{\Omega_R}{2}\frac{-\frac{\Omega_R}{2}v_{12}}{\left(\frac{\Delta}{2} + \frac{\sqrt{\Omega_R^2+\Delta^2}}{2}\right)} \overset{*\ (\text{if } v_{12}\neq 0)}{\Rightarrow}$$

$$\frac{\Delta^2}{4} - \frac{\Omega_R^2}{4} - \frac{\Delta^2}{4} = -\frac{\Omega_R^2}{4},$$

which holds. That is, it is sufficient that $\overset{*}{\boxed{v_{12} \neq 0}}$, thus, e.g., from (1st) it is implied that

$$\Rightarrow \boxed{v_{22} = \frac{\frac{\Delta}{2} - \frac{\sqrt{\Omega_R^2+\Delta^2}}{2}}{\frac{\Omega_R}{2}}v_{12}} \quad \text{ή} \quad v_{22} = \alpha' v_{12} \quad \text{thus} \quad \vec{v}_2 = \begin{bmatrix} \beta' \\ \alpha'\beta' \end{bmatrix}$$

For it to be normalized, it must hold that $\beta'^2 + \alpha'^2\beta'^2 = 1$, e.g., $\beta' = \frac{1}{\sqrt{1+\alpha'^2}} \Rightarrow \boxed{\vec{v}_2 = \begin{bmatrix} \frac{1}{\sqrt{1+\alpha'^2}} \\ \frac{\alpha'}{\sqrt{1+\alpha'^2}} \end{bmatrix}}$

Therefore,

$$\vec{x}(t) = \begin{bmatrix} \mathbb{C}_1(t) \\ \mathbb{C}_2(t) \end{bmatrix} = \begin{bmatrix} C_1(t)e^{-i\frac{\Delta}{2}t} \\ C_2(t)e^{i\frac{\Delta}{2}t} \end{bmatrix} = c_1\vec{v}_1e^{-i\lambda_1 t} + c_2\vec{v}_2e^{-i\lambda_2 t} = \begin{bmatrix} \frac{c_1}{\sqrt{1+\alpha^2}}e^{-i\lambda_1 t} + \frac{c_2}{\sqrt{1+\alpha'^2}}e^{-i\lambda_2 t} \\ \frac{c_1\alpha}{\sqrt{1+\alpha^2}}e^{-i\lambda_1 t} + \frac{c_2\alpha'}{\sqrt{1+\alpha'^2}}e^{-i\lambda_2 t} \end{bmatrix} \quad (5.75)$$

Let the initial conditions be $C_1(0) = 1, C_2(0) = 0$. Thus,

$$\begin{cases} 1 = \frac{c_1}{\sqrt{1+\alpha^2}} + \frac{c_2}{\sqrt{1+\alpha'^2}} \\ 0 = \frac{c_1\alpha}{\sqrt{1+\alpha^2}} + \frac{c_2\alpha'}{\sqrt{1+\alpha'^2}} \Rightarrow c_2 = -\frac{\alpha}{\alpha'}\frac{\sqrt{1+\alpha'^2}}{\sqrt{1+\alpha^2}}c_1 \end{cases}$$

$$\begin{cases} 1 = \dfrac{c_1}{\sqrt{1+\alpha^2}} - \dfrac{\alpha}{\alpha'} \dfrac{\cancel{\sqrt{1+\alpha'^2}}}{\sqrt{1+\alpha^2}} \dfrac{c_1}{\cancel{\sqrt{1+\alpha'^2}}} = c_1 \dfrac{\alpha' - \alpha}{\alpha' \sqrt{1+\alpha^2}} \Rightarrow \boxed{c_1 = \dfrac{\alpha' \sqrt{1+\alpha^2}}{\alpha' - \alpha}} \\ c_2 = -\dfrac{\alpha}{\alpha'} \dfrac{\sqrt{1+\alpha'^2}}{\cancel{\sqrt{1+\alpha^2}}} \dfrac{\alpha' \cancel{\sqrt{1+\alpha^2}}}{\alpha' - \alpha} \Rightarrow \boxed{c_2 = -\dfrac{\alpha \sqrt{1+\alpha'^2}}{\alpha' - \alpha}} \end{cases}$$

Therefore,

$$\begin{bmatrix} C_1(t) e^{-i\frac{\Delta}{2}t} \\ C_2(t) e^{i\frac{\Delta}{2}t} \end{bmatrix} = \begin{bmatrix} \frac{\alpha'}{\alpha'-\alpha} e^{-i\lambda_1 t} - \frac{\alpha}{\alpha'-\alpha} e^{-i\lambda_2 t} \\ \frac{\alpha\alpha'}{\alpha'-\alpha} e^{-i\lambda_1 t} - \frac{\alpha\alpha'}{\alpha'-\alpha} e^{-i\lambda_2 t} \end{bmatrix} \tag{5.76}$$

Let us calculate the coefficients that appear in the first equation of Eq. 5.76.

$$\alpha' - \alpha = \frac{\frac{\Delta}{2} - \frac{\sqrt{\Omega_R^2+\Delta^2}}{2} - \frac{\Delta}{2} - \frac{\sqrt{\Omega_R^2+\Delta^2}}{2}}{\frac{\Omega_R}{2}} = -\frac{2\sqrt{\Omega_R^2 + \Delta^2}}{\Omega_R}$$

$$\frac{\alpha'}{\alpha' - \alpha} = -\frac{\cancel{\Omega_R}}{2\sqrt{\Omega_R^2 + \Delta^2}} \frac{\Delta - \sqrt{\Omega_R^2 + \Delta^2}}{\cancel{\Omega_R}} = \frac{\sqrt{\Omega_R^2 + \Delta^2} - \Delta}{2\sqrt{\Omega_R^2 + \Delta^2}}$$

$$\frac{\alpha}{\alpha' - \alpha} = -\frac{\cancel{\Omega_R}}{2\sqrt{\Omega_R^2 + \Delta^2}} \frac{\Delta + \sqrt{\Omega_R^2 + \Delta^2}}{\cancel{\Omega_R}} = -\frac{\sqrt{\Omega_R^2 + \Delta^2} + \Delta}{2\sqrt{\Omega_R^2 + \Delta^2}}$$

Hence, the first equation becomes

$$C_1(t) e^{i\frac{\Delta}{2}t} = \underbrace{\frac{\sqrt{\Omega_R^2 + \Delta^2} - \Delta}{2\sqrt{\Omega_R^2 + \Delta^2}}}_{k_1} e^{i\lambda t} + \underbrace{\frac{\sqrt{\Omega_R^2 + \Delta^2} + \Delta}{2\sqrt{\Omega_R^2 + \Delta^2}}}_{k_2} e^{-i\lambda t} \Rightarrow$$

$$C_1(t) = (k_1 e^{i\lambda t} + k_2 e^{-i\lambda t}) e^{-i\frac{\Delta}{2}t} \Rightarrow$$

$$|C_1(t)|^2 = k_1^2 + k_2^2 + k_1 k_2 e^{2i\lambda t} + k_1 k_2 e^{-2i\lambda t} = k_1^2 + k_2^2 + 2k_1 k_2 \cos(2\lambda t) \Rightarrow$$

$$|C_1(t)|^2 = \frac{\Omega_R^2 + \Delta^2 + \Delta^2 - \cancel{2\Delta\sqrt{\Omega_R^2 + \Delta^2}}}{4(\Omega_R^2 + \Delta^2)} + \frac{\Omega_R^2 + \Delta^2 + \Delta^2 + \cancel{2\Delta\sqrt{\Omega_R^2 + \Delta^2}}}{4(\Omega_R^2 + \Delta^2)}$$

$$+ 2\frac{\Omega_R^2 + \cancel{\Delta^2} - \cancel{\Delta^2}}{4(\Omega_R^2 + \Delta^2)} \cos(2\lambda t) \Rightarrow$$

$$|C_1(t)|^2 = \frac{2(\Omega_R^2 + 2\Delta^2)}{4(\Omega_R^2 + \Delta^2)} + \frac{2\Omega_R^2}{4(\Omega_R^2 + \Delta^2)} \cos(2\lambda t) = \frac{\Omega_R^2 + 2\Delta^2 + \Omega_R^2 \cos(2\lambda t)}{2(\Omega_R^2 + \Delta^2)} \Rightarrow$$

$$\boxed{\begin{gathered} P_1(t) = |C_1(t)|^2 = 1 - \frac{\Omega_R^2}{\Omega_R^2 + \Delta^2} \sin^2(\lambda t) \\ \text{where } \lambda = \frac{\sqrt{\Omega_R^2 + \Delta^2}}{2} \end{gathered}} \tag{5.77}$$

The maximum value of $|C_1(t)|^2$ is 1, while its minimum value is $1 - \frac{\Omega_R^2}{\Omega_R^2 + \Delta^2}$. Therefore, the maximum transfer percentage is

$$\boxed{\mathscr{A} = \frac{\Omega_R^2}{\Omega_R^2 + \Delta^2}} \tag{5.78}$$

For $\Delta = 0$, $\Rightarrow |C_1(t)|^2 = \cos^2\left(\frac{\Omega_R t}{2}\right)$, as expected (Eq. 5.63).
Let us calculate the coefficient that appears in the second equation of Eq. 5.76.

$$\frac{\alpha\alpha'}{\alpha' - \alpha} = \frac{\sqrt{\Omega_R^2 + \Delta^2} + \Delta}{\Omega_R} \frac{\sqrt{\Omega_R^2 + \Delta^2} - \Delta}{2\sqrt{\Omega_R^2 + \Delta^2}} = \frac{\Omega_R^2 + \cancel{\Delta^2} - \cancel{\Delta^2}}{2\Omega_R\sqrt{\Omega_R^2 + \Delta^2}} = \frac{\Omega_R}{2\sqrt{\Omega_R^2 + \Delta^2}}$$

Hence, $C_2(t)e^{i\frac{\Delta}{2}t} = \frac{\Omega_R}{2\sqrt{\Omega_R^2 + \Delta^2}}e^{+i\lambda t} - \frac{\Omega_R}{2\sqrt{\Omega_R^2 + \Delta^2}}e^{-i\lambda t} = \frac{\Omega_R}{\sqrt{\Omega_R^2 + \Delta^2}}\, i\sin(\lambda t) \Rightarrow$

$$\boxed{\begin{aligned} P_2(t) = |C_2(t)|^2 &= \frac{\Omega_R^2}{\Omega_R^2 + \Delta^2}\ \sin^2(\lambda t) \\ \text{where } \lambda &= \frac{\sqrt{\Omega_R^2 + \Delta^2}}{2} \end{aligned}} \tag{5.79}$$

The maximum value of $|C_2(t)|^2$ is $\frac{\Omega_R^2}{\Omega_R^2 + \Delta^2}$, while its minimum value is 0. Therefore, the maximum transfer percentage is

$$\boxed{\mathscr{A} = \frac{\Omega_R^2}{\Omega_R^2 + \Delta^2}}$$

in accordance with Eq. 5.78.
For $\Delta = 0$, $|C_2(t)|^2 = \sin^2\left(\frac{\Omega_R t}{2}\right)$, as expected (Eq. 5.63).

As evident from Eqs. 5.77 and 5.79, the period of oscillations is

$$\boxed{T_R = \frac{2\pi}{2\lambda} = \frac{2\pi}{\sqrt{\Omega_R^2 + \Delta^2}}} \tag{5.80}$$

and for $\Delta = 0$ it follows that $T = {}^{2\pi}/_{\Omega_R}$, in accordance with Eq. 5.64. Furthermore, the maximum transfer percentage of the oscillations, as given by Eq. 5.78, for $\Delta = 0$ coincides with Eq. 5.65. Oscillations of a two-level system at resonance and out of resonance are presented in Figure 5.8. We remind that $P_k(t) = |C_k(t)|^2,\ k = 1, 2$ are the probabilities to find the electron at level k. From Eqs. 5.80 and 5.78 it is clear that as we move away from resonance, i.e., as $|\Delta|$ increases, the period and maximum transfer percentage of the oscillations become smaller; this is depicted in Figure 5.8.

The maximum transfer rate is

$$\frac{\mathscr{A}}{T_R} = \frac{\Omega_R^2\sqrt{\Omega_R^2 + \Delta^2}}{2\pi(\Omega_R^2 + \Delta^2)} = \frac{\Omega_R^2}{2\pi\sqrt{\Omega_R^2 + \Delta^2}} \tag{5.81}$$

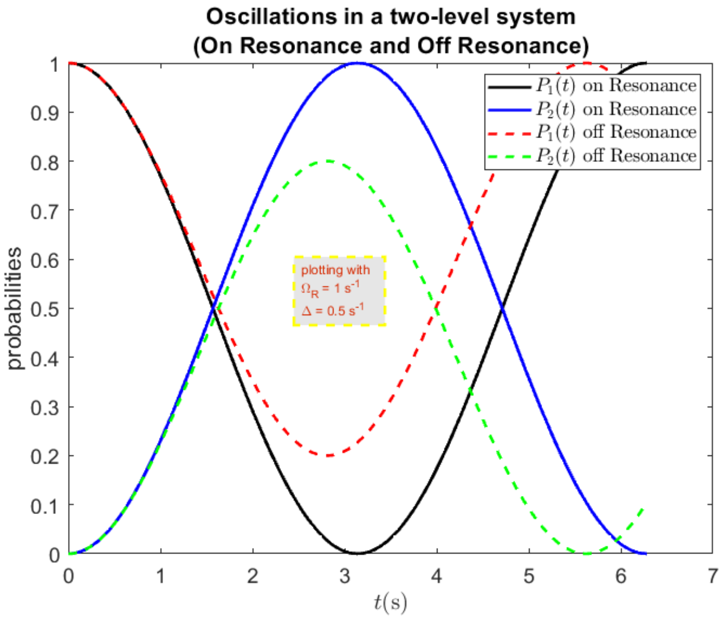

Figure 5.8: Oscillations of a two-level system at resonance ($\Delta = 0$, continuous lines) and out of resonance ($\Delta \neq 0$, dashed lines). The period of the oscillations is $T_{\mathrm{R}} = 2\pi/\sqrt{\Omega_{\mathrm{R}}^2 + \Delta^2}$, while, the maximum transfer percentage is $\mathscr{A} = \frac{\Omega_R^2}{\Omega_R^2+\Delta^2}$. We have assigned some typical values $\Omega_R = 1$ s^{-1} and $\Delta = 0.5$ s^{-1} without referring to a particular system. We observe changes in the period and maximum transfer percentage of the oscillations when the system is out of resonance. In Appendix C, there is the matlab program Oscillations.m, which creates this figure.

The time-averaged probabilities to find the electron at each level are

$$\begin{aligned}\langle |C_1(t)|^2\rangle &= \frac{1}{T_R}\int_0^{T_R} dt \left(1 - \frac{\Omega_R^2}{\Omega_R^2+\Delta^2}\sin^2\left(\frac{2\pi}{T_R}t\right)\right) = 1 - \frac{1}{2T_R}\frac{\Omega_R^2}{\Omega_R^2+\Delta^2}\int_0^{T_R} dt\left(1-\cos\left(\frac{4\pi}{T_R}t\right)\right)\\ &= 1 - \frac{1}{2T_R}\frac{\Omega_R^2}{\Omega_R^2+\Delta^2}\left(T_R - \frac{T_R}{4\pi}\sin\left(\frac{4\pi}{T_R}t\right)\Bigg|_0^{T_R}\right) = 1 - \frac{\Omega_R^2}{2(\Omega_R^2+\Delta^2)} = \frac{\Omega_R^2+2\Delta^2}{2(\Omega_R^2+\Delta^2)},\end{aligned} \tag{5.82}$$

$$\begin{aligned}\langle |C_2(t)|^2\rangle &= \frac{1}{T_R}\int_0^{T_R} dt \frac{\Omega_R^2}{\Omega_R^2+\Delta^2}\sin^2\left(\frac{2\pi}{T_R}t\right) = \frac{1}{2T_R}\frac{\Omega_R^2}{\Omega_R^2+\Delta^2}\int_0^{T_R} dt\left(1-\cos\left(\frac{4\pi}{T_R}t\right)\right)\\ &= \frac{1}{2T_R}\frac{\Omega_R^2}{\Omega_R^2+\Delta^2}\left(T_R - \frac{T_R}{4\pi}\sin\left(\frac{4\pi}{T_R}t\right)\Bigg|_0^{T_R}\right) = \frac{\Omega_R^2}{2(\Omega_R^2+\Delta^2)},\end{aligned} \tag{5.83}$$

while $t_{2\mathrm{mean}}$, i.e., the time it takes so that the probability to find the electron at the upper level becomes equal to its average value for the first time, can be found through the relationship

$$\frac{\Omega_R^2}{2(\Omega_R^2+\Delta^2)} = \frac{\Omega_R^2}{\Omega_R^2+\Delta^2}\sin^2\left(\frac{\sqrt{\Omega_R^2+\Delta^2}}{2}t_{2\mathrm{mean}}\right) \Rightarrow \sin^2\left(\frac{\sqrt{\Omega_R^2+\Delta^2}}{2}t_{2\mathrm{mean}}\right) = \frac{1}{2}$$

$$\Rightarrow \frac{1-\cos\left(\sqrt{\Omega_R^2+\Delta^2}t_{2\mathrm{mean}}\right)}{2} = \frac{1}{2} \Rightarrow \cos\left(\sqrt{\Omega_R^2+\Delta^2}t_{2\mathrm{mean}}\right) = 0 \Rightarrow t_{2\mathrm{mean}} = \frac{\pi}{2\sqrt{\Omega_R^2+\Delta^2}}.$$

Thus, the mean transfer rate to the upper level is

$$k = \frac{\langle |C_2(t)|^2 \rangle}{t_{2\text{mean}}} = \frac{2\sqrt{\Omega_R^2 + \Delta^2 \Omega_R^2}}{2\pi(\Omega_R^2 + \Delta^2)} = \frac{\Omega_R^2}{\pi\sqrt{\Omega_R^2 + \Delta^2}} \tag{5.84}$$

We observe that, again, the ratio between the mean and the maximum transfer rate is equal to 2, hence, the two rates are connected through the relationship

$$k = 2\frac{\mathscr{A}}{T_R}. \tag{5.85}$$

Let us now examine what happens as the magnitude of the perturbation, i.e., the Rabi frequency, becomes smaller with respect to the absolute value of the detuning $|\Delta|$ ($\Omega_R << |\Delta|$).

$$\boxed{\begin{aligned} P_2(t) = |C_2(t)|^2 &= \frac{\Omega_R^2}{\Omega_R^2 + \Delta^2} \sin^2\left(\frac{\sqrt{\Omega_R^2 + \Delta^2}}{2} t\right) \\ &\approx \frac{\Omega_R^2}{\Delta^2} \sin^2\left(\frac{\Delta t}{2}\right), \quad \Omega_R << |\Delta| \end{aligned}} \tag{5.86}$$

Thus, the period becomes $T_R = 2\pi/|\Delta|$. Eq. 5.86 is identical to Eq. 5.89 of Section 5.5, which is derived under the assumption that the time is so small that the solution does not differ much from the initial conditions. This happens since, for a very small Ω_R, a large period T_R occurs, which means that the time evolution is slow.

Let us further examine what happens in the limit of an infinitesimal perturbation.

$$\lim_{\Omega_R \to 0} T_R = \lim_{\Omega_R \to 0} \frac{2\pi}{\sqrt{\Omega_R^2 + \Delta^2}} = \frac{2\pi}{|\Delta|} \tag{5.87}$$

$$\lim_{\Omega_R \to 0} \mathscr{A} = \lim_{\Omega_R \to 0} \frac{\Omega_R^2}{\Omega_R^2 + \Delta^2} = 0 \tag{5.88}$$

Therefore, in the limit of an infinitesimal perturbation, the maximum transfer percentage of the oscillations becomes zero, while their period tends to $\frac{2\pi}{|\Delta|}$, i.e., it depends solely on detuning. To obtain a better idea of what happens at small Ω_R, we present Figure 5.9.

5.5 Solution to the system of differential equations, occurring after RWA, using the simplistic Newton's recursive method.

Let us remember the system of differential equations that occurred after the RWA (Eq. 5.48), which was exactly solved in Section 5.4:

$$\begin{aligned} \dot{C}_1(t) &= C_2(t)\frac{i\mathscr{E}_0\mathscr{P}}{2\hbar} e^{-i(\Omega-\omega)t} \\ \dot{C}_2(t) &= C_1(t)\frac{i\mathscr{E}_0\mathscr{P}}{2\hbar} e^{i(\Omega-\omega)t} \end{aligned} \qquad \begin{aligned} \Omega_R &:= \frac{\mathscr{P}\mathscr{E}_0}{\hbar} \\ \Delta &:= \omega - \Omega \end{aligned}$$

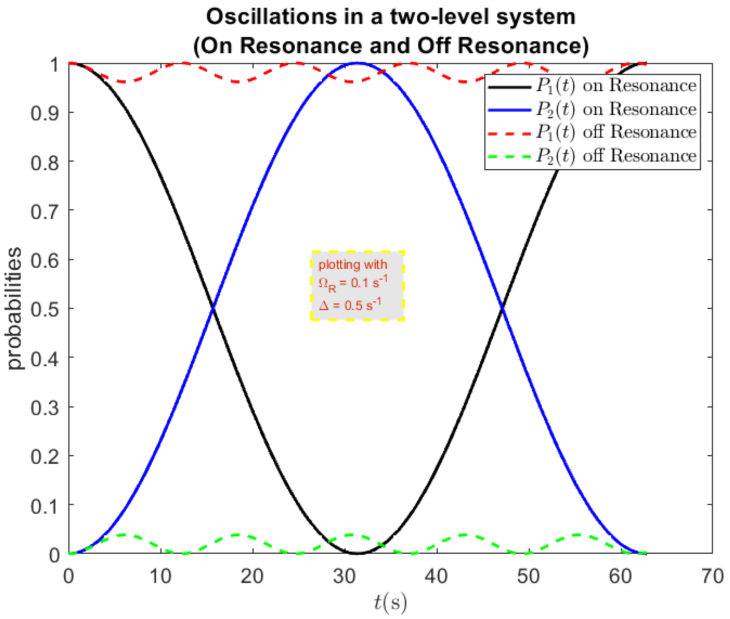

Figure 5.9: Oscillations of a two-level system at resonance ($\Delta = 0$, continuous lines) and out of resonance ($\Delta \neq 0$, dashed lines). The period of the oscillations is $T_{\mathrm{R}} = 2\pi/\sqrt{\Omega_{\mathrm{R}}^2+\Delta^2}$, while, the maximum transfer percentage is $\mathscr{A} = \frac{\Omega_R^2}{\Omega_R^2+\Delta^2}$. We have assigned some typical values $\Omega_R = 0.1\ \mathrm{s}^{-1}$ and $\Delta = 0.5\ \mathrm{s}^{-1}$, i.e., Ω_R is relatively small. In Appendix C, there is the matlab program Oscillations.m, which creates this figure.

Here, we will solve Eqs. 5.48 for the initial conditions $C_1(0) = 1$ and $C_2(0) = 0$, using the **approximate Newton's recursive method**, taking as a zeroth order approximation

$$\begin{aligned} C_1^{(0)}(t) &\approx C_1(0) = 1 \\ C_2^{(0)}(t) &\approx C_2(0) = 0 \end{aligned}$$

i.e., assuming that, at small times, the solution does not differ much from the initial conditions. Thus, the first order approximation is

$$\dot{C}_1^{(1)}(t) = \cancelto{0}{C_2^{(0)}(t)}\ \frac{i\Omega_R}{2}e^{i\Delta t} = 0$$

$$\dot{C}_2^{(1)}(t) = \cancelto{1}{C_1^{(0)}(t)}\ \frac{i\Omega_R}{2}e^{-i\Delta t} \Rightarrow \int_0^{t'} \frac{dC_2^{(1)}(t)}{dt}dt = \frac{i\Omega_R}{2}\int_0^{t'} e^{-i\Delta t}dt \Rightarrow$$

$$C_2^{(1)}(t') - \cancelto{0}{C_2^{(1)}(0)} = \frac{i\Omega_R}{2}\frac{1}{-i\Delta}\left[e^{-i\Delta t}\right]_0^{t'} = -\frac{\Omega_R}{2\Delta}\left(e^{-i\Delta t'}-1\right) \Rightarrow$$

$$\left.\begin{aligned} C_2^{(1)}(t) &= -\frac{\Omega_R}{2\Delta}\left(e^{-i\Delta t}-1\right) \\ \bigstar\ e^{ix}-1 &= 2i\sin\left(\frac{x}{2}\right)e^{i\frac{x}{2}} \end{aligned}\right\} \Rightarrow C_2^{(1)}(t) = -\frac{\Omega_R}{2\Delta}\,2i\sin\left(\frac{-\Delta t}{2}\right)e^{-\frac{i\Delta t}{2}} \Rightarrow$$

$$C_2^{(1)}(t) = \frac{\Omega_R}{\Delta}\,i\sin\left(\frac{\Delta t}{2}\right)e^{-\frac{i\Delta t}{2}}.$$

★ The proof can be found in Appendix B.4. Thus,

$$\boxed{P_2^{(1)}(t) = |C_2^{(1)}(t)|^2 = \frac{\Omega_R^2}{\Delta^2}\sin^2\left(\frac{\Delta t}{2}\right)} \quad \text{or} \quad \boxed{P_2^{(1)}(t) = |C_2^{(1)}(t)|^2 = \frac{\Omega_R^2}{4}\frac{\sin^2\left(\frac{\Delta t}{2}\right)}{\left(\frac{\Delta t}{2}\right)^2}t^2} \tag{5.89}$$

Eq. 5.89 coincides with Eq. 5.86 of Section 5.4, which holds for very small Ω_R, which in turn means that the period T_R is very large, yielding a slow time-evolution.

5.6 Alternative solution to the system of differential equations occurring after RWA.

Let us revisit, once more, the system of differential equations that occurred after the RWA (Eq. 5.48), which was exactly solved in Section 5.4:

$$\begin{aligned}\dot{C}_1(t) &= C_2(t)\frac{i\mathscr{E}_0\mathscr{P}}{2\hbar}e^{-i(\Omega-\omega)t} \\ \dot{C}_2(t) &= C_1(t)\frac{i\mathscr{E}_0\mathscr{P}}{2\hbar}e^{i(\Omega-\omega)t}\end{aligned} \qquad \begin{aligned}\Omega_R &:= \frac{\mathscr{P}\mathscr{E}_0}{\hbar} \\ \Delta &:= \omega - \Omega\end{aligned}$$

Here, we will solve Eqs. 5.48 in an alternative manner, this time by decoupling them.

Let us try to differentiate them with respect to time once more. For the first equation, we have

$$\ddot{C}_1(t) = C_2(t)\frac{i\Omega_R}{2}i\Delta e^{i\Delta t} + \dot{C}_2(t)\frac{i\Omega_R}{2}e^{i\Delta t}.$$

Substituting the expressions for $C_2(t)$ and $\dot{C}_2(t)$ from the second equation, we obtain

$$\ddot{C}_1(t) = \frac{\dot{C}_1(t)}{\cancel{\frac{i\Omega_R}{2}e^{i\Delta t}}}\cancel{\frac{i\Omega_R}{2}}i\Delta\cancel{e^{i\Delta t}} + C_1(t)\frac{i\Omega_R}{2}\cancel{e^{-i\Delta t}}\frac{i\Omega_R}{2}\cancel{e^{i\Delta t}} \Rightarrow \ddot{C}_1(t) = i\Delta\dot{C}_1(t) - \frac{\Omega_R}{4}C_1(t)$$

In a completely analogous manner, for the second equation, we have

$$\ddot{C}_2(t) = -i\Delta\dot{C}_2(t) - \frac{\Omega_R}{4}C_2(t).$$

This way, we arrive at the **independent** equations

$$\boxed{\begin{aligned}\ddot{C}_1(t) - i\Delta\dot{C}_1(t) + \frac{\Omega_R}{4}C_1(t) &= 0 \\ \ddot{C}_2(t) + i\Delta\dot{C}_2(t) + \frac{\Omega_R}{4}C_2(t) &= 0\end{aligned}}. \tag{5.90}$$

We can try solutions of the form

$$\begin{aligned}C_k(t) &= u_k e^{i\mu_k t} \Rightarrow \\ \dot{C}_k(t) &= i\mu_k u_k e^{-i\mu_k t} \Rightarrow \\ \ddot{C}_k(t) &= -\mu_k^2 u_k e^{-i\mu_k t},\end{aligned}$$

for $k = 1, 2$. Substituting to Eqs. 5.90, we conclude that

$$\boxed{\begin{aligned}-\mu_1^2 + \Delta\mu_1 + \frac{\Omega_R}{4} &= 0 \\ -\mu_1^2 - \Delta\mu_2 + \frac{\Omega_R}{4} &= 0\end{aligned}}. \tag{5.91}$$

The above quadratic equations determine the time-evolution of the coefficients C_1 and C_2 and do not depend on $u_1\ u_2$. Their solutions can be easily found to be

$$\begin{aligned} \mu_1 &= \frac{\Delta}{2} \pm \frac{\sqrt{\Delta^2+\Omega^2}}{2} = \frac{\Delta}{2} \pm \lambda \\ \mu_2 &= -\frac{\Delta}{2} \pm \frac{\sqrt{\Delta^2+\Omega^2}}{2} = -\frac{\Delta}{2} \pm \lambda \end{aligned}, \tag{5.92}$$

where $\lambda = \frac{\sqrt{\Delta^2+\Omega_R^2}}{2}$. Therefore, the solutions are of the form

$$\left.\begin{aligned} C_1(t) &= \alpha e^{i\frac{\Delta}{2}} e^{i\lambda t} + \beta e^{i\frac{\Delta}{2}} e^{-i\lambda t} \\ C_2(t) &= \gamma e^{-i\frac{\Delta}{2}} e^{i\lambda t} + \delta e^{-i\frac{\Delta}{2}} e^{-i\lambda t} \end{aligned}\right\} \Rightarrow \left.\begin{aligned} C_1(t) e^{-i\frac{\Delta}{2}} &= \left(\alpha e^{i\lambda t} + \beta e^{-i\lambda t}\right) \\ C_2(t) e^{i\frac{\Delta}{2}} &= \left(\gamma e^{i\lambda t} + \delta e^{-i\lambda t}\right) \end{aligned}\right\} \tag{5.93}$$

- In the case of detuning ($\Delta \neq 0$), the solutions 5.93 have the same form with the ones occurring from the general solution of the coupled differential equations with the eigenvalue method (cf. Eq. 5.75). Therefore, the method used here produces exactly the same results as the ones discussed in Section 5.4, in the case $\Delta \neq 0$.

- In the case of resonance ($\Delta = 0$), the solutions 5.93 become

$$\left.\begin{aligned} C_1(t) &= \alpha e^{i\lambda t} + \beta e^{-i\lambda t} \\ C_2(t) &= \gamma e^{i\lambda t} + \delta e^{-i\lambda t} \end{aligned}\right\}. \tag{5.94}$$

The solutions (5.94) have the same form with the ones occurring from the general solution of the coupled differential equations with the eigenvalue method (cf. Eq. 5.61). Hence, we see that, as expected, the method used here produces exactly the same results as the ones discussed in Section 5.4, in the case of resonance, as well.

5.7 Calculation of Einstein coefficients.

Let us take the equations

$$\boxed{P_2(t) = |C_2(t)|^2 = \frac{\Omega_R^2}{\Delta^2}\sin^2\left(\frac{\Delta t}{2}\right)} \quad \text{or} \quad \boxed{P_2(t) = |C_2(t)|^2 = \frac{\Omega_R^2}{4}\frac{\sin^2\left(\frac{\Delta t}{2}\right)}{\left(\frac{\Delta t}{2}\right)^2}t^2} \tag{5.95}$$

as a starting point. These hold for a very small perturbation, as expressed by Ω_R, which leads to a very large period $T_R = 2\pi/|\Delta|$, which in turn means very slow time-evolution. (As we saw above, the same hold for very small times within the simplistic Newton's recursive method). Given that the electron was initially at the 1st level, $P_2(t)$ essentially describes the probability of absorption in a two-level system for polarized, monochromatic as well as close-to-visible light.

On the other hand, if we are interested in the probability of absorption in two-level system for polarized yet not monochromatic (i.e., containing a large region of angular frequencies around $\omega_0 = \Omega$) close-to-visible light, we ★ REPLACE ★

$$\mathscr{E}_0^2 = \int_{\Omega-\text{something}}^{\Omega+\text{something}} d\omega \frac{\rho(\omega)}{\varepsilon_0}.$$

ε_0 is the vacuum permittivity, with units $[\varepsilon_0] = \dfrac{\mathrm{C}^2}{\mathrm{Nm}^2}$ and ρ is the energy density of EM radiation in an infinitesimal angular frequency interval, with units $[\rho] = \dfrac{\mathrm{Js}}{\mathrm{m}^3}$. Thus, $\left[\int d\omega \dfrac{\rho(\omega)}{\varepsilon_0}\right] = \dfrac{\cancel{(1/s)}\,\mathrm{J}}{\mathrm{m}^3\,\cancel{(1/s)}}\dfrac{\mathrm{Nm}^2}{\mathrm{C}^2} = \dfrac{\mathrm{JN}}{\mathrm{mC}^2} = \dfrac{\mathrm{N}^2\mathrm{m}}{\mathrm{mC}^2} = \dfrac{\mathrm{N}^2}{\mathrm{C}^2} = \left[\mathscr{E}_0^2\right]$.

Thus, from Eq. 5.95, we arrive at

$$P_2(t) = |C_2(t)|^2 = \frac{\mathscr{P}^2}{4\hbar^2} \int\limits_{\Omega-\text{something}}^{\Omega+\text{something}} d\omega\, \frac{\rho(\omega)}{\varepsilon_0} \frac{\sin^2\left(\frac{(\omega-\Omega)t}{2}\right)}{\left(\frac{(\omega-\Omega)t}{2}\right)^2} t^2. \tag{5.96}$$

We set

$$x := \frac{(\omega-\Omega)t}{2} \Rightarrow \omega = \frac{2x}{t} + \Omega \Rightarrow d\omega = \frac{2}{t}dx. \tag{5.97}$$

Thus,

$$P_2(t) = \frac{\mathscr{P}^2}{4\hbar^2}\frac{2}{t}\frac{t^2}{\varepsilon_0} \int\limits_{-\text{something}(t/2)}^{+\text{something}(t/2)} dx\,\rho(x)\frac{\sin^2 x}{x^2} \Rightarrow$$

$$P_2(t) = \frac{\mathscr{P}^2\, t}{2\hbar^2\varepsilon_0} \int\limits_{-\text{something}(t/2)}^{+\text{something}(t/2)} dx\,\rho(x) \underset{\simeq\pi\delta(x)\bigstar}{\boxed{\frac{\sin^2 x}{x^2}}}$$

★ For the approximation of $\delta(x)$, consult Appendix B.3.

$$\left.\begin{array}{r} P_2(t) = \dfrac{\mathscr{P}^2\, t}{2\hbar^2\varepsilon_0}\rho(x=0)\pi \\ \left.\begin{array}{r} x = 0 \Rightarrow \dfrac{\omega-\Omega}{2}t = 0 \\ \text{however } t \text{ is finite} \end{array}\right\} \Rightarrow \omega = \Omega \end{array}\right\} \Rightarrow P_2(t) = \frac{\mathscr{P}^2\, t\, \pi}{2\hbar^2\varepsilon_0}\rho(\Omega) \Rightarrow$$

$$\boxed{\frac{dP_2(t)}{dt} = \frac{\mathscr{P}^2\pi}{2\hbar^2\varepsilon_0}\rho(\Omega)}$$

The EM radiation coming from a black body is not polarized, generally. Thus, the quantity $\rho(\Omega)$ of one polarization should, in some sense, be replaced by $\dfrac{\rho(\Omega)}{3}$ according to the relationship

$$\left\langle \mathscr{E}_0^2 \right\rangle = \left\langle \mathscr{E}_{0x}^2 + \mathscr{E}_{0y}^2 + \mathscr{E}_{0z}^2 \right\rangle = 3\left\langle \mathscr{E}_{0z}^2 \right\rangle \Rightarrow \left\langle \mathscr{E}_{0z}^2 \right\rangle = \frac{1}{3}\left\langle \mathscr{E}_0^2 \right\rangle$$

Hence, it should hold that

$$\boxed{\frac{dP_2(t)}{dt} = \frac{\mathscr{P}^2\pi}{2\hbar^2\varepsilon_0}\frac{\rho(\Omega)}{3}}$$

However, the probability of absorption is

$$dW^{\text{st.}}_{\text{ab.}} = B_{12}\rho(\nu)dt \Rightarrow$$
$$\frac{dW^{\text{st.}}_{\text{ab.}}}{dt} = B_{12}\rho(\nu)$$
$$\text{for } \omega = \Omega \quad \boxed{\frac{dW^{\text{st.}}_{\text{ab.}}}{dt} = B_{12}\rho(\Omega)}$$

Thus,

$$\left.\begin{aligned}\frac{dP_2(t)}{dt} &= \frac{\mathscr{P}^2\pi}{2\hbar^2\varepsilon_0}\frac{\rho(\Omega)}{3}\\ \frac{dW^{\text{st.}}_{\text{ab.}}}{dt} &= B_{12}\rho(\Omega)\end{aligned}\right\} \Rightarrow \tag{5.98}$$

$$\boxed{B_{12} = \frac{\mathscr{P}^2\pi}{6\hbar^2\varepsilon_0}} \tag{5.99}$$

while, we remind that we had found

$$\boxed{\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}} \tag{5.100}$$

and

$$\boxed{B_{12} = B_{21}} \tag{5.101}$$

Notwithstanding the simplifications that were needed for the calculation, the essence is that it is possible to calculate the Einstein coefficients of a two-level system.

5.8 Calculation of the Einstein coefficients using the solutions obtained in Section 5.4.

Let us write down Eq. 5.79 of Section 5.4 and Eq. 5.95 of Section 5.7. Eq. 5.79 can also be written in an analogous manner to Eq. 5.95, i.e.,

$$\boxed{P_2(t) = |C_2(t)|^2 = \frac{\Omega_R^2}{\Omega_R^2+\Delta^2}\sin^2\left(\frac{\sqrt{\Omega_R^2+\Delta^2}}{2}t\right)} \quad \text{or}$$
$$\boxed{P_2(t) = |C_2(t)|^2 = \frac{\Omega_R^2}{4}\frac{\sin^2\left(\frac{\sqrt{\Omega_R^2+\Delta^2}}{2}t\right)}{\left(\frac{\sqrt{\Omega_R^2+\Delta^2}}{2}t\right)^2}t^2} \tag{5.102}$$

just us we wrote

$$\boxed{P_2(t) = |C_2(t)|^2 = \frac{\Omega_R^2}{\Delta^2}\sin^2\left(\frac{\Delta t}{2}\right)} \quad \text{or}$$
$$\boxed{P_2(t) = |C_2(t)|^2 = \frac{\Omega_R^2}{4}\frac{\sin^2\left(\frac{\Delta t}{2}\right)}{\left(\frac{\Delta t}{2}\right)^2}t^2} \tag{5.103}$$

As it is evident, there is an analogy between the second versions of $P_2(t)$. So, we can define

$$x := \frac{\sqrt{\Omega_R^2 + \Delta^2}\; t}{2} \tag{5.104}$$

just as we had defined

$$x := \frac{\Delta t}{2} \tag{5.105}$$

in the previous Section 5.7 (Eq. 5.97). Thus, the calculation of B_{12} would occur just as it was done in the previous Section 5.7.

5.9 ``Eigenenergies'' of a perturbed two-level system, i.e., subjected to an EM field.

We want to solve the problem $\hat{H}\Psi(\vec{r}) = E\Psi(\vec{r})$, assuming that $\Psi(\vec{r})$ can be expanded over the eigenfunctions of the unperturbed system, $\Phi_k(\vec{r})$, with time-independent coefficients g_k. Then

$$\left.\begin{array}{l} \hat{H} = \hat{H}_0 + U_{\mathscr{E}}(\vec{r},t) \\ \hat{H}\Psi(\vec{r}) = E\Psi(\vec{r}) \\ \Psi(\vec{r}) = \sum\limits_k g_k\Phi_k(\vec{r}) \end{array}\right\} \Rightarrow \left.\begin{array}{c} \left[\hat{H}_0 + U_{\mathscr{E}}(\vec{r},t)\right]\sum\limits_k g_k\Phi_k(\vec{r}) = E\left[\sum\limits_k g_k\Phi_k(\vec{r})\right] \\ \text{Let us exploit the orthonormality of } \Phi_k(\vec{r}). \\ \text{We multiply by } \Phi^*_{k'}(\vec{r}) \text{ and integrate over space.} \end{array}\right\} \Rightarrow$$

$$\sum_k g_k \int d^3r\, \Phi^*_{k'}(\vec{r})\hat{H}_0\Phi_k(\vec{r}) + \sum_k g_k \int d^3r\, \Phi^*_{k'}(\vec{r})U_{\mathscr{E}}(\vec{r},t)\Phi_k(\vec{r}) = E\sum_k g_k \int d^3r\, \Phi^*_{k'}(\vec{r})\Phi_k(\vec{r})$$

$$\left.\begin{array}{c} \Rightarrow \sum\limits_k g_k E_k \delta_{k'k} + \sum\limits_k g_k U_{\mathscr{E}k'k}(t) = E\sum\limits_k g_k\delta_{k'k} \Rightarrow \boxed{g_{k'}E_{k'} + \sum\limits_k g_k U_{\mathscr{E}k'k}(t) = E g_{k'}} \\ \text{within the dipole approximation } U = -\vec{\mathscr{P}}\cdot\vec{\mathscr{E}} = +e\vec{r}\cdot\vec{\mathscr{E}}_0 e^{-i\omega t} = U_{\mathscr{E}}(\vec{r},t) \\ U_{\mathscr{E}k'k}(t) = e e^{-i\omega t}\vec{\mathscr{E}}_0\cdot\vec{r}_{k'k} \end{array}\right\} \Rightarrow$$

$$\text{if we average over time within a period } \frac{2\pi}{\omega} \text{ of the EM field, then } \boxed{\langle E\rangle = E_{k'}}$$

Therefore, the eigenenergies are not affected, on average.

5.10 Solution to the equations describing the time-evolution of a three-level system with quantum harmonic oscillator eigenstates.

In the previous sections, we focused on the interaction of a traveling monochromatic and polarized electric field with a two-level system, within the dipole approximation. However, Linear System of First Order Differential Equations (Eq. 5.30)

$$\boxed{\dot{C}_{k'}(t) = \frac{-i}{\hbar}\sum_k C_k(t)e^{i(\Omega_{k'}-\Omega_k)t}U_{\mathscr{E}k'k}(t)} \tag{5.106}$$

can also be solved for a system with three or more levels. In what follows, we will solve this problem, within the RWA, for a three-level system with with quantum harmonic oscillator eigenstates, i.e., for a system described by the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\Omega^2 z^2 \tag{5.107}$$

The eigenenergies of a 1D harmonic oscillator are given by the relationship

$$E_n = \hbar\Omega\left(n + \frac{1}{2}\right) \Rightarrow E_{n+1} - E_n = \hbar\Omega. \tag{5.108}$$

The eigenfunctions that correspond to these levels have the form

$$Z_n(z) = (2^n n! a\sqrt{\pi})^{-\frac{1}{2}} H_n\left(\frac{z}{a}\right) e^{-\frac{z^2}{2a^2}}, \tag{5.109}$$

where $H_n(x)$ are the Hermite polynomials and $a = \sqrt{\hbar/m\Omega}$. Let us assume that we can restrict the problem to the three lowest levels of the harmonic oscillator. Their eigenfunctions are presented in Table 5.1. For convenience, we also perform the change of indices $k = n + 1$.

Table 5.1: Eigenfunctions of the three energetically lowest levels of the 1D harmonic oscillator and their parity.

n	k	$\Phi_k(\vec{r}) = Z_n(z)$	**parity**
0	1	$(a\sqrt{\pi})^{-\frac{1}{2}} e^{-\frac{z^2}{2a^2}}$	even
1	2	$(a\sqrt{\pi})^{-\frac{1}{2}} 2\frac{z}{a} e^{-\frac{z^2}{2a^2}}$	odd
2	3	$(8a\sqrt{\pi})^{-\frac{1}{2}} \left(2 - 4\frac{z}{a}\right) e^{-\frac{z^2}{2a^2}}$	even

In Section 5.3.3, we saw that the matrix elements of the potential energy of the perturbation are

$$U_{\mathscr{E}k'k}(t) = e\mathscr{E}_0 \cos\omega t z_{k'k}$$

where

$$z_{k'k} := \int dV \Phi_{k'}(\vec{r})\, z\, \Phi_k(\vec{r})$$

since, here, the eigenfunctions are real. Observing the above equation together with Table 5.1, we can see that the diagonal elements become zero, the off-diagonal elements are symmetric, while the off-diagonal elements for which it holds that $|k - k'|$ = even become zero, as well.

For our three-level system $(k = 1, 2, 3)$, we can write

$$\begin{aligned}
U_{\mathscr{E}12}(t) &= e\mathscr{E}_0 \cos\omega t\ z_{12} & & U_{\mathscr{E}12}(t) = -\mathscr{P}_{z12}\,\mathscr{E}_0 \cos\omega t\\
U_{\mathscr{E}21}(t) &= e\mathscr{E}_0 \cos\omega t\ z_{21} & & U_{\mathscr{E}21}(t) = -\mathscr{P}_{z21}\,\mathscr{E}_0 \cos\omega t\\
U_{\mathscr{E}13}(t) &= e\mathscr{E}_0 \cos\omega t\ z_{13} = 0 & & U_{\mathscr{E}13}(t) = 0\\
U_{\mathscr{E}31}(t) &= e\mathscr{E}_0 \cos\omega t\ z_{31} = 0 & \text{or} \quad & U_{\mathscr{E}31}(t) = 0\\
U_{\mathscr{E}23}(t) &= e\mathscr{E}_0 \cos\omega t\ z_{23} & & U_{\mathscr{E}23}(t) = -\mathscr{P}_{z23}\,\mathscr{E}_0 \cos\omega t\\
U_{\mathscr{E}32}(t) &= e\mathscr{E}_0 \cos\omega t\ z_{32} & & U_{\mathscr{E}32}(t) = -\mathscr{P}_{z32}\,\mathscr{E}_0 \cos\omega t\\
U_{\mathscr{E}kk}(t) &= e\mathscr{E}_0 \cos\omega t\ z_{kk} = 0 & & U_{\mathscr{E}kk}(t) = 0
\end{aligned}$$

and, given the symmetry of the matrix elements $z_{kk'}$,

$$\mathscr{P}_{z12} = \mathscr{P}_{z21} := \mathscr{P} \qquad \mathscr{P}_{z23} = \mathscr{P}_{z32} := \mathscr{P}' \tag{5.110}$$

At this point, we are in the position to solve the Linear System of First Order Differential Equations (Eq. 5.30) for a three-level system. We will also use the identity $\cos\omega t = \dfrac{e^{i\omega t} + e^{-i\omega t}}{2}$. From Eq. 5.108, we have

$$\boxed{\Omega_2 - \Omega_1 = \Omega_3 - \Omega_2 = \Omega}. \tag{5.111}$$

Therefore,

$$\boxed{k' = 1} \qquad \begin{aligned} \dot{C}_1(t) &= -\frac{i}{\hbar}\, C_2(t)\, e^{i(\Omega_1-\Omega_2)t}\, U_{\mathscr{E}12}(t) \\ \dot{C}_1(t) &= -\frac{i}{\hbar}\, C_2(t)\, e^{-i\Omega t}\, (-\mathscr{E}_0)\, \mathscr{P}\ \cos\omega t \end{aligned}$$

$$\boxed{\dot{C}_1(t) = \frac{i\mathscr{E}_0\,\mathscr{P}}{2\hbar}\left[e^{-i(\Omega-\omega)t} + e^{-i(\Omega+\omega)t}\right] C_2(t)} \tag{5.112}$$

$$\boxed{k' = 2} \qquad \begin{aligned} \dot{C}_2(t) &= -\frac{i}{\hbar}\, C_1(t)\, e^{i(\Omega_2-\Omega_1)t}\, U_{\mathscr{E}21}(t) - \frac{i}{\hbar}\, C_3(t)\, e^{i(\Omega_2-\Omega_3)t}\, U_{\mathscr{E}23}(t) \\ \dot{C}_2(t) &= -\frac{i}{\hbar}\, C_1(t)\, e^{i\Omega t}\, (-\mathscr{E}_0)\, \mathscr{P}\ \cos\omega t - \frac{i}{\hbar}\, C_3(t)\, e^{-i\Omega t}\, (-\mathscr{E}_0)\, \mathscr{P}'\ \cos\omega t \end{aligned}$$

$$\boxed{\dot{C}_2(t) = \frac{i\mathscr{E}_0\,\mathscr{P}}{2\hbar}\left[e^{i(\Omega+\omega)t} + e^{i(\Omega-\omega)t}\right] C_1(t) + \frac{i\mathscr{E}_0\,\mathscr{P}'}{2\hbar}\left[e^{-i(\Omega+\omega)t} + e^{-i(\Omega-\omega)t}\right] C_3(t)} \tag{5.113}$$

$$\boxed{k' = 3} \qquad \begin{aligned} \dot{C}_3(t) &= -\frac{i}{\hbar}\, C_2(t)\, e^{i(\Omega_3-\Omega_2)t}\, U_{\mathscr{E}32}(t) \\ \dot{C}_3(t) &= -\frac{i}{\hbar}\, C_2(t)\, e^{i\Omega t}\, (-\mathscr{E}_0)\, \mathscr{P}'\ \cos\omega t \end{aligned}$$

$$\boxed{\dot{C}_3(t) = \frac{i\mathscr{E}_0\,\mathscr{P}'}{2\hbar}\left[e^{i(\Omega-\omega)t} + e^{i(\Omega+\omega)t}\right] C_2(t)} \tag{5.114}$$

We observe that level (2) acts as an intermediate between levels 1 and 3. **Within RWA**, we will ignore the rapidly evolving terms containing $(\Omega + \omega)$. Moreover, as we did for the two-level system, we will define detuning as

$$\boxed{\Delta := \omega - \Omega}$$

as well as the frequencies

$$\boxed{\Omega_R := \frac{\mathscr{P}\mathscr{E}_0}{\hbar}, \quad \Omega_R' := \frac{\mathscr{P}'\mathscr{E}_0}{\hbar}}. \tag{5.115}$$

This, after the RWA, we arrive at the system

$$\boxed{\begin{aligned} \dot{C}_1(t) &= \frac{i\Omega_R}{2} C_2(t) e^{i\Delta t} \\ \dot{C}_2(t) &= \frac{i\Omega_R}{2} C_1(t) e^{-i\Delta t} + \frac{i\Omega_R'}{2} C_3(t) e^{i\Delta t} \\ \dot{C}_3(t) &= \frac{i\Omega_R'}{2} C_2(t) e^{-i\Delta t} \end{aligned}} \tag{5.116}$$

Next, we will make a transformation to obtain a system of differential equations with time-independent coefficients. In other words,

$$\begin{aligned} C_1(t) &= \mathbb{C}_1(t)\, e^{\frac{i\Delta t}{2}} \\ C_2(t) &= \mathbb{C}_2(t)\, e^{-\frac{i\Delta t}{2}} \\ C_3(t) &= \mathbb{C}_3(t)\, e^{-\frac{i3\Delta t}{2}} \end{aligned} \tag{5.117}$$

Inserting the transformations of Equation 5.117 to the above system, we arrive at the system of differential equations

$$\begin{cases} \dot{\mathbb{C}}_1(t) = -\dfrac{i\Delta}{2}\,\mathbb{C}_1(t) + \dfrac{i\Omega_R}{2}\,\mathbb{C}_2(t) \\ \dot{\mathbb{C}}_2(t) = +\dfrac{i\Omega_R}{2}\,\mathbb{C}_1(t) + \dfrac{i\Delta}{2}\,\mathbb{C}_2(t) + \dfrac{i\Omega'_R}{2}\,\mathbb{C}_3(t)\,, \\ \dot{\mathbb{C}}_3(t) = \dfrac{i\Omega'_R}{2}\,\mathbb{C}_2(t) + \dfrac{i3\Delta}{2}\,\mathbb{C}_3(t) \end{cases}$$

which can be written in the form of a matrix differential equation as

$$\boxed{\begin{bmatrix} \dot{\mathbb{C}}_1(t) \\ \dot{\mathbb{C}}_2(t) \\ \dot{\mathbb{C}}_3(t) \end{bmatrix} = \begin{bmatrix} -\frac{i\Delta}{2} & \frac{i\Omega_R}{2} & 0 \\ \frac{i\Omega_R}{2} & \frac{i\Delta}{2} & \frac{i\Omega'_R}{2} \\ 0 & \frac{i\Omega'_R}{2} & \frac{i3\Delta}{2} \end{bmatrix} \begin{bmatrix} \mathbb{C}_1(t) \\ \mathbb{C}_2(t) \\ \mathbb{C}_3(t) \end{bmatrix}} \tag{5.118}$$

To solve the system of Eq. 5.118, we introduce the vector

$$\vec{x}(t) = \begin{bmatrix} \mathbb{C}_1(t) \\ \mathbb{C}_2(t) \\ \mathbb{C}_3(t) \end{bmatrix}. \tag{5.119}$$

Thus,

$$\dot{\vec{x}}(t) = \begin{bmatrix} \dot{\mathbb{C}}_1(t) \\ \dot{\mathbb{C}}_2(t) \\ \dot{\mathbb{C}}_3(t) \end{bmatrix}, \tag{5.120}$$

and denoting

$$\tilde{A} = \begin{bmatrix} -\frac{i\Delta}{2} & \frac{i\Omega_R}{2} & 0 \\ \frac{i\Omega_R}{2} & \frac{i\Delta}{2} & \frac{i\Omega'_R}{2} \\ 0 & \frac{i\Omega'_R}{2} & \frac{i3\Delta}{2} \end{bmatrix} := -i\mathrm{A} \Rightarrow \qquad \mathrm{A} = \begin{bmatrix} \frac{\Delta}{2} & -\frac{\Omega_R}{2} & 0 \\ -\frac{\Omega_R}{2} & -\frac{\Delta}{2} & -\frac{\Omega'_R}{2} \\ 0 & -\frac{\Omega'_R}{2} & -\frac{3\Delta}{2} \end{bmatrix} \tag{5.121}$$

the system of Eq. 5.118 is written as

$$\boxed{\dot{\vec{x}}(t) = \tilde{A}\,\vec{x}(t)} \tag{5.122}$$

Let us try solutions of the form

$$\vec{x}(t) = \vec{v}\, e^{\tilde{\lambda} t}, \tag{5.123}$$

hence,

$$\vec{v}\,\tilde{\lambda}\, e^{\tilde{\lambda} t} = \tilde{A}\,\vec{v}\, e^{\tilde{\lambda} t} \Rightarrow \left.\begin{matrix} \tilde{A}\vec{v} = \tilde{\lambda}\vec{v} \\ \tilde{\lambda} := -i\lambda \end{matrix}\right\} \Rightarrow -i\mathrm{A}\vec{v} = -i\lambda\vec{v} \Rightarrow \underbrace{\mathrm{A}\vec{v} = \lambda\vec{v}}_{\text{eigenvalue problem}}$$

Thus, the whole thing is essentially reduced to the eigenvalue problem

$$\boxed{\mathrm{A}\vec{v} = \lambda\vec{v}} \tag{5.124}$$

from which the normalized eigenvectors $\vec{v}_1, \vec{v}_2, \vec{v}_3$, which correspond to the eigenvalues $\lambda_1, \lambda_2, \lambda_3$, will occur. Having checked that the normalized eigenvectors $\vec{v}_1, \vec{v}_2, \vec{v}_3$, which correspond to the eigenvalues $\lambda_1, \lambda_2, \lambda_3$, are linearly independent, the solution to our problem is

$$\boxed{\vec{x}(t) = \sum_{k=1}^{3} c_k \, \vec{v}_k \, e^{-i\lambda_k t}}$$

where, of course, $\tilde{\lambda}_k = -i\lambda_k$. The initial conditions determine the coefficients c_k.

$\boxed{\text{SOLUTION for } \Delta = 0.}$

We present the analytical SOLUTION for $\Delta = 0$, i.e., at resonance. The matrix A has the form

$$\mathrm{A} = \begin{bmatrix} 0 & -\frac{\Omega_R}{2} & 0 \\ -\frac{\Omega_R}{2} & 0 & -\frac{\Omega'_R}{2} \\ 0 & -\frac{\Omega'_R}{2} & 0 \end{bmatrix} \tag{5.125}$$

Its eigenvalues occur by the roots of the determinant

$$\det(\mathrm{A} - \lambda \mathrm{I}),$$

where I is the unit 3×3 matrix. Thus,

$$\begin{aligned} \det(\mathrm{A} - \lambda\mathrm{I}) = 0 \Rightarrow -\lambda \begin{vmatrix} -\lambda & -\frac{\Omega'_R}{2} \\ -\frac{\Omega'_R}{2} & -\lambda \end{vmatrix} + \frac{\Omega_R}{2} \begin{vmatrix} -\frac{\Omega_R}{2} & 0 \\ -\frac{\Omega'_R}{2} & -\lambda \end{vmatrix} = 0 \\ \Rightarrow -\lambda\left(\lambda^2 - \frac{\Omega'^2_R}{4}\right) + \lambda\frac{\Omega^2_R}{4} = 0 \Rightarrow -\lambda\left(\lambda^2 - \frac{\Omega'^2_R}{4} - \frac{\Omega^2_R}{4}\right) = 0 \\ \Rightarrow \lambda = 0 \text{ ή } \lambda = \pm\frac{\sqrt{\Omega^2_R + \Omega'^2_R}}{2} \end{aligned}$$

Hence,

$$\boxed{\lambda_1 = -\frac{\sqrt{\Omega^2_R + \Omega'^2_R}}{2} := -\Lambda, \qquad \lambda_2 = 0, \qquad \lambda_3 = \frac{\sqrt{\Omega^2_R + \Omega'^2_R}}{2} := \Lambda} \tag{5.126}$$

Let us now obtain the eigenvectors of A.

For $\boxed{\lambda_1 = -\frac{\sqrt{\Omega_R^2 + \Omega_R'^2}}{2} := -\Lambda}$

$$\begin{bmatrix} \Lambda & -\frac{\Omega_R}{2} & 0 \\ -\frac{\Omega_R}{2} & \Lambda & -\frac{\Omega_R'}{2} \\ 0 & -\frac{\Omega_R'}{2} & \Lambda \end{bmatrix} \begin{bmatrix} v_{11} \\ v_{21} \\ v_{31} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \Rightarrow$$

$$\left. \begin{aligned} v_{11} &= \frac{\Omega_R}{2\Lambda} v_{21} \\ -\frac{\Omega_R}{2} v_{11} + \Lambda v_{21} - \frac{\Omega_R'}{2} v_{31} &= 0 \\ v_{31} &= \frac{\Omega_R'}{2\Lambda} v_{21} \end{aligned} \right\}$$

Substituting the first and the third relationship to the second one, we obtain

$$\underbrace{\left(\Lambda - \frac{\sqrt{\Omega_R^2 + \Omega_R'^2}}{2} \right)}_{=0} v_{22} = 0.$$

Thus, the choice of v_{22} arbitrary (albeit non-zero). We choose $v_{22} = 1$. Thus,

$$\vec{v}_1 = \beta \begin{bmatrix} \frac{\Omega_R}{2\Lambda} \\ 1 \\ \frac{\Omega_R'}{2\Lambda} \end{bmatrix}$$

For $\vec{v}_1$ to be normalized, it must hold that

$$\left|\vec{v}_1\right|^2 = 1 \Rightarrow |\beta|^2 \underbrace{\frac{\Omega_R + 4\Lambda^2 + \Omega_R'}{4\Lambda^2}}_{=2} = 1 \Rightarrow |\beta|^2 = \frac{1}{2}.$$

Hence, e.g., $\beta = \frac{1}{\sqrt{2}}$. Therefore,

$$\vec{v}_1 = \frac{1}{\sqrt{2}} \begin{bmatrix} \frac{\Omega_R}{2\Lambda} \\ 1 \\ \frac{\Omega_R'}{2\Lambda} \end{bmatrix} \tag{5.127}$$

For $\boxed{\lambda_2 = 0}$

$$\begin{bmatrix} 0 & -\frac{\Omega_R}{2} & 0 \\ -\frac{\Omega_R}{2} & 0 & -\frac{\Omega_R'}{2} \\ 0 & -\frac{\Omega_R'}{2} & 0 \end{bmatrix} \begin{bmatrix} v_{12} \\ v_{22} \\ v_{32} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \Rightarrow$$

$$\left. \begin{aligned} v_{22} &= 0 \\ v_{32} &= -\frac{\Omega_R}{\Omega_R'} v_{12} \\ v_{22} &= 0 \end{aligned} \right\}$$

Thus,

$$\vec{v}_2 = v_{12}\begin{bmatrix} 1 \\ 0 \\ -\frac{\Omega_R}{\Omega_R'} \end{bmatrix}.$$

For $\vec{v}_2$ to be normalized, it must hold that

$$\left|\vec{v}_2\right|^2 = 1 \Rightarrow |v_{12}|^2\left(1 + \frac{\Omega_R^2}{\Omega_R'^2}\right) = 1 \Rightarrow |v_{12}|^2 = \frac{\Omega_R'^2}{\Omega_R^2 + \Omega_R'^2} = \frac{\Omega_R'^2}{4\Lambda^2}.$$

Hence, e.g., $v_{12} = \frac{\Omega_R'}{2\Lambda}$. Thus,

$$\vec{v}_2 = \begin{bmatrix} \frac{\Omega_R'}{2\Lambda} \\ 0 \\ -\frac{\Omega_R}{2\Lambda} \end{bmatrix} \tag{5.128}$$

For $\boxed{\lambda_3 = \frac{\sqrt{\Omega_R^2 + \Omega_R'^2}}{2} := \Lambda}$

$$\begin{bmatrix} -\Lambda & -\frac{\Omega_R}{2} & 0 \\ -\frac{\Omega_R}{2} & -\Lambda & -\frac{\Omega_R'}{2} \\ 0 & -\frac{\Omega_R'}{2} & -\Lambda \end{bmatrix}\begin{bmatrix} v_{13} \\ v_{23} \\ v_{33} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \Rightarrow$$

$$\left.\begin{aligned} v_{13} &= -\frac{\Omega_R}{2\Lambda}v_{23} \\ -\frac{\Omega_R}{2}v_{13} - \Lambda v_{23} - \frac{\Omega_R'}{2}v_{33} &= 0 \\ v_{33} &= -\frac{\Omega_R'}{2\Lambda}v_{23} \end{aligned}\right\}$$

Substituting the first and the third relationship to the second one, we obtain

$$\underbrace{\frac{\sqrt{\Omega_R^2 - 4\Lambda^2 + \Omega_R'^2}}{4\Lambda}}_{=0} v_{23} = 0.$$

Thus, the choice of v_{23} arbitrary (albeit non-zero). We choose $v_{23} = 1$. Thus,

$$\vec{v}_3 = \beta\begin{bmatrix} -\frac{\Omega_R}{2\Lambda} \\ 1 \\ -\frac{\Omega_R'}{2\Lambda} \end{bmatrix}$$

For $\vec{v}_3$ to be normalized, it must hold that

$$\left|\vec{v}_3\right|^2 = 1 \Rightarrow |\beta|^2 \underbrace{\frac{\Omega_R + 4\Lambda^2 + \Omega_R'}{4\Lambda^2}}_{=2} = 1 \Rightarrow |\beta|^2 = \frac{1}{2}.$$

Hence, e.g., $\beta = -\frac{1}{\sqrt{2}}$. Therefore,

$$\vec{v}_3 = \frac{1}{\sqrt{2}} \begin{bmatrix} \frac{\Omega_R}{2\Lambda} \\ -1 \\ \frac{\Omega'_R}{2\Lambda} \end{bmatrix} \tag{5.129}$$

Finally,

$$\vec{x}(t) = \begin{bmatrix} \mathbb{C}_1(t) \\ \mathbb{C}_2(t) \\ \mathbb{C}_3(t) \end{bmatrix} = c_1\,\vec{v}_1\,e^{-i\lambda_1 t} + c_2\,\vec{v}_2\,e^{-i\lambda_2 t} + c_3\,\vec{v}_3\,e^{-i\lambda_3 t}$$

$$\begin{bmatrix} C_1(t)\,e^{-i\frac{\Delta}{2}t} \\ C_2(t)\,e^{i\frac{\Delta}{2}t} \\ C_3(t)\,e^{i\frac{3\Delta}{2}t} \end{bmatrix} = \frac{c_1}{\sqrt{2}} \begin{bmatrix} \frac{\Omega_R}{2\Lambda} \\ 1 \\ \frac{\Omega'_R}{2\Lambda} \end{bmatrix} e^{i\Lambda t} + c_2 \begin{bmatrix} \frac{\Omega'_R}{2\Lambda} \\ 0 \\ -\frac{\Omega_R}{2\Lambda} \end{bmatrix} + \frac{c_3}{\sqrt{2}} \begin{bmatrix} \frac{\Omega_R}{2\Lambda} \\ -1 \\ \frac{\Omega'_R}{2\Lambda} \end{bmatrix} e^{-i\Lambda t} \Rightarrow \text{(we assumed } \Delta = 0) \Rightarrow$$

$$\begin{bmatrix} C_1(t) \\ C_2(t) \\ C_3(t) \end{bmatrix} = \frac{c_1}{\sqrt{2}} \begin{bmatrix} \frac{\Omega_R}{2\Lambda} \\ 1 \\ \frac{\Omega'_R}{2\Lambda} \end{bmatrix} e^{i\Lambda t} + c_2 \begin{bmatrix} \frac{\Omega'_R}{2\Lambda} \\ 0 \\ -\frac{\Omega_R}{2\Lambda} \end{bmatrix} + \frac{c_3}{\sqrt{2}} \begin{bmatrix} \frac{\Omega_R}{2\Lambda} \\ -1 \\ \frac{\Omega'_R}{2\Lambda} \end{bmatrix} e^{-i\Lambda t} \tag{5.130}$$

Let the initial conditions be $C_1(0) = 1$, $C_2(0) = 0$ and $C_3(0) = 0$. Hence, for $t = 0$, the system of Eq. 5.130 becomes

$$\left.\begin{aligned} 1 &= \frac{c_1}{\sqrt{2}}\frac{\Omega_R}{2\Lambda} + c_2\frac{\Omega'_R}{2\Lambda} + \frac{c_3}{\sqrt{2}}\frac{\Omega_R}{2\Lambda} \\ 0 &= \frac{c_1}{\sqrt{2}} - \frac{c_3}{\sqrt{2}} \Rightarrow c_1 = c_3 := c \\ 0 &= \frac{c_1}{\sqrt{2}}\frac{\Omega'_R}{2\Lambda} - c_2\frac{\Omega_R}{2\Lambda} + \frac{c_3}{\sqrt{2}}\frac{\Omega'_R}{2\Lambda} \end{aligned}\right\}$$

Substituting the condition occurring from the second equation of the system to the third equation, we obtain

$$c_2 = c\sqrt{2}\frac{\Omega'_R}{\Omega_R}.$$

Now, substituting to the first equation of the system, we obtain

$$2\Lambda = c\frac{\Omega_R}{\sqrt{2}} + c\sqrt{2}\frac{\Omega'^2_R}{\Omega_R} + c\frac{\Omega_R}{\sqrt{2}} = c\frac{2\Omega^2_R + 2\Omega'^2_R}{\sqrt{2}\Omega_R} \Rightarrow c = \frac{\sqrt{2}\Omega_R\Lambda}{\Omega^2_R + \Omega'^2_R} = \frac{\sqrt{2}\Omega_R}{2\sqrt{\Omega^2_R + \Omega'^2_R}} = \frac{\Omega_R}{2\sqrt{2}\Lambda}.$$

Thus, finally, the system of Eq. 5.130 reaches the form

$$\begin{bmatrix} C_1(t) \\ C_2(t) \\ C_3(t) \end{bmatrix} = \begin{bmatrix} \frac{\Omega^2_R}{8\Lambda^2}e^{i\Lambda t} + \frac{\Omega'^2_R}{4\Lambda^2} + \frac{\Omega^2_R}{8\Lambda^2}e^{-i\Lambda t} \\ \frac{\Omega_R}{4\Lambda}e^{i\Lambda t} - \frac{\Omega_R}{4\Lambda}e^{-i\Lambda t} \\ \frac{\Omega_R\Omega'_R}{8\Lambda^2}e^{i\Lambda t} - \frac{\Omega_R\Omega'_R}{4\Lambda^2} + \frac{\Omega_R\Omega'_R}{8\Lambda^2}e^{-i\Lambda t} \end{bmatrix} \Rightarrow$$

$$\begin{bmatrix} C_1(t) \\ C_2(t) \\ C_3(t) \end{bmatrix} = \begin{bmatrix} \frac{\Omega^2_R}{4\Lambda^2}\cos(\Lambda t) + \frac{\Omega'^2_R}{4\Lambda^2} \\ i\frac{\Omega_R}{2\Lambda}\sin(\Lambda t) \\ \frac{\Omega_R\Omega'_R}{4\Lambda^2}\cos(\Lambda t) - \frac{\Omega_R\Omega'_R}{4\Lambda^2} \end{bmatrix}. \tag{5.131}$$

These are the equations that describe the time-evolution of the three-level system. The probability that, at time t, the electron is at level k is, of course, $P_k(t) := |C_k(t)|^2$.

- For level 1, Eq. 5.131 yields

$$|C_1(t)|^2 = \frac{\Omega_R^4}{16\Lambda^4}\cos^2(\Lambda t) + \frac{\Omega_R'^4}{16\Lambda^4} + \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^4}\cos(\Lambda t) \Rightarrow$$

$$\boxed{P_1(t) = |C_1(t)|^2 = \frac{\Omega_R^4}{32\Lambda^4}(\cos(2\Lambda t)+1) + \frac{\Omega_R'^4}{16\Lambda^4} + \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^4}\cos(\Lambda t)}. \tag{5.132}$$

We see that there are two periods involved in the above equation, namely $T_1 = \frac{2\pi}{\Lambda}$ and $T_2 = \frac{2\pi}{2\Lambda}$. Since the ratio between the two periods is a rational number, specifically $\frac{T_1}{T_2} = 2$, the probability to find the electron at level 1 will be a periodic function, with period

$$\boxed{T_1 = \frac{2\pi}{\Lambda} = \frac{4\pi}{\sqrt{\Omega_R^2 + \Omega_R'^2}} = 2T_2}. \tag{5.133}$$

Let us examine Equation 5.132 a bit more.

- After a full period, i.e., at $t = T_1 = \frac{2\pi}{\Lambda}$,

$$\begin{aligned}\left|C_1\left(\frac{2\pi}{\Lambda}\right)\right|^2 &= \frac{\Omega_R^4}{32\Lambda^4}(\cos(4\pi)+1) + \frac{\Omega_R'^4}{16\Lambda^4} + \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^4}\cos(2\pi) = \frac{\Omega_R^4}{16\Lambda^4} + \frac{\Omega_R'^4}{16\Lambda^4} + \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^4}\\ &= \frac{(\Omega_R^2 + \Omega_R'^2)^2}{16\Lambda^4} = 1,\end{aligned}$$

which is expected, since after one period, the probability will return to its initial value, i.e., $|C_1(0)|^2 = 1$.

- After half a period, i.e., at $t = T_2 = \frac{2\pi}{2\Lambda}$,

$$\begin{aligned}\left|C_1\left(\frac{2\pi}{2\Lambda}\right)\right|^2 &= \frac{\Omega_R^4}{32\Lambda^4}(\cos(2\pi)+1) + \frac{\Omega_R'^4}{16\Lambda^4} + \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^4}\cos(\pi) = \frac{\Omega_R^4}{16\Lambda^4} + \frac{\Omega_R'^4}{16\Lambda^4} - \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^4}\\ &= \frac{(\Omega_R^2 - \Omega_R'^2)^2}{16\Lambda^4} = \frac{(\Omega_R^2 - \Omega_R'^2)^2}{(\Omega_R^2 + \Omega_R'^2)^2}.\end{aligned}$$

- The first derivative of $|C_1(t)|^2$ is

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}|C_1(t)|^2 &= -\frac{\Omega_R^4}{16\Lambda^3}\sin(2\Lambda t) - \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^3}\sin(\Lambda t) = -\frac{\Omega_R^4}{8\Lambda^3}\sin(\Lambda t)\cos(\Lambda t) - \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^3}\sin(\Lambda t)\\ &= -\frac{\Omega_R^2}{8\Lambda^3}\sin(\Lambda t)\left(\Omega_R^2\cos(\Lambda t) + \Omega_R'^2\right)\end{aligned} \tag{5.134}$$

The second derivative of $|C_1(t)|^2$ is

$$\begin{aligned}\frac{\mathrm{d}^2}{\mathrm{d}t^2}|C_1(t)|^2 &= -\frac{\Omega_R^2}{8\Lambda^2}\cos(\Lambda t)\left(\Omega_R^2\cos(\Lambda t) + \Omega_R'^2\right) + \frac{\Omega_R^4}{8\Lambda^2}\sin^2(\Lambda t)\\ &= \frac{\Omega_R^4}{8\Lambda^2}\left(\sin^2(\Lambda t) - \cos^2(\Lambda t)\right) - \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^2}\cos(\Lambda t)\end{aligned} \tag{5.135}$$

From Equation 5.134 it occurs that there are two cases in which extrema occur:

1. When $\cos(\Lambda t) = -\frac{\Omega_R'^2}{\Omega_R^2}$. *Attention:* in this case, it must hold that $\Omega_R'^2 \le \Omega_R^2$. Then, Equation 5.135 becomes

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}|C_1(t)|^2 = \frac{\Omega_R^4}{8\Lambda^2}\left(\sin^2(\Lambda t) - \frac{\Omega_R'^4}{\Omega_R^4}\right) + \frac{\Omega_R'^4}{8\Lambda^2} = \frac{\Omega_R^4}{8\Lambda^2}\sin^2(\Lambda t) > 0.$$

In other words, we have a minimum. Actually, substituting the value $\cos(\Lambda t) = -\frac{\Omega_R'^2}{\Omega_R^2}$ to Equation 5.132, we can easily find that then $|C_1| = 0$. Additionally, within a period $T_1 = \frac{2\pi}{\Lambda}$, there will be two times at which it will hold that $\cos(\Lambda t) = -\frac{\Omega_R'^2}{\Omega_R^2}$, i.e., there will be two zeros in a single period T_1. Therefore, in this case, the maximum transfer percentage from level 1 is

$$\boxed{\mathscr{A}_1 = 1} \tag{5.136}$$

2. When $\sin(\Lambda t) = 0$, thus $\cos(\Lambda t) = \pm 1$. Hence, there are two subcases:
   (a) $\sin(\Lambda t) = 0$ and $\cos(\Lambda t) = 1$. Thus, $\Lambda t = 0, 2\pi, 4\pi, \dots$. In other words, we are at integer multiples of the period T_1. Then, Equation 5.135 becomes

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}|C_1(t)|^2 = -\frac{\Omega_R^4}{8\Lambda^2} - \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^2} < 0.$$

   Hence, we have a maximum. However, as we saw above, after a full period, $|C_1(t)|^2 = 1$. Therefore, this is a global maximum.

   (b) $\sin(\Lambda t) = 0$ and $\cos(\Lambda t) = -1$. Thus, $\Lambda t = \pi, 3\pi, 5\pi \dots$. In other words, we are at half-integer multiples of the period T_1. Then, Equation 5.135 becomes

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}|C_1(t)|^2 = -\frac{\Omega_R^4}{8\Lambda^2} + \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^2} = \frac{\Omega_R^2}{8\Lambda^2}(\Omega_R'^2 - \Omega_R^2) > 0$$

   Hence, we have a minimum. However, as we saw above, after half a period, $|C_1(t)|^2 = \frac{(\Omega_R^2-\Omega_R'^2)^2}{(\Omega_R^2+\Omega_R'^2)^2}$. Therefore, in this case, the maximum transfer percentage from level 1 is

$$\boxed{\mathscr{A}_1 = 1 - \frac{(\Omega_R^2 - \Omega_R'^2)^2}{(\Omega_R^2 + \Omega_R'^2)^2} = \frac{4\Omega_R^2\Omega_R'^2}{(\Omega_R^2 + \Omega_R'^2)^2}} \tag{5.137}$$

* When $\Omega_R = \Omega_R'$, we have $\Lambda = \frac{\sqrt{2}\Omega_R}{2}$ and

$$\boxed{T_1 = \sqrt{2}\frac{2\pi}{\Omega_R}}. \tag{5.138}$$

The period of the oscillation is equal to $\sqrt{2}$ times the period of the respective two-level system (see Equation 5.64). Additionally, then, the above cases 1. and 2. coincide, and the maximum transfer percentage from level 1 is $\mathscr{A}_1 = 1$. Moreover, the expression for the time-evolution of the probability $|C_1(t)|^2$ reaches the simpler form

$$|C_1(t)|^2 = \frac{1}{8}\left(\cos\left(\sqrt{2}\Omega_R t\right) + 1\right) + \frac{1}{4} + \frac{1}{2}\cos\left(\frac{\sqrt{2}\Omega_R}{2}t\right)$$
$$= \frac{1}{4}\cos^2\left(\frac{\sqrt{2}\Omega_R}{2}t\right) + \frac{1}{4} + \frac{1}{2}\cos\left(\frac{\sqrt{2}\Omega_R}{2}t\right) = \left(\frac{1}{2}\cos\left(\frac{\sqrt{2}\Omega_R}{2}t\right) + \frac{1}{2}\right)^2$$
$$|C_1(t)|^2 = \cos^4\left(\frac{\sqrt{2}\Omega_R}{4}t\right). \tag{5.139}$$

- For level 2, Eq. 5.131 yields

$$|C_2(t)|^2 = \frac{\Omega_R^2}{4\Lambda^2}\sin^2(\Lambda t) \Rightarrow$$
$$\boxed{P_2(t) = |C_2(t)|^2 = \frac{\Omega_R^2}{8\Lambda^2} - \frac{\Omega_R^2}{8\Lambda^2}\cos(2\Lambda t)}. \tag{5.140}$$

We see that there is one period involved in the above equation, namely

$$T_2 = \frac{2\pi}{2\Lambda} = \frac{2\pi}{\sqrt{\Omega_R^2 + \Omega_R'^2}}. \tag{5.141}$$

Thus, the probability to find the electron at level 2 will be a periodic function, with period T_2. Moreover, the maximum transfer percentage to level 2 is

$$\boxed{\mathscr{A}_2 = \frac{\Omega_R^2}{4\Lambda^2} = \frac{\Omega_R^2}{\Omega_R^2 + \Omega_R'^2}} \tag{5.142}$$

In the case $\Omega_R = \Omega_R'$, we have $\Lambda = \frac{\sqrt{2}\Omega_R}{2}$ and $T_2 = \frac{1}{\sqrt{2}}\frac{2\pi}{\Omega_R}$. Thus, the period of the oscillation is equal to $1/\sqrt{2}$ times the period of the respective two-level system (see Equation 5.64). Moreover, the expression for the time-evolution of the probability $|C_2(t)|^2$ reaches the simpler form

$$|C_2(t)|^2 = \frac{1}{4} - \frac{1}{4}\cos\left(\sqrt{2}\Omega_R t\right) \Rightarrow$$
$$|C_2(t)|^2 = \frac{1}{2}\sin^2\left(\frac{\sqrt{2}\Omega_R}{2}t\right) \tag{5.143}$$

- For level 3, Eq. 5.131 yields

$$\left|C_3(t)\right|^2 = \frac{\Omega_R^2\Omega_R'^2}{16\Lambda^4}\cos^2(\Lambda t) + \frac{\Omega_R^2\Omega_R'^2}{16\Lambda^4} - \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^4}\cos(\Lambda t) \Rightarrow$$
$$\boxed{P_3(t) = \left|C_3(t)\right|^2 = \frac{\Omega_R^2\Omega_R'^2}{32\Lambda^4}\left(\cos(2\Lambda t) + 1\right) + \frac{\Omega_R^2\Omega_R'^2}{16\Lambda^4} - \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^4}\cos(\Lambda t)}. \tag{5.144}$$

We see that there are two periods involved in the above equation, namely $T_1 = \frac{2\pi}{\Lambda}$ and $T_2 = \frac{2\pi}{2\Lambda}$. Since the ratio between the two periods is a rational number, specifically $\frac{T_1}{T_2} = 2$, the probability to find the electron at level 3 will be a periodic function, with period

$$\boxed{T_1 = \frac{2\pi}{\Lambda} = \frac{4\pi}{\sqrt{\Omega_R^2 + \Omega_R'^2}} = 2T_2}. \tag{5.145}$$

Let us examine Equation 5.144 a bit more.

- After a full period, i.e., at $t = T_1 = \frac{2\pi}{\Lambda}$,

$$\begin{aligned}\left|C_3\left(\tfrac{2\pi}{\Lambda}\right)\right|^2 &= \frac{\Omega_R^2\Omega_R'^2}{32\Lambda^4}(\cos(4\pi)+1) + \frac{\Omega_R^2\Omega_R'^2}{16\Lambda^4} - \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^4}\cos(2\pi)\\ &= \frac{\Omega_R^2\Omega_R'^2}{16\Lambda^4} + \frac{\Omega_R^2\Omega_R'^2}{16\Lambda^4} - \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^4} = 0,\end{aligned}$$

which is expected, since after one period, the probability will return to its initial value, i.e., $\left|C_3(0)\right|^2 = 0$.

- After half a period, i.e., at $t = T_2 = \frac{2\pi}{2\Lambda}$,

$$\begin{aligned}\left|C_3\left(\tfrac{2\pi}{2\Lambda}\right)\right|^2 &= \frac{\Omega_R^2\Omega_R'^2}{32\Lambda^4}(\cos(2\pi)+1) + \frac{\Omega_R^2\Omega_R'^2}{16\Lambda^4} - \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^4}\cos(\pi)\\ &= \frac{\Omega_R^2\Omega_R'^2}{16\Lambda^4} + \frac{\Omega_R^2\Omega_R'^2}{16\Lambda^4} + \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^4} = \frac{\Omega_R^2\Omega_R'^2}{4\Lambda^4} = \frac{4\Omega_R^2\Omega_R'^2}{(\Omega_R^2+\Omega_R'^2)^2}\end{aligned}$$

- The first derivative of $\left|C_3(t)\right|^2$ is

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\left|C_3(t)\right|^2 &= -\frac{\Omega_R^2\Omega_R'^2}{16\Lambda^3}\sin(2\Lambda t) + \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^3}\sin(\Lambda t)\\ &= -\frac{\Omega_R^2\Omega_R'^2}{8\Lambda^3}\sin(\Lambda t)\cos(\Lambda t) + \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^3}\sin(\Lambda t) = \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^3}\sin(\Lambda t)\,(1-\cos(\Lambda t))\end{aligned} \tag{5.146}$$

The second derivative of $\left|C_3(t)\right|^2$ is

$$\begin{aligned}\frac{\mathrm{d}^2}{\mathrm{d}t^2}\left|C_3(t)\right|^2 &= \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^2}\cos(\Lambda t)\,(1-\cos(\Lambda t)) + \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^2}\sin^2(\Lambda t)\\ &= \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^2}\left[\cos(\Lambda t) - \cos^2(\Lambda t) + \sin^2(\Lambda t)\right] = \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^2}[\cos(\Lambda t) - \cos(2\Lambda t)]\end{aligned} \tag{5.147}$$

From Equation 5.146 it occurs that there are two cases in which extrema occur:

1. $\sin(\Lambda t) = 0$. This means that $\cos(\Lambda t) = \pm 1$. Hence, there are two subcases:
   (a) $\cos(\Lambda t) = 1$. Thus, $\Lambda t = 0, 2\pi, 4\pi, \ldots$. In other words, we are at integer multiples of the period T_1. Then, Equation 5.147 becomes

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\left|C_3(t)\right|^2 = \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^2}[1-1] = 0$$

Hence, the second derivative does not provide additional information about the extremum. However, we have already seen that after a full period, it holds that $\left|C_3(t)\right|^2 = 0$. Given that this is a function describing a probability, this value is a global minimum.

Let us verify this by expanding the first derivative around the limits $\Lambda t = 0 \pm \epsilon$, where ϵ is an infinitesimally small positive quantity:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left|C_3\left(\frac{\epsilon}{\Lambda}\right)\right|^2 \approx \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^3}\epsilon\left[1-\left(1-\frac{\epsilon^2}{2}\right)\right] = \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^3}\frac{\epsilon^3}{3} > 0$$
$$\frac{\mathrm{d}}{\mathrm{d}t}\left|C_3\left(-\frac{\epsilon}{\Lambda}\right)\right|^2 \approx \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^3}(-\epsilon)\left[1-\left(1-\frac{\epsilon^2}{2}\right)\right] = -\frac{\Omega_R^2\Omega_R'^2}{8\Lambda^3}\frac{\epsilon^3}{3} < 0$$

Hence, we have a minimum.

(b) $\cos(\Lambda t) = -1$. Thus, $\Lambda t = \pi, 3\pi, 5\pi \ldots$. In other words, we are at half-integer multiples of the period T_1. Then, Equation 5.147 becomes

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\left|C_3(t)\right|^2 = \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^2}(-1-1) = -\frac{\Omega_R^2\Omega_R'^2}{4\Lambda^2} < 0.$$

Hence, we have a local maximum. As we saw above, after half a period, $\left|C_3(t)\right|^2 = \frac{4\Omega_R^2\Omega_R'^2}{(\Omega_R^2+\Omega_R'^2)^2}$. Hence, in this case, the maximum transfer percentage to level 3 is

$$\boxed{\mathscr{A}_3 = \frac{4\Omega_R^2\Omega_R'^2}{(\Omega_R^2+\Omega_R'^2)^2}} \tag{5.148}$$

(c) $\cos(\Lambda t) = 1$. Thus, $\sin(\Lambda t) = 0$. This reduces to case $1(\alpha)$.

2. When $\Omega_R = \Omega_R'$, we have $\Lambda = \frac{\sqrt{2}\Omega_R}{2}$ and

$$\boxed{T_1 = \sqrt{2}\frac{2\pi}{\Omega_R}}. \tag{5.149}$$

The period of the oscillation is equal to $\sqrt{2}$ times the period of the respective two-level system (see Equation 5.64). Additionally, then, the maximum transfer percentage from level 1 is $\mathscr{A}_1 = 1$. Moreover, the expression for the time-evolution of the probability $\left|C_3(t)\right|^2$ reaches the simpler form

$$\begin{aligned}\left|C_3(t)\right|^2 &= \frac{1}{8}\left(\cos\left(\sqrt{2}\Omega_R t\right)+1\right)+\frac{1}{4}-\frac{1}{2}\cos\left(\frac{\sqrt{2}\Omega_R}{2}t\right)\\ &= \frac{1}{4}\cos^2\left(\frac{\sqrt{2}\Omega_R}{2}t\right)+\frac{1}{4}-\frac{1}{2}\cos\left(\frac{\sqrt{2}\Omega_R}{2}t\right) = \left(\frac{1}{2}\cos\left(\frac{\sqrt{2}\Omega_R}{2}t\right)-\frac{1}{2}\right)^2\\ \left|C_3(t)\right|^2 &= \sin^4\left(\frac{\sqrt{2}\Omega_R}{4}t\right).\end{aligned} \tag{5.150}$$

The above conclusions are summarized in Figure 5.10, where the oscillations of a three-level system at resonance are presented.

The maximum transfer rate from level 1 to level 3 is

$$\frac{\mathscr{A}_3}{T_1} = \frac{4\Omega_R^2\Omega_R'^2}{(\Omega_R^2+\Omega_R'^2)^2}\frac{\sqrt{\Omega_R^2+\Omega_R'^2}}{4\pi} = \frac{\Omega_R^2\Omega_R'^2}{\pi(\Omega_R^2+\Omega_R'^2)^{\frac{3}{2}}} \tag{5.151}$$

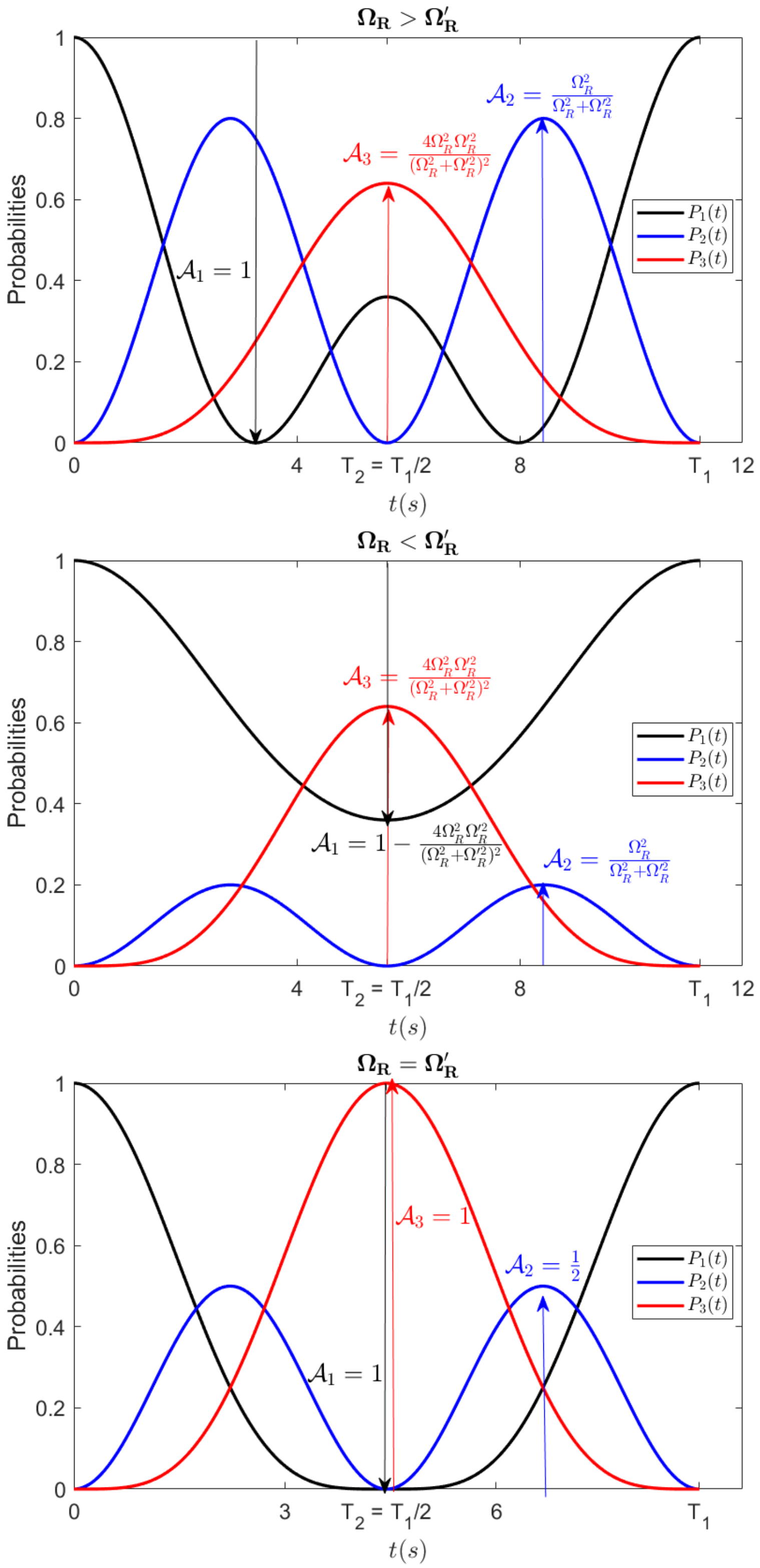

Figure 5.10: Oscillations of a three-level system at resonance, i.e., for $\omega = \Omega \Leftrightarrow \Delta = 0$, for $\Omega_R > \Omega'_R$ (top), $\Omega_R < \Omega'_R$ (middle) and $\Omega_R = \Omega'_R$ (bottom). Without having in mind a particular system, we have assigned typical values (top) $\Omega_R = 1\ \mathrm{s}^{-1}$ and $\Omega'_R = 0.5\ \mathrm{s}^{-1}$, (middle) $\Omega_R = 0.5\ \mathrm{s}^{-1}$ and $\Omega'_R = 1\ \mathrm{s}^{-1}$, and (bottom) $\Omega_R = \Omega'_R = 1\ \mathrm{s}^{-1}$.

The time-averaged probability to find the electron at each level is

$$\boxed{\begin{aligned} \langle|C_1(t)|^2\rangle &= \frac{\Omega_R^4}{32\Lambda^4} + \frac{\Omega_R'^4}{16\Lambda^4} = \frac{\Omega_R^4 + 2\Omega_R'^4}{32\Lambda^4} \\ \langle|C_2(t)|^2\rangle &= \frac{\Omega_R^2}{8\Lambda^2} \end{aligned}} . \qquad (5.152)$$

The time $t_{3\text{mean}}$, i.e., the time it takes so that the probability to find the electron to the upper level becomes equal to its average for the first time can be found from the relationship

$$\begin{aligned}
\frac{3\Omega_R^2\Omega_R'^2}{32\Lambda^4} &= \frac{\Omega_R^2\Omega_R'^2}{32\Lambda^4}(\cos(2\Lambda t_{3\text{mean}})+1) + \frac{\Omega_R^2\Omega_R'^2}{16\Lambda^4} - \frac{\Omega_R^2\Omega_R'^2}{8\Lambda^4}\cos(\Lambda t_{3\text{mean}}) \Rightarrow \\
\frac{3}{32} &= \frac{1}{32}(\cos(2\Lambda t_{3\text{mean}})+1) + \frac{1}{16} - \frac{1}{8}\cos(\Lambda t_{3\text{mean}}) \Rightarrow \\
\frac{3}{4} &= \frac{1}{4}(\cos(2\Lambda t_{3\text{mean}})+1) + \frac{1}{2} - \cos(\Lambda t_{3\text{mean}}) \Rightarrow \\
\frac{3}{4} &= \frac{1}{2}\cos^2(\Lambda t_{3\text{mean}}) + \frac{1}{2} - \cos(\Lambda t_{3\text{mean}}) \Rightarrow \\
\frac{3}{2} &= \cos^2(\Lambda t_{3\text{mean}}) + 1 - 2\cos(\Lambda t_{3\text{mean}}) \Rightarrow \\
0 &= \cos^2(\Lambda t_{3\text{mean}}) - 2\cos(\Lambda t_{3\text{mean}}) - \frac{1}{2}
\end{aligned}$$

Thus, we arrived at a quadratic equation in $\cos(\Lambda t_{3\text{mean}})$. Its roots are

$$\cos(\Lambda t_{3\text{mean}}) = 1 \pm \sqrt{\frac{3}{2}}. \tag{5.153}$$

The root $1 \pm \sqrt{\frac{3}{2}} > 1$ is rejected. Therefore,

$$\begin{aligned}
\cos(\Lambda t_{3\text{mean}}) = 1 - \sqrt{\frac{3}{2}} \Rightarrow \Lambda t_{3\text{mean}} = \arccos\left(1 - \sqrt{\frac{3}{2}}\right) = 1.797478 \Rightarrow \\
t_{3\text{mean}} \approxeq \frac{1.797478}{\Lambda}
\end{aligned} \tag{5.154}$$

Hence, the mean transfer rate from level 1 to level 3 is

$$k \overset{\text{def}}{=} \frac{\langle |C_3(t)|^2 \rangle}{t_{3\text{mean}}} = \frac{3\Omega_R^2\Omega_R'^2}{32\Lambda^3 \times 1.797478} = \frac{3\Omega_R^2\Omega_R'^2}{4(\Omega_R^2+\Omega_R'^2)^{\frac{3}{2}} \times 1.797478}. \tag{5.155}$$

Finally, the ratio between the mean and the maximum transfer rate is

$$\frac{k}{\frac{\mathscr{A}_3}{T_1}} = \frac{3\Omega_R^2\Omega_R'^2}{4(\Omega_R^2+\Omega_R'^2)^{\frac{3}{2}} \times 1.797478}\,\frac{\pi(\Omega_R^2+\Omega_R'^2)^{\frac{3}{2}}}{\Omega_R^2\Omega_R'^2} = \frac{3\pi}{4 \times 1.797478}. \tag{5.156}$$

Therefore, the two rates are connected through the relationship

$$k \approxeq 1.31083\frac{\mathscr{A}_3}{T_1}. \tag{5.157}$$

Let the initial conditions be $C_1(0) = 0$, $C_2(0) = 0$ and $C_3(0) = 1$. Hence, for $t = 0$, the system of Eq. 5.130 becomes

$$\left.\begin{aligned}
0 &= \frac{c_1}{\sqrt{2}}\frac{\Omega_R}{2\Lambda} + c_2\frac{\Omega_R'}{2\Lambda} + \frac{c_3}{\sqrt{2}}\frac{\Omega_R}{2\Lambda} \\
0 &= \frac{c_1}{\sqrt{2}} - \frac{c_3}{\sqrt{2}} \Rightarrow c_1 = c_3 := c \\
1 &= \frac{c_1}{\sqrt{2}}\frac{\Omega_R'}{2\Lambda} - c_2\frac{\Omega_R}{2\Lambda} + \frac{c_3}{\sqrt{2}}\frac{\Omega_R'}{2\Lambda}
\end{aligned}\right\}$$

Substituting the condition occurring from the second equation of the system to the first equation, we obtain

$$c_2 = -c\sqrt{2}\frac{\Omega_R}{\Omega'_R}.$$

Now, substituting to the third equation of the system, we obtain

$$2\Lambda = c\frac{\Omega'_R}{\sqrt{2}} + c\sqrt{2}\frac{\Omega_R^2}{\Omega'_R} + c\frac{\Omega'_R}{\sqrt{2}} = c\frac{2\Omega_R^2 + 2\Omega_R'^2}{\sqrt{2}\Omega'_R} \Rightarrow c = \frac{\sqrt{2}\Omega'_R\Lambda}{\Omega_R^2 + \Omega_R'^2} = \frac{\sqrt{2}\Omega'_R}{2\sqrt{\Omega_R^2 + \Omega_R'^2}} = \frac{\Omega'_R}{2\sqrt{2}\Lambda}.$$

Thus, finally, the system of Eq. 5.130 reaches the form

$$\begin{bmatrix} C_1(t) \\ C_2(t) \\ C_3(t) \end{bmatrix} = \begin{bmatrix} \frac{\Omega_R\Omega'_R}{8\Lambda^2}e^{i\Lambda t} - \frac{\Omega_R\Omega'_R}{4\Lambda^2} + \frac{\Omega_R\Omega'_R}{8\Lambda^2}e^{-i\Lambda t} \\ \frac{\Omega'_R}{4\Lambda}e^{i\Lambda t} - \frac{\Omega'_R}{4\Lambda}e^{-i\Lambda t} \\ \frac{\Omega_R'^2}{8\Lambda^2}e^{i\Lambda t} + \frac{\Omega_R^2}{4\Lambda^2} + \frac{\Omega_R'^2}{8\Lambda^2}e^{-i\Lambda t} \end{bmatrix} \Rightarrow$$

$$\begin{bmatrix} C_1(t) \\ C_2(t) \\ C_3(t) \end{bmatrix} = \begin{bmatrix} \frac{\Omega_R\Omega'_R}{4\Lambda^2}\cos(\Lambda t) - \frac{\Omega_R\Omega'_R}{4\Lambda^2} \\ i\frac{\Omega'_R}{2\Lambda}\sin(\Lambda t) \\ \frac{\Omega_R'^2}{4\Lambda^2}\cos(\Lambda t) + \frac{\Omega_R^2}{4\Lambda^2} \end{bmatrix}. \tag{5.158}$$

Comparing between Equations 5.158 and 5.131, i.e., the one that occurred for initial placement of the electron on the lower level, we observe that the transformation $C_(t) \longleftrightarrow C_3(t)$, $\Omega_R \longleftrightarrow \Omega'_R$ leads to exactly the same system of equations. Therefore, the above discussion will hold for this initial condition, as well, if we consider this transformation.

$\boxed{\text{SOLUTION for } \Delta \neq 0}$

In the presence of detuning, the matrix A has the form

$$\mathrm{A} = \begin{bmatrix} \frac{\Delta}{2} & -\frac{\Omega_R}{2} & 0 \\ -\frac{\Omega_R}{2} & -\frac{\Delta}{2} & -\frac{\Omega'_R}{2} \\ 0 & -\frac{\Omega'_R}{2} & -\frac{3\Delta}{2} \end{bmatrix} \tag{5.159}$$

To make calculations easier, we will solve the problem for the special case

$$\Omega_R = \Omega'_R = \Delta := 2\beta$$

Thus, in this case, we have the matrix

$$\mathrm{A} = \beta\begin{bmatrix} 1 & -1 & 0 \\ -1 & -1 & -1 \\ 0 & -1 & -3 \end{bmatrix}. \tag{5.160}$$

Its eigenvalues are obtained by by the roots of the determinant

$$\det(\mathrm{A} - \lambda\mathrm{I}),$$

where I is the unit 3 × 3 matrix. Thus,

$$\det(\mathrm{A} - \lambda\mathrm{I}) = 0 \Rightarrow (\beta - \lambda)\begin{vmatrix} -\beta - \lambda & -\beta \\ -\beta & -3\beta - \lambda \end{vmatrix} + \beta\begin{vmatrix} -\beta & 0 \\ -\beta & -3\beta - \lambda \end{vmatrix} = 0$$

$$\Rightarrow (\beta - \lambda)\left[(\beta + \lambda)(3\beta + \lambda) - \beta^2\right] + \beta^2(3\beta + \lambda) = 0$$

$$\Rightarrow -\lambda^3 - 3\beta\lambda^2 + 3\beta\lambda^2 + 5\beta^3 = 0.$$

We can verify that the value $\lambda = -\beta$ satisfies the above relationship. Hence, the rest eigenvalues can by found by dividing the left-hand side of the above relationship by $\lambda + \beta$, i.e.,

$$\begin{array}{rrrrr|l}
 & -\lambda^3 & -3\beta\lambda^2 & +3\beta\lambda^2 & +5\beta^3 & \lambda+\beta \\ \cline{6-6}
\ominus & -\lambda^3 & -\beta\lambda^2 & & & -\lambda^2-2\beta\lambda+5\beta^2 \\ \cline{2-3}
 & & -2\beta\lambda^2 & +3\beta^2\lambda & +5\beta^3 & \\
\ominus & & -2\beta\lambda^2 & -2\beta^2\lambda & & \\ \cline{3-4}
 & & & 5\beta\lambda^2 & +5\beta^3 & \\
\ominus & & & 5\beta\lambda^2 & +5\beta^3 & \\ \cline{4-5}
 & & & & 0 &
\end{array}$$

Hence, the condition that the determinant becomes zero is factored as

$$(\lambda+\beta)(\lambda^2+2\beta\lambda-5\beta^2)=0$$

and the eigenvalues are

$$\boxed{\lambda_1=-\beta(1+\sqrt{6}), \qquad \lambda_2=-\beta(1-\sqrt{6}), \qquad \lambda_3=-\beta}. \tag{5.161}$$

Let us now find the eigenvectors of A.

For $\boxed{\lambda_1=-\beta(1+\sqrt{6})}$

$$\begin{bmatrix} 1 & -1 & 0 \\ -1 & -1 & -1 \\ 0 & -1 & -3 \end{bmatrix}\begin{bmatrix} v_{11} \\ v_{21} \\ v_{31} \end{bmatrix} = -(1+\sqrt{6})\begin{bmatrix} v_{11} \\ v_{21} \\ v_{31} \end{bmatrix} \Rightarrow \left.\begin{aligned} v_{11}-v_{21} &= -(1+\sqrt{6})v_{11} \\ -v_{11}-v_{21}-v_{31} &= -(1+\sqrt{6})v_{21} \\ -v_{21}-3v_{31} &= -(1+\sqrt{6})v_{31} \end{aligned}\right\}$$

$$\Rightarrow \left.\begin{aligned} v_{21} &= (2+\sqrt{6})v_{11} \\ v_{11}+v_{31} &= \sqrt{6}v_{21} \\ v_{21} &= -(2-\sqrt{6})v_{31} \end{aligned}\right\} \Rightarrow \left.\begin{aligned} v_{31} &= -\frac{2+\sqrt{6}}{2-\sqrt{6}}v_{11} \\ v_{21} &= (2+\sqrt{6})v_{11} \end{aligned}\right\}$$

Thus,

$$\vec{v}_1 = v_{11}\begin{bmatrix} 1 \\ 2+\sqrt{6} \\ -\frac{2+\sqrt{6}}{2-\sqrt{6}} \end{bmatrix}$$

For $\vec{v}_1$ to be normalized, it must hold that

$$\left|\vec{v}_1\right|^2=1.$$

Hence, e.g., $v_{11}=\frac{2-\sqrt{6}}{2\sqrt{6}}$. Therefore,

$$\vec{v}_1=\frac{1}{2\sqrt{6}}\begin{bmatrix} 2-\sqrt{6} \\ -2 \\ -(2+\sqrt{6}) \end{bmatrix} \tag{5.162}$$

For $\boxed{\lambda_2 = -\beta(1-\sqrt{6})}$

$$\begin{bmatrix} 1 & -1 & 0 \\ -1 & -1 & -1 \\ 0 & -1 & -3 \end{bmatrix} \begin{bmatrix} v_{12} \\ v_{22} \\ v_{32} \end{bmatrix} = -(1-\sqrt{6}) \begin{bmatrix} v_{12} \\ v_{22} \\ v_{32} \end{bmatrix} \Rightarrow \left.\begin{aligned} v_{12} - v_{22} &= -(1-\sqrt{6})v_{12} \\ -v_{12} - v_{22} - v_{32} &= -(1-\sqrt{6})v_{22} \\ -v_{22} - 3v_{32} &= -(1-\sqrt{6})v_{32} \end{aligned}\right\}$$

$$\Rightarrow \left.\begin{aligned} v_{22} &= (2-\sqrt{6})v_{12} \\ v_{12} + v_{32} &= -\sqrt{6}v_{22} \\ v_{22} &= -(2+\sqrt{6})v_{32} \end{aligned}\right\} \Rightarrow \left.\begin{aligned} v_{32} &= -\frac{2-\sqrt{6}}{2+\sqrt{6}}v_{12} \\ v_{22} &= (2-\sqrt{6})v_{12} \end{aligned}\right\}$$

Thus,

$$\vec{v}_2 = v_{12} \begin{bmatrix} 1 \\ 2-\sqrt{6} \\ -\frac{2-\sqrt{6}}{2+\sqrt{6}} \end{bmatrix}$$

For $\vec{v}_2$ to be normalized, it must hold that

$$\left|\vec{v}_2\right|^2 = 1.$$

Hence, e.g., $v_{12} = \frac{2+\sqrt{6}}{2\sqrt{6}}$. Therefore,

$$\vec{v}_2 = \frac{1}{2\sqrt{6}} \begin{bmatrix} 2+\sqrt{6} \\ -2 \\ -(2-\sqrt{6}) \end{bmatrix} \tag{5.163}$$

For $\boxed{\lambda_3 = -\beta}$

$$\begin{bmatrix} 1 & -1 & 0 \\ -1 & -1 & -1 \\ 0 & -1 & -3 \end{bmatrix} \begin{bmatrix} v_{13} \\ v_{23} \\ v_{33} \end{bmatrix} = - \begin{bmatrix} v_{13} \\ v_{23} \\ v_{33} \end{bmatrix} \Rightarrow \left.\begin{aligned} v_{13} - v_{23} &= -v_{13} \\ -v_{13} - v_{23} - v_{33} &= -v_{23} \\ -v_{23} - 3v_{33} &= -v_{33} \end{aligned}\right\}$$

$$\Rightarrow \left.\begin{aligned} v_{23} &= 2v_{13} \\ v_{33} = -v_{13}v_{23} &= -2v_{33} \end{aligned}\right\}$$

Thus,

$$\vec{v}_3 = v_{13} \begin{bmatrix} 1 \\ 2 \\ -1 \end{bmatrix}$$

For $\vec{v}_3$ to be normalized, it must hold that

$$\left|\vec{v}_3\right|^2 = 1.$$

Hence, e.g., $v_{13} = \frac{1}{\sqrt{6}}$. Therefore,

$$\vec{v}_3 = \frac{1}{\sqrt{6}} \begin{bmatrix} 1 \\ 2 \\ -1 \end{bmatrix} \tag{5.164}$$

After all, the general solution is

$$\vec{x}(t) = \begin{bmatrix}\mathbb{C}_1(t)\\ \mathbb{C}_2(t)\\ \mathbb{C}_3(t)\end{bmatrix} = c_1\,\vec{v}_1\,e^{-i\lambda_1 t} + c_2\,\vec{v}_2\,e^{-i\lambda_2 t} + c_3\,\vec{v}_3\,e^{-i\lambda_3 t}$$

$$\begin{bmatrix}C_1(t)\,e^{-i\beta t}\\ C_2(t)\,e^{i\beta t}\\ C_3(t)\,e^{i3\beta t}\end{bmatrix} = \frac{c_1}{2\sqrt{6}}\begin{bmatrix}2-\sqrt{6}\\ -2\\ 2+\sqrt{6}\end{bmatrix}e^{i\beta(1+\sqrt{6})t} + \frac{c_2}{2\sqrt{6}}\begin{bmatrix}2+\sqrt{6}\\ -2\\ 2-\sqrt{6}\end{bmatrix}e^{i\beta(1-\sqrt{6})t} + \frac{c_3}{2\sqrt{6}}\begin{bmatrix}1\\ 2\\ -1\end{bmatrix}e^{i\beta t} \tag{5.165}$$

As in the previous cases we examined, imposing initial conditions determines the coefficients c_1, c_2, c_3 and, subsequently, the time evolution of the probability to find the electron at each level.

5.11 Multi-level system with equidistant levels within the RWA.

At this point, we will solve the problem of the multi-level system (MLS), i.e., with N levels, within the RWA. To simplify the problem and make its solution feasible, we will suppose that the energy levels of the system are equidistant. This is the same we did in the previous section, where we considered a system with quantum harmonic oscillator eigenstates, whose energy levels are indeed equidistant. From Eq. (5.30), we have

$$\boxed{\dot{C}_{k'}(t) = \frac{-i}{\hbar}\sum_k C_k(t)e^{i(\Omega_{k'}-\Omega_k)t}U_{\mathscr{E}k'k}(t)}, \tag{5.166}$$

where,

$$\boxed{U_{\mathscr{E}k'k}(t) = e\mathscr{E}_0\cos\omega t\int dV\Phi^*_{k'}(\vec{r})\,z\,\Phi_k(\vec{r})}. \tag{5.167}$$

The matrix elements of the z-coordinate are

$$z_{k'k} := \int dV\Phi^*_{k'}(\vec{r})\,z\,\Phi_k(\vec{r}). \tag{5.168}$$

We note that, for $k = 1, 3, 5, \ldots$, Φ_k are even functions, while, for $k' = 2, 4, 6, \ldots$, they are odd functions. Therefore, given this fact, and knowing that the z-coordinate is an odd function, the following hold:

- For $k = k'$, $z_{k,k} = 0$ since

$$z_{k,k} = \int dV\,\underbrace{|\Phi_k(\vec{r})|^2}_{\text{Even}}\;\underbrace{z}_{\text{Odd}} = 0 \tag{5.169}$$

- For $k \neq k'$,
  - If, e.g. $k' = k-1$, then $z_{k-1,k} \neq 0$. This happens since, from the relation,

$$z_{k-1,k} = \int dV\Phi^*_{k-1}(\vec{r})\,z\,\Phi_k(\vec{r}). \tag{5.170}$$

  we notice that if $\Phi^*_{k-1}(\vec{r}) \longrightarrow$ EVEN, then $\Phi_k(\vec{r}) \longrightarrow$ ODD, while, on the contrary, if $\Phi^*_{k-1}(\vec{r}) \longrightarrow$ ODD, then $\Phi_k(\vec{r}) \longrightarrow$ EVEN. Thus, in both cases, the result will be either EVEN · ODD · ODD or ODD · ODD · EVEN, i.e., non-zero.
  - Similarly, it can be demonstrated that, for $k' = k-2$, $z_{k-2,k} = 0$, etc.

Thus, to summarize,

$$\begin{aligned} z_{k-1,k} &= z_{k,k-1} \neq 0 \\ z_{k-2,k} &= z_{k,k-2} = 0 \\ z_{k-3,k} &= z_{k,k-3} \neq 0 \\ z_{k-4,k} &= z_{k,k-4} = 0 \\ &\vdots \\ z_{k-(N-1),k} &= z_{k,k-(N-1)} \begin{cases} \neq 0\,, \text{for } N = \text{even} \\ = 0\,, \ \text{for } N = \text{odd} \end{cases} \end{aligned}$$

Given that the matrix element of the potential energy of the perturbation can be written as (see Eq. 5.41)

$$U_{\mathscr{E}k'k}(t) = -\mathscr{P}_{zk'k}\,\mathscr{E}_0 \cos\omega t = -\mathscr{P}_{zk'k}\mathscr{E}_0 \frac{e^{i\omega t} + e^{-i\omega t}}{2}, \tag{5.171}$$

Eq. (5.166) becomes

$$\dot{C}_{k'}(t) = \frac{i}{2\hbar} \sum_{k} \mathscr{E}_0 \mathscr{P}_{zk'k} C_k(t) \left(e^{i(\Omega_{k'} - \Omega_k + \omega)t} + e^{i(\Omega_{k'} - \Omega_k - \omega)t} \right)$$

Assuming that the energy levels are equidistant, we have $\Omega_{k'} - \Omega_k = (k' - k)\Omega$. Thus,

$$\begin{aligned} \dot{C}_{k'}(t) = & \frac{i\mathscr{E}_0}{2\hbar} \sum_{k=1}^{k'} \mathscr{P}_{zk'k} C_k(t) \left(e^{i[(k'-k)\Omega+\omega]t} + e^{i[(k'-k)\Omega-\omega]t} \right) + \\ & \frac{i\mathscr{E}_0}{2\hbar} \sum_{k=k'+1}^{N} \mathscr{P}_{zk'k} C_k(t) \left(e^{i[(k'-k)\Omega+\omega]t} + e^{i[(k'-k)\Omega-\omega]t} \right). \end{aligned}$$

The coefficients $k' - k$ are presented in the table below:

$k \setminus k'$	1	2	3	4	$\cdots$	N
1	0	1	2	3	$\cdots$	$N-1$
2	-1	0	1	2	$\cdots$	$N-2$
3	-2	-1	0	1	$\cdots$	$N-3$
4	-3	-2	-1	0	$\cdots$	$N-4$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$
N	$-(N-1)$	$-(N-2)$	$-(N-3)$	$-(N-4)$	$\cdots$	0

The terms that correspond to slow changes are, for $k' - k = -1$, the exponential $e^{i[(k'-k)\Omega+\omega]t}$, and, for $k' - k = 1$ the exponential $e^{i[(k'-k)\Omega-\omega]t}$. In any other case, changes are fast, hence, we can omit them within the RWA. Therefore, from the N occurring equations, we have, for $k' = 1, k' = 2, 3, ..., N-1$ and $k' = N$, respectively,

$$\begin{aligned} \dot{C}_1(t) &= \frac{i\mathscr{P}_{1,2}\mathscr{E}_0}{2\hbar} C_2(t) e^{i\Delta t} \\ \dot{C}_{k'}(t) &= \frac{i\mathscr{P}_{k',k'-1}\mathscr{E}_0}{2\hbar} C_{k'-1}(t) e^{-i\Delta t} + \frac{i\mathscr{P}_{k',k'+1}\mathscr{E}_0}{2\hbar} C_{k'+1}(t) e^{i\Delta t} \\ \dot{C}_N(t) &= \frac{i\mathscr{P}_{N,N-1}\mathscr{E}_0}{2\hbar} C_{N-1}(t) e^{-i\Delta t}, \end{aligned}$$

where $\Delta = \omega - \Omega$ is the detuning. Alternatively, setting $\Omega_{Rk'k} = \frac{\mathscr{P}_{k'k}\mathscr{E}_0}{\hbar}$, the above equations can be written as

$$\dot{C}_1(t) = \frac{i\Omega_{R1,2}}{2} C_2(t)e^{i\Delta t} \tag{5.172}$$

$$\dot{C}_{k'}(t) = \frac{i\Omega_{Rk',k'-1}}{2} C_{k'-1}(t)e^{-i\Delta t} + \frac{i\Omega_{Rk',k'+1}}{2} C_{k'+1}(t)e^{i\Delta t} \tag{5.173}$$

$$\dot{C}_N(t) = \frac{i\Omega_{RN,N-1}}{2} C_{N-1}(t)e^{-i\Delta t}. \tag{5.174}$$

These equations can be solved using the following transformations:

- For even N,

$$\begin{aligned} C_{k'}(t) &= \mathbb{C}_{k'}(t)e^{i((N+1)-2k')\frac{\Delta}{2}t} \Rightarrow \\ \dot{C}_{k'}(t) &= \dot{\mathbb{C}}_{k'}(t)e^{i((N+1)-2k')\frac{\Delta}{2}t} + i((N+1)-2k')\frac{\Delta}{2}\mathbb{C}_{k'}(t)e^{i((N+1)-2k')\frac{\Delta}{2}t} \end{aligned}$$

- For odd N,

$$\begin{aligned} C_{k'}(t) &= \mathbb{C}_{k'}(t)e^{i(N-2k')\frac{\Delta}{2}t} \Rightarrow \\ \dot{C}_{k'}(t) &= \dot{\mathbb{C}}_{k'}(t)e^{i(N-2k')\frac{\Delta}{2}t} + i(N-2k')\frac{\Delta}{2}\mathbb{C}_{k'}(t)e^{i(N-2k')\frac{\Delta}{2}t} \end{aligned}$$

Substituting the transformations, we have

- For even N,
  - for $k' = 1$,

$$\dot{\mathbb{C}}_1(t)\cancel{e^{i(N-1)\frac{\Delta}{2}t}} + i(N-1)\frac{\Delta}{2}\mathbb{C}_1(t)\cancel{e^{i(N-1)\frac{\Delta}{2}t}} = \frac{i\Omega_{R1,2}}{2}\mathbb{C}_2(t)\cancel{e^{i(N-3)\frac{\Delta}{2}t}e^{i\Delta t}} \Rightarrow$$

$$\boxed{\dot{\mathbb{C}}_1(t) = -i(N-1)\frac{\Delta}{2}\mathbb{C}_1(t) + \frac{i\Omega_{R1,2}}{2}\mathbb{C}_2(t)} \tag{5.175}$$

  - for $k' = 2, 3, .., N-1$,

$$\begin{aligned} &\dot{\mathbb{C}}_{k'}(t)\cancel{e^{i[(N+1)-2k']\frac{\Delta}{2}t}} + i(N+1-2k')\frac{\Delta}{2}\mathbb{C}_{k'}(t)\cancel{e^{i[(N+1)-2k']\frac{\Delta}{2}t}} = \\ &= \frac{i\Omega_{Rk',k'-1}}{2}\mathbb{C}_{k'-1}(t)\cancel{e^{i[(N+1)-2(k'-1)]\frac{\Delta}{2}t}e^{-i\Delta t}} + \frac{i\Omega_{Rk',k'+1}}{2}\mathbb{C}_{k'+1}(t)\cancel{e^{i[(N+1)-2(k'+1)]\frac{\Delta}{2}t}e^{i\Delta t}} \Rightarrow \end{aligned}$$

$$\boxed{\dot{\mathbb{C}}_{k'}(t) = \frac{i\Omega_{Rk',k'-1}}{2}\mathbb{C}_{k'-1}(t) - i(N+1-2k')\frac{\Delta}{2}\mathbb{C}_{k'}(t) + \frac{i\Omega_{Rk',k'+1}}{2}\mathbb{C}_{k'+1}(t)} \tag{5.176}$$

  - for $k' = N$,

$$\dot{\mathbb{C}}_N(t)\cancel{e^{i(1-N)\frac{\Delta}{2}t}} + i((1-N)\frac{\Delta}{2}\mathbb{C}_N(t)\cancel{e^{i(1-N)\frac{\Delta}{2}t}} = \frac{i\Omega_{RN,N-1}}{2}\mathbb{C}_{N-1}(t)\cancel{e^{i((N+1)-2(N-1))\frac{\Delta}{2}t}e^{-i\Delta t}} \Rightarrow$$

$$\boxed{\dot{\mathbb{C}}_N(t) = i(N-1)\frac{\Delta}{2}\mathbb{C}_N(t) + \frac{i\Omega_{RN,N-1}}{2}\mathbb{C}_{N-1}(t)} \tag{5.177}$$

- For odd N,
  - $*$ for $k' = 1$,

$$\dot{\mathbb{C}}_1(t)\cancel{e^{i(N-2)\frac{\Delta}{2}t}} + i(N-2)\frac{\Delta}{2}\mathbb{C}_1(t)\cancel{e^{i(N-2)\frac{\Delta}{2}t}} = \frac{i\Omega_{R1,2}}{2}\mathbb{C}_2(t)\cancel{e^{i(N-4)\frac{\Delta}{2}t}}e^{i\Delta t} \Rightarrow$$

$$\boxed{\dot{\mathbb{C}}_1(t) = -i(N-2)\frac{\Delta}{2}\mathbb{C}_1(t) + \frac{i\Omega_{R1,2}}{2}\mathbb{C}_2(t)} \tag{5.178}$$

  - $*$ for $k' = 2, 3, .., N-1$,

$$\dot{\mathbb{C}}_{k'}(t)\cancel{e^{i(N-2k')\frac{\Delta}{2}t}} + i(N-2k')\frac{\Delta}{2}\mathbb{C}_{k'}(t)\cancel{e^{i(N-2k')\frac{\Delta}{2}t}} =$$

$$= \frac{i\Omega_{Rk',k'-1}}{2}\mathbb{C}_{k'-1}(t)\cancel{e^{i[N-2(k'-1)]\frac{\Delta}{2}t}}e^{-i\Delta t} + \frac{i\Omega_{Rk',k'+1}}{2}\mathbb{C}_{k'+1}(t)\cancel{e^{i[N-2(k'+1)]\frac{\Delta}{2}t}}e^{i\Delta t} \Rightarrow$$

$$\boxed{\dot{\mathbb{C}}_{k'}(t) = \frac{i\Omega_{Rk',k'-1}}{2}\mathbb{C}_{k'-1}(t) - i(N-2k')\frac{\Delta}{2}\mathbb{C}_{k'}(t) + \frac{i\Omega_{Rk',k'+1}}{2}\mathbb{C}_{k'+1}(t)} \tag{5.179}$$

  - $*$ for $k' = N$,

$$\dot{\mathbb{C}}_N(t)\cancel{e^{-iN\frac{\Delta}{2}t}} - iN\frac{\Delta}{2}\mathbb{C}_N(t)\cancel{e^{-iN\frac{\Delta}{2}t}} = \frac{i\Omega_{RN,N-1}}{2}\mathbb{C}_{N-1}(t)\cancel{e^{i(N-2(N-1))\frac{\Delta}{2}t}}e^{-i\Delta t} \Rightarrow$$

$$\boxed{\dot{\mathbb{C}}_N(t) = +iN\frac{\Delta}{2}\mathbb{C}_N(t) + \frac{i\Omega_{RN,N-1}}{2}\mathbb{C}_{N-1}(t)} \tag{5.180}$$

Hence, three different forms occur in each case (i.e., three forms for even N and three forms for odd N). We notice that in both cases, we have arrived at a system of first-order differential equations of the form

$$\begin{bmatrix} \dot{\mathbb{C}}_1(t) \\ \dot{\mathbb{C}}_2(t) \\ \dot{\mathbb{C}}_3(t) \\ \vdots \\ \dot{\mathbb{C}}_N(t) \end{bmatrix} = \tilde{A} \begin{bmatrix} \mathbb{C}_1(t) \\ \mathbb{C}_2(t) \\ \mathbb{C}_3(t) \\ \vdots \\ \mathbb{C}_N(t) \end{bmatrix}, \tag{5.181}$$

where

- for even N,

$$\tilde{A} = \frac{i}{2}\begin{bmatrix} -(N-1)\Delta & \Omega_{R1,2} & 0 & 0 & 0 & \cdots & 0 \\ \Omega_{R1,2} & -(N-3)\Delta & \Omega_{R2,3} & 0 & 0 & \cdots & 0 \\ 0 & \ddots & \ddots & \ddots & \cdots & \cdots & \vdots \\ \vdots & \cdots & \Omega_{Rk'-1,k'} & -(N+1-2k')\Delta & \Omega_{Rk',k'+1} & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & 0 & \cdots & (N-1)\Delta \end{bmatrix},$$

- for odd N,

$$\tilde{A} = \frac{i}{2}\begin{bmatrix} -(N-2)\Delta & \Omega_{R1,2} & 0 & 0 & 0 & \cdots & 0 \\ \Omega_{R1,2} & -(N-4)\Delta & \Omega_{R2,3} & 0 & 0 & \cdots & 0 \\ 0 & \ddots & \ddots & \ddots & \cdots & \cdots & \vdots \\ \vdots & \cdots & \Omega_{Rk'-1,k'} & -(N-2k')\Delta & \Omega_{Rk',k'+1} & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & 0 & \cdots & N\Delta \end{bmatrix}.$$

In other words, in both cases, we arrive at a problem of the form

$$\dot{\vec{x}}(t) = \tilde{A}\vec{x}(t) := -i\mathrm{A}\vec{x}(t) \tag{5.182}$$

We try solutions of the form $\vec{x}(t) = \vec{u}e^{\tilde{\lambda}t}$, with $\tilde{\lambda} = -i\lambda$. Thus, we conclude that,

$$\tilde{\lambda}\vec{u}\cancel{e^{\tilde{\lambda}t}} = \tilde{A}\vec{u}\cancel{e^{\tilde{\lambda}t}} \Rightarrow -i\lambda\vec{u} = -i\mathrm{A}\vec{u} \Rightarrow$$

$$\boxed{\mathrm{A}\vec{u} = \lambda\vec{u}}.$$

Hence, for a given N, we arrive at an eigenvalue-eigenvector problem, the solution of which is feasible, using the methods described in the previous Sections.

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CHAPTER 6

SEMICLASSICAL APPROXIMATION II

In this Chapter:
We continue studying Rabi oscillations with the semiclassical approach. However, here we focus on numerical solutions. Also, we compare our numerical results with approximative methods like the Rotating Wave Approximation (RWA), which we analyzed in the previous chapter, and the Averaging Method, of 1st and of 2nd order. We solve for various initial conditions either on resonance or off resonance. Relevant references for further reading: [1, 3, 4, 5, 6, 7, 8, 9, 10, 2].
Prerequisite knowledge: Basic knowledge of Quantum Physics and Mathematics.

The purpose of this chapter is to solve the linear system of first-order differential equations (Eq. 5.30) without the rotating wave approximation (RWA). The method we use to this end are the numerical solution with *matlab* (no RWA, NRWA) and the averaging method (AM). The linear system will be solved for a 2LS, both in-resonance and out-of-resonance, with initial conditions

1. $C_1(0) = 1, C_2(0) = 0$, i.e., placing the electron, at time zero, at the lower level,
2. $C_1(0) = 0, C_2(0) = 1$, i.e., placing the electron, at time zero, at the higher level
3. $C_1(0) = \frac{1}{\sqrt{2}}e^{i\theta}, C_2(0) = \frac{1}{\sqrt{2}}e^{i\phi}$, i.e., placing the electron, at time zero, with equal probability $|C_1(0)|^2 = |C_2(0)|^2 = \frac{1}{2}$ at both levels.

The linear system of first-order differential equation for the 2LS is

$$\boxed{\begin{aligned} \dot{C}_1(t) &= C_2(t)\frac{i\mathscr{E}_0\mathscr{P}}{2\hbar}\left[e^{-i(\Omega-\omega)t} + e^{-i(\Omega+\omega)t}\right] \\ \dot{C}_2(t) &= C_1(t)\frac{i\mathscr{E}_0\mathscr{P}}{2\hbar}\left[e^{i(\Omega+\omega)t} + e^{i(\Omega-\omega)t}\right] \end{aligned}} \tag{6.1}$$

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6.1 Rabi oscillations in a 2LS without Rotating Wave Approximation.

The significance of the full numerical solution (NRWA) is that it is the most accurate approach to obtain the actual solution to our problem. Therefore, the numerical solution provides the opportunity to compare it with the approximate ones (RWA - AM), in order to obtain a criterion for their range of successful application.

The 2LS (6.1) is numerically solved utilizing *matlab*; specifically, we used an algorithm based on the trapezoid and Runge-Kutta (4,5) methods (*ode*45). The algorithm *ode*45 selects a certain partition of the chosen interval, in our case for time t, producing at each point in time a column vector $C_k(t)$, where $k = 1, 2$. It is important to notice that this particion can be controlled. Additionally, Two important options of the algorithm are the relative and absolute tolerance, $RelTol$ and $AbsTol$, respectively. At each step of the *ode*45 algorithm, an error is approximated.. If y_k is the approximation of $y(x_k)$ at step k and e_k is the approximate error at this step, then *matlab* chooses its partition to ensure that

$$e_k \leq \max(RelTol \cdot y_k, AbsTol)$$

where the default values are $RelTol = 0.001$ and $AbsTol = 0.000001$. In the following, we set $RelTol = 10^{-10}$ and $AbsTol = 10^{-10}$, since our tests have shown that these values give the optimal results.

6.2 The averaging method.

The Averaging Method (AM) in nonlinear dynamical systems belongs to asymptotic methods. The simplest form of averaging is *periodic* averaging, which deals with solving a perturbation problem of the standard form

$$\dot{\mathbf{x}} = \epsilon f(\mathbf{x}, t) + \epsilon^2 g(\mathbf{x}, t) + \dots \tag{6.2}$$

where $\epsilon << 1$ and $f(\mathbf{x}, t)$, $g(\mathbf{x}, t)$ periodic functions with period T. We write the function f as

$$f(\mathbf{x}, t) = \overline{f}(\mathbf{x}) + \tilde{f}(\mathbf{x}, t). \tag{6.3}$$

$\overline{f}(\mathbf{x})$ is an *idiotypic* temporal average of f in the regime $[0, T]$: We average over t, but assuming $\mathbf{x}(t)$ constant, hypothesizing that $\mathbf{x}(t)$ is a slowly varying function. The functions $\mathbf{y}(t)$ and $\mathbf{z}(t)$ are confronted with the same hypothesis, which are defined the Eqs. (6.7), (6.22) respectively. Therefore, for $\overline{f}(\mathbf{x})$ we have,

$$\overline{f}(\mathbf{x}) = \frac{1}{T}\int_0^T f(\mathbf{x}, t)dt. \tag{6.4}$$

Similarly with $f(\mathbf{x}, t)$, we treat $g(\mathbf{x}, t)$, … . Below we use similar separation of functions f, g, h … to $\overline{f}, \overline{g}, \overline{h}$, … and $\tilde{f}, \tilde{g}, \tilde{h}$, … .

6.2.1 Averaging method of first and second order.

As above, we start by writing the periodic function $f(\mathbf{x}, t)$, i.e.,

$$f(\mathbf{x}, t) := \bar{f}(\mathbf{x}) + \tilde{f}(\mathbf{x}, t), \tag{6.5}$$

where

$$\bar{f}(\mathbf{x}) = \frac{1}{T}\int_0^T f(\mathbf{x}, t)dt. \tag{6.6}$$

Furthermore, we define,

$$\mathbf{x}(t) = \mathbf{y}(t) + \epsilon\, \mathbf{w}(\mathbf{y}(t), t) \tag{6.7}$$

where $\mathbf{w}$ is a function of $\mathbf{y}(t)$ and the time, t, which defined below, in Eq. (6.17). The differential of $\mathbf{x}(t)$ is

$$d\mathbf{x}(t) = d\mathbf{y}(t) + \epsilon\, d\mathbf{w}(\mathbf{y}(t), t), \tag{6.8}$$

$$d\mathbf{w}(\mathbf{y}, t) = \frac{\partial \mathbf{w}}{\partial \mathbf{y}} d\mathbf{y} + \frac{\partial \mathbf{w}}{\partial t} dt, \tag{6.9}$$

where $\frac{\partial \mathbf{w}}{\partial t}$ is the derivative of $\mathbf{w}$ with respect to t, keeping $\mathbf{y}(t)$ constant, hypothesizing that $\mathbf{y}(t)$ is a slowly varying function. Hence,

$$\dot{\mathbf{x}} = \dot{\mathbf{y}} + \epsilon \frac{\partial \mathbf{w}}{\partial \mathbf{y}} \dot{\mathbf{y}} + \epsilon \frac{\partial \mathbf{w}}{\partial t}. \tag{6.10}$$

Eq. (6.3), with Eq. (6.7), becomes

$$f(\mathbf{y} + \epsilon \mathbf{w}, t) = \bar{f}(\mathbf{y} + \epsilon \mathbf{w}) + \tilde{f}(\mathbf{y} + \epsilon \mathbf{w}, t). \tag{6.11}$$

Therefore, using Eqs. (6.7), (6.10), (6.11), Eq. (6.2) becomes

$$\dot{\mathbf{y}} + \epsilon \frac{\partial \mathbf{w}}{\partial \mathbf{y}} \dot{\mathbf{y}} + \epsilon \frac{\partial \mathbf{w}}{\partial t} = \epsilon \left(\bar{f}(\mathbf{y} + \epsilon \mathbf{w}) + \tilde{f}(\mathbf{y} + \epsilon \mathbf{w}, t) \right) + \epsilon^2 g(\mathbf{y} + \epsilon \mathbf{w}, t) \tag{6.12}$$

Using a Taylor expansion vs. $\mathbf{y}$, we obtain

$$\bar{f}(\mathbf{y} + \epsilon \mathbf{w}) = \bar{f}(\mathbf{y}) + \epsilon \frac{\partial \bar{f}(\mathbf{y})}{\partial \mathbf{y}} \mathbf{w} + \mathscr{O}(\epsilon^2 \mathbf{w}^2) \tag{6.13}$$

$$\tilde{f}(\mathbf{y} + \epsilon \mathbf{w}, t) = \tilde{f}(\mathbf{y}, t) + \epsilon \frac{\partial \tilde{f}(\mathbf{y}, t)}{\partial \mathbf{y}} \mathbf{w} + \mathscr{O}(\epsilon^2 \mathbf{w}^2) \tag{6.14}$$

$$g(\mathbf{y} + \epsilon \mathbf{w}, t) = g(\mathbf{y}, t) + \epsilon \frac{\partial g(\mathbf{y}, t)}{\partial \mathbf{y}} \mathbf{w} + \mathscr{O}(\epsilon^2 \mathbf{w}^2) \tag{6.15}$$

Thus, using Eqs. (6.13), (6.14), (6.15), Eq. (6.12) becomes

$$\dot{\mathbf{y}} + \epsilon \frac{\partial \mathbf{w}}{\partial \mathbf{y}} \dot{\mathbf{y}} + \epsilon \frac{\partial \mathbf{w}}{\partial t} = \epsilon (\bar{f}(\mathbf{y}) + \tilde{f}(\mathbf{y}, t)) + \epsilon^2 \left(\frac{\partial \bar{f}(\mathbf{y})}{\partial \mathbf{y}} \mathbf{w} + \frac{\partial \tilde{f}(\mathbf{y}, t)}{\partial \mathbf{y}} \mathbf{w} + g(\mathbf{y}, t) \right) + \mathscr{O}(\epsilon^3)$$

Rearranging, we have

$$\left(I + \epsilon \frac{\partial \mathbf{w}}{\partial \mathbf{y}} \right) \dot{\mathbf{y}} = \epsilon \left(\bar{f}(\mathbf{y}) + \tilde{f}(\mathbf{y}, t) - \frac{\partial \mathbf{w}}{\partial t} \right) + \epsilon^2 \left(\frac{\partial f(\mathbf{y}, t)}{\partial \mathbf{y}} \mathbf{w} + g(\mathbf{y}, t) \right) + \mathscr{O}(\epsilon^3), \tag{6.16}$$

where I is the unit relevant to the nature of $\mathbf{y}$. If $\mathbf{y}$ is a simple function of t, $I = 1$. If $\mathbf{y}$ is a column matrix, as in our case, $I = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$. We define the function $\mathbf{w}$ through the relationship

$$\tilde{f}(\mathbf{y}, t) = \frac{\partial \mathbf{w}}{\partial t}. \tag{6.17}$$

The use of Eq. (6.17) to simplify Eq. (6.16) is obvious. Therefore,

$$\left.\begin{aligned} \dot{\mathbf{y}} = \left(I + \epsilon \frac{\partial \mathbf{w}}{\partial \mathbf{y}} \right)^{-1} \left[\epsilon \bar{f}(\mathbf{y}) + \epsilon^2 \left(\frac{\partial f(\mathbf{y}, t)}{\partial \mathbf{y}} \mathbf{w} + g(\mathbf{y}, t) \right) + \mathscr{O}(\epsilon^3) \right] \\ \left(I + \epsilon \frac{\partial \mathbf{w}}{\partial \mathbf{y}} \right)^{-1} = I - \epsilon \frac{\partial \mathbf{w}}{\partial \mathbf{y}} + \mathscr{O}(\epsilon^2) \end{aligned}\right\} \Rightarrow$$

$$\boxed{\dot{\mathbf{y}} = \epsilon \bar{f}(\mathbf{y}) + \epsilon^2 \left(\frac{\partial f(\mathbf{y}, t)}{\partial \mathbf{y}} \mathbf{w} + g(\mathbf{y}, t) - \frac{\partial \mathbf{w}}{\partial \mathbf{y}} \bar{f}(\mathbf{y}) \right) + \mathcal{O}(\epsilon^3)} \tag{6.18}$$

If we ignore terms of order ϵ^2 and above in Eq. (6.18), we obtain the **first-order AM** of Eq. (6.2), i.e.,

$$\boxed{\dot{\mathbf{y}} = \epsilon \bar{f}(\mathbf{y})} \tag{6.19}$$

It is worth-noticing that the functions of the problem of Eq. (6.19) are independent of time. As a result, this problem is easier to solve than the initial problem of Eq. (6.2).

Continuing towards the second-order AM, from Eq. (6.18), we have

$$\dot{\mathbf{y}} = \epsilon \bar{f}(\mathbf{y}) + \epsilon^2 \underbrace{\left(\frac{\partial f(\mathbf{y}, t)}{\partial \mathbf{y}} \mathbf{w} + g(\mathbf{y}, t) - \frac{\partial \mathbf{w}}{\partial \mathbf{y}} \bar{f}(\mathbf{y}) \right)}_{h(\mathbf{y},t)} + \mathcal{O}(\epsilon^3) \Rightarrow$$

$$\dot{\mathbf{y}} = \epsilon \bar{f}(\mathbf{y}) + \epsilon^2 h(\mathbf{y}, t) + \mathcal{O}(\epsilon^3) \tag{6.20}$$

Just as we did previously with the function $f(\mathbf{x}, t)$ of Eq. (6.3), we write the function $h(\mathbf{y}, t)$ as

$$h(\mathbf{y}, t) = \bar{h}(\mathbf{y}) + \tilde{h}(\mathbf{y}, t), \tag{6.21}$$

where

$$\mathbf{y}(t) = \mathbf{z}(t) + \epsilon^2 \mathbf{u}(\mathbf{z}(t), t). \tag{6.22}$$

$\mathbf{u}$ is a function of $\mathbf{z}(t)$ and the time, t, which defined below, in Eq. (6.33). The differential of $\mathbf{y}(t)$ is

$$d\mathbf{y}(t) = d\mathbf{z}(t) + \epsilon^2 \, d\mathbf{u}[\mathbf{z}(t), t], \tag{6.23}$$

$$d\mathbf{u}[\mathbf{z}(t), t] = \frac{\partial \mathbf{u}}{\partial \mathbf{z}} d\mathbf{z} + \frac{\partial \mathbf{u}}{\partial t} dt, \tag{6.24}$$

where $\frac{\partial \mathbf{u}}{\partial t}$ is the derivative of $\mathbf{u}$ with respect to t, keeping $\mathbf{z}(t)$ constant, hypothesizing that $\mathbf{z}(t)$ is a slowly varying function. Hence,

$$\dot{\mathbf{y}} = \dot{\mathbf{z}} + \epsilon^2 \frac{\partial \mathbf{u}}{\partial \mathbf{z}} \dot{\mathbf{z}} + \epsilon^2 \frac{\partial \mathbf{u}}{\partial t} \tag{6.25}$$

Eq. (6.21), with Eq. (6.22), becomes

$$h(\mathbf{z} + \epsilon^2 \mathbf{u}, t) = \bar{h}(\mathbf{z} + \epsilon^2 \mathbf{u}) + \tilde{h}(\mathbf{z} + \epsilon^2 \mathbf{u}, t) \tag{6.26}$$

Therefore, using Eqs. (6.22), (6.25), (6.26), Eq. (6.20) becomes

$$\dot{\mathbf{z}} + \epsilon^2 \frac{\partial \mathbf{u}}{\partial \mathbf{z}} \dot{\mathbf{z}} + \epsilon^2 \frac{\partial \mathbf{u}}{\partial t} = \epsilon \bar{f}(\mathbf{z} + \epsilon^2 \mathbf{u}) + \epsilon^2 \left(\bar{h}(\mathbf{z} + \epsilon^2 \mathbf{u}) + \tilde{h}(\mathbf{z} + \epsilon^2 \mathbf{u}, t) \right) + \mathcal{O}(\epsilon^3) \tag{6.27}$$

Using a Taylor expansion vs. $\mathbf{z}$, we obtain

$$\bar{f}(\mathbf{z} + \epsilon^2 \mathbf{u}) = \bar{f}(\mathbf{z}) + \epsilon^2 \frac{\partial \bar{f}(\mathbf{z})}{\partial \mathbf{z}} \mathbf{u} + \mathcal{O}(\epsilon^4 \mathbf{u}^2), \tag{6.28}$$

$$\bar{h}(\mathbf{z} + \epsilon^2 \mathbf{u}) = \bar{h}(\mathbf{z}) + \epsilon^2 \frac{\partial \bar{h}(\mathbf{z})}{\partial \mathbf{z}} \mathbf{u} + \mathcal{O}(\epsilon^4 \mathbf{u}^2), \tag{6.29}$$

$$\tilde{h}(\mathbf{z} + \epsilon^2 \mathbf{u}, t) = \tilde{h}(\mathbf{z}, t) + \epsilon^2 \frac{\partial \tilde{h}(\mathbf{z}, t)}{\partial \mathbf{z}} \mathbf{u} + \mathcal{O}(\epsilon^4 \mathbf{u}^2) \tag{6.30}$$

Thus, using Eqs. (6.28), (6.29), (6.30), Eq. (6.27) becomes

$$\dot{\mathbf{z}} + \epsilon^2 \frac{\partial \mathbf{u}}{\partial \mathbf{z}} \dot{\mathbf{z}} + \epsilon^2 \frac{\partial \mathbf{u}}{\partial t} = \epsilon \bar{f}(\mathbf{z}) + \epsilon^2 \left(\bar{h}(\mathbf{z}) + \tilde{h}(\mathbf{z}, t) \right) + \mathscr{O}(\epsilon^3) \tag{6.31}$$

Rearranging, we have

$$\left(I + \epsilon^2 \frac{\partial \mathbf{u}}{\partial \mathbf{z}} \right) \dot{\mathbf{z}} = \epsilon \bar{f}(\mathbf{z}) + \epsilon^2 \left(\bar{h}(\mathbf{z}) + \tilde{h}(\mathbf{z}, t) - \frac{\partial \mathbf{u}}{\partial t} \right) + \mathscr{O}(\epsilon^3) \tag{6.32}$$

where I is the unit relevant to the nature of $\mathbf{z}$. If $\mathbf{z}$ is a simple function of t, $I = 1$. If $\mathbf{z}$ is a column matrix, as in our case, $I = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$. We define the function $\mathbf{u}$ through the relationship

$$\tilde{h}(\mathbf{z}, t) = \frac{\partial \mathbf{u}}{\partial t}. \tag{6.33}$$

The use of Eq. (6.33) to simplify Eq. (6.32) is obvious. Therefore,

$$\left. \begin{aligned} \dot{\mathbf{z}} &= \left(I + \epsilon^2 \frac{\partial \mathbf{u}}{\partial \mathbf{z}} \right)^{-1} \left[\epsilon \bar{f}(\mathbf{z}) + \epsilon^2 \bar{h}(\mathbf{z}) + \mathscr{O}(\epsilon^3) \right] \\ \left(I + \epsilon^2 \frac{\partial \mathbf{u}}{\partial \mathbf{z}} \right)^{-1} &= I - \epsilon^2 \frac{\partial \mathbf{u}}{\partial \mathbf{z}} + \mathscr{O}(\epsilon^4) \end{aligned} \right\} \Rightarrow$$

$$\boxed{\dot{\mathbf{z}} = \epsilon \ \bar{f}(\mathbf{z}) + \epsilon^2 \ \bar{h}(\mathbf{z}) + \mathscr{O}(\epsilon^3)} \tag{6.34}$$

If we ignore terms of order ϵ^3 and above in Eq. (6.34), we obtain the **second-order AM** of Eq. (6.2), i.e.,

$$\boxed{\dot{\mathbf{z}} = \epsilon \ \bar{f}(\mathbf{z}) + \epsilon^2 \ \bar{h}(\mathbf{z})} \tag{6.35}$$

We notice again that the functions of the problem of Eq. (6.35) are independent of time. As a result, this problem is also easier to solve than the initial problem of Eq. (6.2).

6.2.2 Averaging method for Rabi oscillations in a 2LS.

labelsubsec:AMRabi The Rabi oscillations of electron probabilities of a 2LS interacting with an electromagnetic field, are described by Eq. (6.1)

$$\boxed{\begin{aligned} \dot{C}_1(t) &= C_2(t) \frac{i \mathscr{E}_0 \mathscr{P}}{2\hbar} \left[e^{-i(\Omega-\omega)t} + e^{-i(\Omega+\omega)t} \right] \\ \dot{C}_2(t) &= C_1(t) \frac{i \mathscr{E}_0 \mathscr{P}}{2\hbar} \left[e^{i(\Omega+\omega)t} + e^{i(\Omega-\omega)t} \right] \end{aligned}} \tag{6.36}$$

where we have already defined the detuning, in Eq. (5.49), as

$$\boxed{\Delta := \omega - \Omega} \tag{6.37}$$

and the Rabi[1] (angular) frequency, in Eq. (5.50), as

$$\boxed{\Omega_R := \frac{\mathscr{P} \mathscr{E}_0}{\hbar}} \tag{6.38}$$

---

[1] After Isidor Isaak Rabi (1898-1988).

Our aim at this point is to apply the AM in Eq. (6.1). Before proceeding, it is important to remind the reader of the solving process for the above equations within the RWA, where we assumed that the terms containing $(\Omega - \omega)$ are slow, while the terms containing $(\Omega + \omega)$ are fast. Hence, in any remarkable time scale, these fast terms are somehow expected to have negligible effect. The RWA is the claim that we can ignore these fast terms. Afterwards, using the transformation of Eq. (5.51), we obtained a system of differential equations with time-independent coefficients, i.e., manageable case of differential equations. The AM arrives at this result via a different path. If we also define the sum of angular frequencies as

$$\boxed{\Sigma := \omega + \Omega}, \tag{6.39}$$

Eq. (6.1) can be written in matrix form as

$$\begin{bmatrix} \dot{C}_1(t) \\ \dot{C}_2(t) \end{bmatrix} = \frac{i\Omega_R}{2} \begin{bmatrix} 0 & e^{+i\Delta t} + e^{-i\Sigma t} \\ e^{-i\Delta t} + e^{+i\Sigma t} & 0 \end{bmatrix} \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} \tag{6.40}$$

$\boxed{\text{Solution for } \Delta \neq 0}$

We write Eq. (6.40) in the form

$$\dot{\mathbf{x}}(t) = \underbrace{\frac{i\Omega_R}{2} \begin{bmatrix} 0 & e^{+i\Delta t} + e^{-i\Sigma t} \\ e^{-i\Delta t} + e^{+i\Sigma t} & 0 \end{bmatrix} \mathbf{x}(t),}_{\epsilon f(\mathbf{x},t)} \tag{6.41}$$

where $\mathbf{x}(t) = \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix}$, we define $\epsilon f(\mathbf{x}, t)$ as the right-hand side of Eq. (6.40), and

$$g(\mathbf{x}, t) = 0. \tag{6.42}$$

For the AM to be applicable, f must be periodic. Eq. (6.41) involves two periods, $T_1 = \frac{2\pi}{\Delta}$ and $T_2 = \frac{2\pi}{\Sigma}$. If $\frac{T_1}{T_2}$ is a rational number, then the system is *periodic* with a common period, T, which is the least common multiple of T_1 and T_2. In other words,

$$\left.\begin{aligned} \frac{T_1}{T_2} = \frac{\Sigma}{\Delta} = N, \text{where: } N = \text{Rational} \\ N = \frac{\alpha}{\beta}, \quad \text{where: } \alpha, \beta = \text{Integers} \end{aligned}\right\} \Rightarrow T = \alpha T_2 = \beta T_1.$$

On the contrary, if $\frac{T_1}{T_2}$ is not a rational number, then, we can choose any close rational and solve approximately the problem. We notice that in numerical calculations, since T_1 and T_2 are represented as floats, $\frac{T_1}{T_2}$ is always a rational number. For example, if

$$\frac{T_1}{T_2} = \sqrt{2}$$

in a computer, it will be approximated by $\sqrt{2} = 1.41...$, with a finite number of decimal places. Moreover, in this case, we would choose, for example, $\sqrt{2} = 1.41 = \frac{141}{100}$.

The average of $f(\mathbf{x}, t)$ is

$$\epsilon \bar{f}(\mathbf{x}) := \frac{1}{T} \int_0^T \epsilon f(\mathbf{x}, t) dt = \frac{1}{T} \begin{bmatrix} 0 & \int_0^T (e^{+i\Delta t} + e^{-i\Sigma t}) dt \\ \int_0^T (e^{-i\Delta t} + e^{+i\Sigma t}) dt & 0 \end{bmatrix} \mathbf{x}(t) = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix} \mathbf{x}(t),$$

since

$$
\begin{aligned}
&\int_0^T e^{\pm i\Sigma t}dt = \pm\frac{1}{i\Sigma}(e^{\pm i\Sigma T}-1) = 0, \text{ because}\\
&e^{\pm i\Sigma T} = e^{\pm i\Sigma\alpha\frac{2\pi}{\Sigma}} = e^{\pm i2\pi\alpha} = (e^{i2\pi})^{\pm\alpha} = 1^{\pm\alpha} = 1, \text{ and}\\
&\int_0^T e^{\pm i\Delta t}dt = \pm\frac{1}{i\Delta}(e^{\pm i\Delta T}-1) = 0, \text{ because}\\
&e^{\pm i\Delta T} = e^{\pm i\Delta\beta\frac{2\pi}{\Delta}} = e^{\pm i2\pi\beta} = (e^{i2\pi})^{\pm\beta} = 1^{\pm\beta} = 1.
\end{aligned}
$$

Therefore,

$$\boxed{\bar{f}(\mathbf{x}) = \begin{bmatrix} 0 & 0\\ 0 & 0\end{bmatrix}} \tag{6.43}$$

Thus, from Eq. (6.3), we obtain

$$f(\mathbf{x},t) = \cancelto{0}{\bar{f}(\mathbf{x})} + \tilde{f}(\mathbf{x},t) \Rightarrow$$

$$\boxed{\epsilon\tilde{f}(\mathbf{x},t) = \frac{i\Omega_R}{2}\begin{bmatrix} 0 & e^{+i\Delta t}+e^{-i\Sigma t}\\ e^{-i\Delta t}+e^{+i\Sigma t} & 0\end{bmatrix}\mathbf{x}(t)}. \tag{6.44}$$

For the first-order AM, from Eq. (6.19) we have

$$\dot{\mathbf{y}} = \epsilon\bar{f}(\mathbf{y}). \tag{6.45}$$

However, in our case, $\bar{f}(\mathbf{y}) = 0$. Thus,

$$\dot{\mathbf{y}} = 0 \tag{6.46}$$

Therefore, $\mathbf{y}$ is a constant matrix, i.e.,

$$\boxed{\mathbf{y} = \begin{bmatrix} y_{10}\\ y_{20}\end{bmatrix}}. \tag{6.47}$$

y_{10}, y_{20} can be determined by applying the initial conditions. Finally, we obtain $\mathbf{w}$ by Eq. (6.17) as

$$\epsilon\frac{\partial\mathbf{w}}{\partial t} = \epsilon\tilde{f}(\mathbf{y},t) \Rightarrow$$

$$\boxed{\epsilon\mathbf{w}(\mathbf{y},t) = \frac{i\Omega_R}{2}\begin{bmatrix} 0 & \frac{e^{+i\Delta t}}{i\Delta}-\frac{e^{-i\Sigma t}}{i\Sigma}\\ -\frac{e^{-i\Delta t}}{i\Delta}+\frac{e^{+i\Sigma t}}{i\Sigma} & 0\end{bmatrix}\mathbf{y}(t)}. \tag{6.48}$$

For the second-order AM, from Eq. (6.35) we have

$$\dot{\mathbf{z}} = \epsilon\,\bar{f}(\mathbf{z}) + \epsilon^2\,\bar{h}(\mathbf{z}). \tag{6.49}$$

In our case, $\bar{f}(\mathbf{z}) = 0$. From Eq. (6.20) where we have defined the function $h(\mathbf{y},t)$, we have

$$h(\mathbf{z},t) = \frac{\partial\tilde{f}(\mathbf{z},t)}{\partial\mathbf{z}}\mathbf{w}(\mathbf{z},t). \tag{6.50}$$

Using Eq. (6.50), Eq. (6.35) becomes

$$\dot{\mathbf{z}} = \epsilon^2\,\overline{\frac{\partial\tilde{f}(\mathbf{z},t)}{\partial\mathbf{z}}\mathbf{w}(\mathbf{z},t)}. \tag{6.51}$$

Substituting Eqs. (6.44) and (6.48), Eq. (6.50) becomes

$$\begin{aligned}\epsilon^2 h(\mathbf{z}(t),t) &= i\left(\frac{\Omega_R}{2}\right)^2\left(\frac{1}{\Sigma}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}+\frac{1}{\Delta}\begin{bmatrix}-1 & 0\\ 0 & 1\end{bmatrix}\right)\mathbf{z}(t)\\ &+ i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{\Delta}\begin{bmatrix}-e^{-i(\Delta+\Sigma)t} & 0\\ 0 & e^{i(\Delta+\Sigma)t}\end{bmatrix}\mathbf{z}(t)+i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{\Sigma}\begin{bmatrix}e^{i(\Delta+\Sigma)t} & 0\\ 0 & -e^{-i(\Delta+\Sigma)t}\end{bmatrix}\mathbf{z}(t).\end{aligned} \tag{6.52}$$

The average of Eq. (6.52) is

$$\epsilon^2\bar{h}(\mathbf{z}) = \epsilon^2\overline{\left[\frac{\partial\tilde{f}(\mathbf{z},t)}{\partial\mathbf{z}}\mathbf{w}(\mathbf{z},t)\right]} = i\left(\frac{\Omega_R}{2}\right)^2\left(\frac{1}{\Sigma}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}+\frac{1}{\Delta}\begin{bmatrix}-1 & 0\\ 0 & 1\end{bmatrix}\right)\mathbf{z}(t). \tag{6.53}$$

From Eqs. (6.21), (6.52), (6.53), and since $\Delta+\Sigma = 2\omega$, we have

$$\epsilon^2\tilde{h}(\mathbf{z},t) = i\left(\frac{\Omega_R}{2}\right)^2\left(\frac{1}{\Delta}\begin{bmatrix}-e^{-i2\omega t} & 0\\ 0 & e^{i2\omega t}\end{bmatrix}+\frac{1}{\Sigma}\begin{bmatrix}e^{i2\omega t} & 0\\ 0 & -e^{-i2\omega t}\end{bmatrix}\right)\mathbf{z}(t). \tag{6.54}$$

Therefore, Eq. (6.51) becomes

$$\dot{\mathbf{z}} = iA\begin{bmatrix}-1 & 0\\ 0 & 1\end{bmatrix}\mathbf{z}(t), \tag{6.55}$$

where

$$A = \left(\frac{\Omega_R}{2}\right)^2\frac{2\Omega}{\omega^2-\Omega^2}. \tag{6.56}$$

The solution to Eq. (6.55) is

$$\boxed{\mathbf{z}(t) = \begin{bmatrix}z_1(t)\\ z_2(t)\end{bmatrix} = \begin{bmatrix}z_{10}e^{-iAt}\\ z_{20}e^{iAt}.\end{bmatrix}} \tag{6.57}$$

The coefficients z_{10}, z_{20} are determined by the initial conditions. Finally, from Eq. (6.33), we conclude that

$$\boxed{\epsilon^2\mathbf{u}(\mathbf{z},t) = i\left(\frac{\Omega_R}{2}\right)^2\begin{bmatrix}\frac{e^{-i2\omega t}}{i2\omega\Delta}+\frac{e^{i2\omega t}}{i2\omega\Sigma} & 0\\ 0 & \frac{e^{i2\omega t}}{i2\omega\Delta}+\frac{e^{-i2\omega t}}{i2\omega\Sigma}\end{bmatrix}\mathbf{z}(t)}. \tag{6.58}$$

To sum up, we present the results for the first- and second-order AM.

- First order:

$$\left\{\begin{aligned}&\mathbf{x}(t) = \mathbf{y}+\epsilon\,\mathbf{w}(\mathbf{y},t)\\ &\mathbf{y} = \begin{bmatrix}y_{10}\\ y_{20}\end{bmatrix}\\ &\epsilon\mathbf{w}(\mathbf{y},t) = \frac{i\Omega_R}{2}\begin{bmatrix}0 & \frac{e^{+i\Delta t}}{i\Delta}-\frac{e^{-i\Sigma t}}{i\Sigma}\\ -\frac{e^{-i\Delta t}}{i\Delta}+\frac{e^{+i\Sigma t}}{i\Sigma} & 0\end{bmatrix}\mathbf{y}\end{aligned}\right\} \tag{6.59}$$

- Second order:

$$\left\{\begin{array}{l}
\mathbf{x}(t) = \mathbf{z}(t) + \epsilon\mathbf{w}(\mathbf{z}(t), t) + \epsilon^2\mathbf{u}(\mathbf{z}(t), t) \\
\mathbf{z}(t) = \begin{bmatrix} z_{10}e^{-iAt} \\ z_{20}e^{iAt} \end{bmatrix} \\
\epsilon\mathbf{w}(\mathbf{z}(t), t) = \dfrac{i\Omega_R}{2}\begin{bmatrix} 0 & \dfrac{e^{+i\Delta t}}{i\Delta} - \dfrac{e^{-i\Sigma t}}{i\Sigma} \\ -\dfrac{e^{-i\Delta t}}{i\Delta} + \dfrac{e^{+i\Sigma t}}{i\Sigma} & 0 \end{bmatrix}\mathbf{z}(t) \\
\epsilon^2\mathbf{u}(\mathbf{z}(t), t) = i\left(\dfrac{\Omega_R}{2}\right)^2\left[\dfrac{1}{i2\omega\Delta}\begin{bmatrix} e^{-i2\omega t} & 0 \\ 0 & e^{i2\omega t} \end{bmatrix} + \dfrac{1}{i2\omega\Sigma}\begin{bmatrix} e^{i2\omega t} & 0 \\ 0 & e^{-i2\omega t} \end{bmatrix}\right]\mathbf{z}(t)
\end{array}\right\} \tag{6.60}$$

We observe that in Eqs. (6.59), (6.60) there are three types of ϵ, i.e., $\frac{\Omega_R}{\Delta}$, $\frac{\Omega_R}{\Sigma}$ and $\frac{\Omega_R}{\omega}$. These three distinct, small, ϵ reflect the relative magnitude of the perturbation, which is described by the Rabi (angular) frequency with respect to the detuning $\Delta = \omega - \Omega$, the sum of frequencies $\Sigma = \omega + \Omega$ and the frequency ω, respectively. These considerations give us the opportunity to confront different numerical cases.

Solution for $\Delta = 0$

The need to re-solve the problem for $\Delta = 0$ stems from the fact that, unavoidably, as Δ becomes smaller, $\frac{\Omega_R}{\Delta}$ gets so large that non-resonant AM is not successful anymore. Hence, we have to start again from the initial problem, i.e., Eq. (6.40), and set $\Delta = 0$. Therefore,

$$\dot{\mathbf{x}}(t) = \underbrace{\frac{i\Omega_R}{2}\begin{bmatrix} 0 & 1 + e^{-i2\omega t} \\ 1 + e^{+i2\omega t} & 0 \end{bmatrix}\mathbf{x}(t),}_{\epsilon f(\mathbf{x},t)} \tag{6.61}$$

where $\mathbf{x}(t) = \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix}$, we define $\epsilon f(\mathbf{x}, t)$ as the right-hand side of Eq. (6.40), and

$$g(\mathbf{x}, t) = 0. \tag{6.62}$$

For the AM to be applicable, f must be periodic. We notice that, indeed, $\epsilon f(\mathbf{x}, t)$ is periodic, with period $T = \frac{\pi}{\omega}$.

The average value of $f(\mathbf{x}, t)$ is

$$\epsilon\bar{f}(\mathbf{x}) = \frac{1}{T}\int_0^T \epsilon f(\mathbf{x}, t)dt = \frac{1}{T}\frac{i\Omega_R}{2}\begin{bmatrix} 0 & T \\ T & 0 \end{bmatrix}\mathbf{x}(t) = \frac{i\Omega_R}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\mathbf{x}(t)$$

Therefore,

$$\boxed{\epsilon\bar{f}(\mathbf{x}) = \frac{i\Omega_R}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\mathbf{x}(t)} \tag{6.63}$$

Thus, from Eq. (6.3), we obtain

$$f(\mathbf{x}, t) = \bar{f}(\mathbf{x}) + \tilde{f}(\mathbf{x}, t) \Rightarrow$$

$$\epsilon\tilde{f}(\mathbf{x}, t) = \epsilon f(\mathbf{x}, t) - \epsilon\bar{f}(\mathbf{x}) = \frac{i\Omega_R}{2}\begin{bmatrix} 0 & 1 + e^{-i2\omega t} \\ 1 + e^{+i2\omega t} & 0 \end{bmatrix}\mathbf{x}(t) - \frac{i\Omega_R}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\mathbf{x}(t) \Rightarrow$$

$$\boxed{\epsilon \tilde{f}(\mathbf{x}, t) = \frac{i\Omega_R}{2}\begin{bmatrix} 0 & e^{-i2\omega t} \\ e^{i2\omega t} & 0 \end{bmatrix}\mathbf{x}(t)} \tag{6.64}$$

For the first-order AM, from Eq. (6.19) we have

$$\dot{\mathbf{y}} = \epsilon \bar{f}(\mathbf{y}). \tag{6.65}$$

In our case, due to Eq. (6.63),

$$\dot{\mathbf{y}}(t) = \frac{i\Omega_R}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\mathbf{y}(t) \Rightarrow \left\{\begin{array}{l} \dot{y}_1(t) = \dfrac{i\Omega_R}{2} y_2(t) \\ \dot{y}_2(t) = \dfrac{i\Omega_R}{2} y_1(t) \end{array}\right\} \Rightarrow \left\{\begin{array}{l} \ddot{y}_1(t) + \left(\dfrac{\Omega_R}{2}\right)^2 y_1(t) = 0 \\ \ddot{y}_2(t) + \left(\dfrac{\Omega_R}{2}\right)^2 y_2(t) = 0 \end{array}\right\} \Rightarrow$$

$$\boxed{\begin{array}{l} y_1(t) = A_{11}\cos\left(\dfrac{\Omega_R}{2}t\right) + B_{11}\sin\left(\dfrac{\Omega_R}{2}t\right) \\ y_2(t) = A_{21}\cos\left(\dfrac{\Omega_R}{2}t\right) + B_{21}\sin\left(\dfrac{\Omega_R}{2}t\right) \end{array}} \tag{6.66}$$

with

$$\left\{\begin{array}{l} y_1(0) = A_{11} \\ y_2(0) = A_{21} \end{array}\right\} \text{ and } \left\{\begin{array}{l} \dot{y}_1(0) = \dfrac{\Omega_R}{2}B_{11} = i\dfrac{\Omega_R}{2}y_2(0) \\ \dot{y}_2(0) = \dfrac{\Omega_R}{2}B_{21} = i\dfrac{\Omega_R}{2}y_1(0) \end{array}\right\} \tag{6.67}$$

A_{11}, B_{11}, A_{21}, B_{21} are determined by applying the initial conditions. Finally, $\mathbf{w}$ is calculated from the Eq. (6.17),

$$\epsilon\frac{\partial \mathbf{w}}{\partial t} = \epsilon \tilde{f}(\mathbf{y}, t) \Rightarrow$$

$$\boxed{\epsilon \mathbf{w}(\mathbf{y}, t) = \frac{\Omega_R}{4\omega}\begin{bmatrix} 0 & -e^{-i2\omega t} \\ e^{i2\omega t} & 0 \end{bmatrix}\mathbf{y}(t)} \tag{6.68}$$

For the second-order AM, from Eq. (6.35) we have

$$\dot{\mathbf{z}} = \epsilon\ \bar{f}(\mathbf{z}) + \epsilon^2\ \bar{h}(\mathbf{z}). \tag{6.69}$$

From Eq. (6.20) where we have defined the function $h(\mathbf{y}, t)$, we have

$$h(\mathbf{z}, t) = \frac{\partial \bar{f}(\mathbf{z})}{\partial \mathbf{z}}\mathbf{w}(\mathbf{z}, t) + \frac{\partial \tilde{f}(\mathbf{z}, t)}{\partial \mathbf{z}}\mathbf{w}(\mathbf{z}, t) + g(\mathbf{z}, t) - \frac{\partial \mathbf{w}(\mathbf{z}, t)}{\partial \mathbf{z}}\bar{f}(\mathbf{z}). \tag{6.70}$$

We want the average of $h(\mathbf{z}, t)$, hence,

$$\bar{h}(\mathbf{z}) = \overline{\left(\frac{\partial \bar{f}(\mathbf{z})}{\partial \mathbf{z}}\mathbf{w}(\mathbf{z}, t) + \frac{\partial \tilde{f}(\mathbf{z}, t)}{\partial \mathbf{z}}\mathbf{w}(\mathbf{z}, t) + g(\mathbf{z}, t) - \frac{\partial \mathbf{w}(\mathbf{z}, t)}{\partial \mathbf{z}}\bar{f}(\mathbf{z})\right)}. \tag{6.71}$$

We will calculate the above terms one-by-one.

$$1^{\text{st}}\text{ term: }\frac{\partial \bar{f}(\mathbf{z})}{\partial \mathbf{z}}\mathbf{w}(\mathbf{z},t)=\frac{i\Omega_R}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}\frac{\Omega_R}{4\omega}\begin{bmatrix}0&-e^{-i2\omega t}\\e^{i2\omega t}&0\end{bmatrix}\mathbf{z}(t)=i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\begin{bmatrix}e^{i2\omega t}&0\\0&-e^{-i2\omega t}\end{bmatrix}\mathbf{z}(t)$$

$$2^{\text{nd}}\text{ term: }\frac{\partial \tilde{f}(\mathbf{z},t)}{\partial \mathbf{z}}\mathbf{w}(\mathbf{z},t)=+\frac{i\Omega_R}{2}\begin{bmatrix}0&e^{-i2\omega t}\\e^{i2\omega t}&0\end{bmatrix}\frac{\Omega_R}{4\omega}\begin{bmatrix}0&-e^{-i2\omega t}\\e^{i2\omega t}&0\end{bmatrix}\mathbf{z}(t)=i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\begin{bmatrix}1&0\\0&-1\end{bmatrix}\mathbf{z}(t)$$

$$3^{\text{rd}}\text{ term: }g(\mathbf{z},t)=0$$

$$4^{\text{th}}\text{ term: }\frac{\partial \mathbf{w}(\mathbf{z},t)}{\partial \mathbf{z}}\bar{f}(\mathbf{z})=\frac{\Omega_R}{4\omega}\begin{bmatrix}0&-e^{-i2\omega t}\\e^{i2\omega t}&0\end{bmatrix}\frac{i\Omega_R}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}\mathbf{z}(t)=i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\begin{bmatrix}-e^{-i2\omega t}&0\\0&e^{i2\omega t}\end{bmatrix}\mathbf{z}(t)$$

Thus, $h(\mathbf{z},t)$ in our case is

$$\boxed{\begin{aligned}h(\mathbf{z},t)=&i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\begin{bmatrix}e^{i2\omega t}&0\\0&-e^{-i2\omega t}\end{bmatrix}\mathbf{z}(t)+i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\begin{bmatrix}1&0\\0&-1\end{bmatrix}\mathbf{z}(t)\\&-i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\begin{bmatrix}-e^{-i2\omega t}&0\\0&e^{i2\omega t}\end{bmatrix}\mathbf{z}(t)\end{aligned}} \tag{6.72}$$

Therefore, the averages of the above terms are

$$1^{\text{st}}\text{ term: }\overline{\left(\frac{\partial \bar{f}(\mathbf{z})}{\partial \mathbf{z}}\mathbf{w}(\mathbf{z},t)\right)}=i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\begin{bmatrix}0&0\\0&0\end{bmatrix}\mathbf{z}(t)=\begin{bmatrix}0&0\\0&0\end{bmatrix}$$

$$2^{\text{nd}}\text{ term: }\overline{\left(\frac{\partial \tilde{f}(\mathbf{z},t)}{\partial \mathbf{z}}\mathbf{w}(\mathbf{z},t)\right)}=i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\begin{bmatrix}1&0\\0&-1\end{bmatrix}\mathbf{z}(t)$$

$$3^{\text{rd}}\text{ term: }\bar{g}(\mathbf{z},t)=0$$

$$4^{\text{th}}\text{ term: }\overline{\left(\frac{\partial \mathbf{w}(\mathbf{z},t)}{\partial \mathbf{z}}\bar{f}(\mathbf{z})\right)}=i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\begin{bmatrix}0&0\\0&0\end{bmatrix}\mathbf{z}(t)=\begin{bmatrix}0&0\\0&0\end{bmatrix}$$

We finally obtain that

$$\boxed{\bar{h}(\mathbf{z})=i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\begin{bmatrix}1&0\\0&-1\end{bmatrix}\mathbf{z}(t)} \tag{6.73}$$

$\tilde{h}(\mathbf{z},t)$ occurs from Eqs.. (6.21), (6.72), (6.73):

$$\boxed{\tilde{h}(\mathbf{z},t)=i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\begin{bmatrix}e^{i2\omega t}&0\\0&-e^{-i2\omega t}\end{bmatrix}\mathbf{z}(t)-i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\begin{bmatrix}-e^{-i2\omega t}&0\\0&e^{i2\omega t}\end{bmatrix}\mathbf{z}(t)} \tag{6.74}$$

Using Eqs. (6.63), (6.73), Eq. (6.35) becomes

$$\dot{\mathbf{z}}(t)=\frac{i\Omega_R}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}\mathbf{z}(t)+i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\begin{bmatrix}1&0\\0&-1\end{bmatrix}\mathbf{z}(t)\Rightarrow$$

$$\boxed{\dot{\mathbf{z}}(t)=i\begin{bmatrix}\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}&\frac{\Omega_R}{2}\\\frac{\Omega_R}{2}&-\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\end{bmatrix}\mathbf{z}(t)} \tag{6.75}$$

Setting $\alpha := \left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega}$ and $\beta := \frac{\Omega_R}{2}$, the system of differential equations of Eq. (6.75) becomes

$$\left.\begin{array}{l} \dot{z}_1(t) = i\alpha z_1(t) + i\beta z_2(t) \\ \dot{z}_2(t) = i\beta z_1(t) - i\alpha z_2(t) \end{array}\right\} \Rightarrow \left\{\begin{array}{l} \ddot{z}_1(t) = i\alpha \dot{z}_1(t) + i\beta \dot{z}_2(t) \\ \ddot{z}_2(t) = i\beta \dot{z}_1(t) - i\alpha \dot{z}_2(t) \end{array}\right\} \Rightarrow$$

$$\left\{\begin{array}{l} \ddot{z}_1(t) = i\alpha(i\alpha z_1(t) + i\beta z_2(t)) + i\beta(i\beta z_1(t) - i\alpha z_2(t)) \\ \ddot{z}_2(t) = i\beta(i\alpha z_1(t) + i\beta z_2(t)) - i\alpha(i\beta z_1(t) - i\alpha z_2(t)) \end{array}\right\} \Rightarrow$$

$$\boxed{\begin{array}{l} \ddot{z}_1(t) + B^2 z_1(t) = 0 \\ \ddot{z}_2(t) + B^2 z_2(t) = 0 \end{array}}, \tag{6.76}$$

where $B^2 := \alpha^2 + \beta^2$. The solutions to the above equations are known:

$$\left\{\begin{array}{l} z_1(t) = A_{12}\cos(Bt) + B_{12}\sin(Bt) \\ z_2(t) = A_{22}\cos(Bt) + B_{22}\sin(Bt) \end{array}\right\} \tag{6.77}$$

with

$$\left\{\begin{array}{l} z_1(0) = A_{12} \\ z_2(0) = A_{22} \end{array}\right\} \text{ and } \left\{\begin{array}{l} \dot{z}_1(0) = B \cdot B_{12} = i\alpha z_1(0) + i\beta z_2(0) \\ \dot{z}_2(0) = B \cdot B_{22} = i\beta z_1(0) - i\alpha z_2(0) \end{array}\right\} \tag{6.78}$$

$A_{12}, B_{12}, A_{22}, B_{22}$ are determined by applying the initial conditions. Finally, $\mathbf{u}$ is calculated from the Eq. (6.33),

$$\epsilon^2 \mathbf{u}(\mathbf{z}, t) = i\left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega^2} \sin 2\omega t \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \mathbf{z}(t). \tag{6.79}$$

To sum up, we present the results for the first- and second-order AM.

- First order:

$$\left\{\begin{array}{l} \mathbf{x}(t) = \mathbf{y}(t) + \epsilon\, \mathbf{w}(\mathbf{y}(t), t) \\[2ex] \mathbf{y}(t) = \begin{bmatrix} A_{11}\cos\left(\frac{\Omega_R}{2}t\right) + B_{11}\sin\left(\frac{\Omega_R}{2}t\right) \\ A_{21}\cos\left(\frac{\Omega_R}{2}t\right) + B_{21}\sin\left(\frac{\Omega_R}{2}t\right) \end{bmatrix} \\[2ex] \epsilon \mathbf{w}(\mathbf{y}, t) = \frac{\Omega_R}{4\omega} \begin{bmatrix} 0 & -e^{-i2\omega t} \\ e^{i2\omega t} & 0 \end{bmatrix} \mathbf{y}(t) \end{array}\right\} \tag{6.80}$$

- Second order:

$$\left\{\begin{array}{l} \mathbf{x}(t) = \mathbf{z}(t) + \epsilon \mathbf{w}(\mathbf{z}(t), t) + \epsilon^2 \mathbf{u}(\mathbf{z}(t), t) \\[2ex] \mathbf{z}(t) = \begin{bmatrix} A_{12}\cos(Bt) + B_{12}\sin(Bt) \\ A_{22}\cos(Bt) + B_{22}\sin(Bt) \end{bmatrix} \\[2ex] \epsilon \mathbf{w}(\mathbf{z}(t), t) = \frac{\Omega_R}{4\omega} \begin{bmatrix} 0 & -e^{-i2\omega t} \\ e^{i2\omega t} & 0 \end{bmatrix} \mathbf{z}(t) \\[2ex] \epsilon^2 \mathbf{u}(\mathbf{z}(t), t) = i\left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega^2} \sin 2\omega t \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \mathbf{z}(t) \end{array}\right\} \tag{6.81}$$

We observe that in Eqs (6.80) and (6.81) the three distinct values of ϵ are reduced to one, $\frac{\Omega_R}{\omega}$. Thus, when in-resonance ($\Delta = 0$), this ϵ reflects the relative magnitude of the perturbation, which is described by the Rabi (angular) frequency with respect to the frequency ω. These considerations give us the opportunity to confront different numerical cases.

6.2.3 Solutions for different initial conditions.

There is another step we have to take before we can arrive at some final equations which allow as to describe the behavior of Rabi oscillations in the 2LS; that is, to set the initial conditions. We will assume the probability that the electron is located each energy level, at time zero. This allows as to calculate the unknown factors obtained for each case of the AM, discussed above, and reach the final equations. The initial conditions that will be used are

1. $C_1(0) = 1, C_2(0) = 0$, i.e., initial placement of the electron at the lower level,
2. $C_1(0) = 0, C_2(0) = 1$, i.e., initial placement of the electron at the higher level, and
3. $C_1(0) = \frac{1}{\sqrt{2}}e^{i\theta}, C_2(0) = \frac{1}{\sqrt{2}}e^{i\phi}$, i.e., initial placement of the electron at both levels with probability $|C_1(0)|^2 = |C_2(0)|^2 = \frac{1}{2}$.

1. Let the initial conditions be $C_1(0) = 1, C_2(0) = 0.$

Solution for $\Delta \neq 0, 1^{\text{st}}$ order AM

Using Eqs. (6.59) for $\mathbf{x}(0) = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$, we have

$$\mathbf{x}(0) = \begin{bmatrix} y_{10} \\ y_{20} \end{bmatrix} + \frac{\Omega_R}{2}\begin{bmatrix} 0 & \frac{1}{\Delta} - \frac{1}{\Sigma} \\ \frac{1}{\Sigma} - \frac{1}{\Delta} & 0 \end{bmatrix}\begin{bmatrix} y_{10} \\ y_{20} \end{bmatrix} \Rightarrow \left\{\begin{aligned} 1 &= y_{10} + \frac{\Omega_R}{2}\left(\frac{1}{\Delta} - \frac{1}{\Sigma}\right) y_{20} \\ 0 &= y_{20} + \frac{\Omega_R}{2}\left(\frac{1}{\Sigma} - \frac{1}{\Delta}\right) y_{10} \end{aligned}\right\} \Rightarrow$$

$$\left\{\begin{aligned} &1 = y_{10} + \frac{2A}{\Omega_R} y_{20} \\ &0 = y_{20} - \frac{2A}{\Omega_R} y_{10} \Rightarrow y_{20} = \frac{2A}{\Omega_R} y_{10} \end{aligned}\right\} \Rightarrow 1 = y_{10} + \left(\frac{2A}{\Omega_R}\right)^2 y_{10} \Rightarrow$$

$$\boxed{y_{10} = \frac{1}{1 + \left(\frac{2A}{\Omega_R}\right)^2}}\ ,\ \boxed{y_{20} = \frac{\frac{2A}{\Omega_R}}{1 + \left(\frac{2A}{\Omega_R}\right)^2}}, \tag{6.82}$$

where

$$A = \left(\frac{\Omega_R}{2}\right)^2 \frac{2\Omega}{\omega^2 - \Omega^2} \tag{6.83}$$

Therefore, the solution is,

$$\mathbf{x}(t) = \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \begin{bmatrix} 1 & \frac{i\Omega_R}{2}\left(\frac{e^{+i\Delta t}}{i\Delta} - \frac{e^{-i\Sigma t}}{i\Sigma}\right) \\ \frac{i\Omega_R}{2}\left(-\frac{e^{-i\Delta t}}{i\Delta} + \frac{e^{+i\Sigma t}}{i\Sigma}\right) & 1 \end{bmatrix} \begin{bmatrix} \frac{1}{1+\left(\frac{2A}{\Omega_R}\right)^2} \\ \frac{\frac{2A}{\Omega_R}}{1+\left(\frac{2A}{\Omega_R}\right)^2} \end{bmatrix} \Rightarrow$$

$$\boxed{\begin{aligned} C_1(t) &= \frac{1}{1+\left(\frac{2A}{\Omega_R}\right)^2}\left[1 + A\left(\frac{e^{+i\Delta t}}{\Delta} - \frac{e^{-i\Sigma t}}{\Sigma}\right)\right] \\ C_2(t) &= \frac{1}{1+\left(\frac{2A}{\Omega_R}\right)^2}\left[\frac{2A}{\Omega_R} + \frac{\Omega_R}{2}\left(-\frac{e^{-i\Delta t}}{\Delta} + \frac{e^{+i\Sigma t}}{\Sigma}\right)\right]\end{aligned}}, \tag{6.84}$$

where $|C_1(t)|^2$ is the probability to find the electron at lower level and $|C_2(t)|^2$ is the probability to find the electron at higher level.

$\boxed{\text{Solution for } \Delta \neq 0, 2^{\text{nd}} \text{ order AM}}$

Using Eqs. (6.60) for $\mathbf{x}(0) = \begin{bmatrix}1\\0\end{bmatrix}$, we have

$$\mathbf{x}(0) = \begin{bmatrix}z_{10}\\z_{20}\end{bmatrix} + \frac{\Omega_R}{2}\left\{\begin{bmatrix}0 & \frac{1}{\Delta}-\frac{1}{\Sigma}\\ \frac{1}{\Sigma}-\frac{1}{\Delta} & 0\end{bmatrix}\right)\begin{bmatrix}z_{10}\\z_{20}\end{bmatrix} + i\left(\frac{\Omega_R}{2}\right)^2\left\{\frac{1}{i2\omega\Delta}\begin{bmatrix}1&0\\0&1\end{bmatrix} + \frac{1}{i2\omega\Sigma}\begin{bmatrix}1&0\\0&1\end{bmatrix}\right\}\begin{bmatrix}z_{10}\\z_{20}\end{bmatrix} \Rightarrow$$

$$\left\{\begin{aligned} 1 &= z_{10} + \frac{\Omega_R}{2}\left(\frac{1}{\Delta}-\frac{1}{\Sigma}\right)z_{20} + \left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\left(\frac{1}{\Delta}+\frac{1}{\Sigma}\right)z_{10} \Rightarrow 1 = \left(1+\frac{A}{2\Omega}\right)z_{10} + \frac{2A}{\Omega_R}z_{20} \\ 0 &= z_{20} + \frac{\Omega_R}{2}\left(\frac{1}{\Sigma}-\frac{1}{\Delta}\right)z_{10} + \left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\left(\frac{1}{\Delta}+\frac{1}{\Sigma}\right)z_{20} \Rightarrow \frac{2A}{\Omega_R}z_{10} = \left(1+\frac{A}{2\Omega}\right)z_{20}\end{aligned}\right\} \Rightarrow$$

$$\left\{\begin{aligned} 1 &= \left(1+\frac{A}{2\Omega}\right)z_{10} + \frac{\left(\frac{2A}{\Omega_R}\right)^2}{\left(1+\frac{A}{2\Omega}\right)}z_{10} \\ z_{20} &= \frac{\frac{2A}{\Omega_R}}{\left(1+\frac{A}{2\Omega}\right)}z_{10}\end{aligned}\right\} \Rightarrow \left\{\begin{aligned} &\boxed{z_{10} = \frac{1+\frac{A}{2\Omega}}{\left(1+\frac{A}{2\Omega}\right)^2 + \left(\frac{2A}{\Omega_R}\right)^2}} \\ &\boxed{z_{20} = \frac{\frac{2A}{\Omega_R}}{\left(1+\frac{A}{2\Omega}\right)^2 + \left(\frac{2A}{\Omega_R}\right)^2}}\end{aligned}\right\}$$

Therefore, the solution is

$$\mathbf{x}(t) = \begin{bmatrix}C_1(t)\\C_2(t)\end{bmatrix} = \begin{bmatrix} 1 + \left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\left(\frac{e^{-i2\omega t}}{\Delta} + \frac{e^{i2\omega t}}{\Sigma}\right) & \frac{\Omega_R}{2}\left(\frac{e^{i\Delta t}}{\Delta} - \frac{e^{-i\Sigma t}}{\Sigma}\right) \\ \frac{\Omega_R}{2}\left(-\frac{e^{-i\Delta t}}{\Delta} + \frac{e^{+i\Sigma t}}{\Sigma}\right) & 1 + \left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\left(\frac{e^{i2\omega t}}{\Delta} + \frac{e^{-i2\omega t}}{\Sigma}\right)\end{bmatrix}\begin{bmatrix}z_{10}e^{-iAt}\\ z_{20}e^{iAt}\end{bmatrix} \Rightarrow$$

$$\boxed{\begin{aligned} C_1(t) &= \left[1 + \left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\left(\frac{e^{-i2\omega t}}{\Delta} + \frac{e^{i2\omega t}}{\Sigma}\right)\right]z_{10}e^{-iAt} + \left[\frac{\Omega_R}{2}\left(\frac{e^{i\Delta t}}{\Delta} - \frac{e^{-i\Sigma t}}{\Sigma}\right)\right]z_{20}e^{iAt} \\ C_2(t) &= \left[\frac{\Omega_R}{2}\left(-\frac{e^{-i\Delta t}}{\Delta} + \frac{e^{+i\Sigma t}}{\Sigma}\right)\right]z_{10}e^{-iAt} + \left[1 + \left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\left(\frac{e^{i2\omega t}}{\Delta} + \frac{e^{-i2\omega t}}{\Sigma}\right)\right]z_{20}e^{iAt}\end{aligned}}. \tag{6.85}$$

Solution for $\Delta = 0, 1^{\text{st}}$ order AM

Using Eqs. (6.80) for $\mathbf{x}(0) = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$, we have

$$\mathbf{x}(0) = \begin{bmatrix} A_{11} \\ A_{21} \end{bmatrix} + \frac{\Omega_R}{4\omega}\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} A_{11} \\ A_{21} \end{bmatrix} \Rightarrow \left\{\begin{matrix} 1 = A_{11} - \dfrac{\Omega_R}{4\omega}A_{21} \\ 0 = A_{21} + \dfrac{\Omega_R}{4\omega}A_{11} \Rightarrow A_{21} = -\dfrac{\Omega_R}{4\omega}A_{11} \end{matrix}\right\} \Rightarrow$$

$$\left\{\begin{matrix} 1 = A_{11} + (\dfrac{\Omega_R}{4\omega})^2 A_{11} \\ A_{21} = -\dfrac{\Omega_R}{4\omega}A_{11} \end{matrix}\right\} \Rightarrow \boxed{A_{11} = \frac{1}{1 + (\frac{\Omega_R}{4\omega})^2}}, \boxed{A_{21} = \frac{-\frac{\Omega_R}{4\omega}}{1 + (\frac{\Omega_R}{4\omega})^2}}$$

Furthermore, through Eq. (6.67), we know that

$$\left\{\begin{matrix} \dot{y}_1(0) = \dfrac{\Omega_R}{2}B_{11} = i\dfrac{\Omega_R}{2}y_2(0) \\ \dot{y}_2(0) = \dfrac{\Omega_R}{2}B_{21} = i\dfrac{\Omega_R}{2}y_1(0) \end{matrix}\right\} \Rightarrow \left\{\begin{matrix} B_{11} = iA_{21} = \dfrac{-i\frac{\Omega_R}{4\omega}}{1 + (\frac{\Omega_R}{4\omega})^2} \\ B_{21} = iA_{11} = \dfrac{i}{1 + (\frac{\Omega_R}{4\omega})^2} \end{matrix}\right\}$$

Therefore, the solution is

$$\mathbf{x}(t) = \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} + \frac{\Omega_R}{4\omega}\begin{bmatrix} 0 & -e^{-i2\omega t} \\ e^{i2\omega t} & 0 \end{bmatrix}\begin{bmatrix} y_1 \\ y_2 \end{bmatrix} \Rightarrow$$

$$\boxed{\begin{aligned} C_1(t) &= A_{11}\cos\left(\frac{\Omega_R}{2}t\right) + iA_{21}\sin\left(\frac{\Omega_R}{2}t\right) - \frac{\Omega_R}{4\omega}e^{-i2\omega t}\left[A_{21}\cos\left(\frac{\Omega_R}{2}t\right) + iA_{11}\sin\left(\frac{\Omega_R}{2}t\right)\right] \\ C_2(t) &= A_{21}\cos\left(\frac{\Omega_R}{2}t\right) + iA_{11}\sin\left(\frac{\Omega_R}{2}t\right) + \frac{\Omega_R}{4\omega}e^{i2\omega t}\left[A_{11}\cos\left(\frac{\Omega_R}{2}t\right) + iA_{21}\sin\left(\frac{\Omega_R}{2}t\right)\right] \end{aligned}}. \tag{6.86}$$

Solution for $\Delta = 0, 2^{\text{nd}}$ order AM

Using Eqs. (6.81) for $\mathbf{x}(0) = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$, we have

$$\mathbf{x}(0) = \begin{bmatrix} A_{12} \\ A_{22} \end{bmatrix} + \frac{\Omega_R}{4\omega}\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} A_{12} \\ A_{22} \end{bmatrix} \Rightarrow \left\{\begin{matrix} 1 = A_{12} - \dfrac{\Omega_R}{4\omega}A_{22} \\ 0 = A_{22} + \dfrac{\Omega_R}{4\omega}A_{12} \Rightarrow A_{22} = -\dfrac{\Omega_R}{4\omega}A_{12} \end{matrix}\right\} \Rightarrow$$

$$\left\{\begin{matrix} 1 = A_{12} + \left(\dfrac{\Omega_R}{4\omega}\right)^2 A_{12} \\ A_{22} = -\dfrac{\Omega_R}{4\omega}A_{12} \end{matrix}\right\} \Rightarrow \boxed{A_{12} = \frac{1}{1 + \left(\frac{\Omega_R}{4\omega}\right)^2}}, \boxed{A_{22} = \frac{-\frac{\Omega_R}{4\omega}}{1 + \left(\frac{\Omega_R}{4\omega}\right)^2}}$$

Furthermore, through Eq. (6.78), we know that

$$\left\{\begin{matrix} \dot{z}_1(0) = B \cdot B_{12} = i\alpha z_1(0) + i\beta z_2(0) \\ \dot{z}_2(0) = B \cdot B_{22} = i\beta z_1(0) - i\alpha z_2(0) \end{matrix}\right\} \Rightarrow$$

$$\left\{\begin{array}{l} B_{12}=\dfrac{i\alpha A_{12}+iBA_{22}}{B}=i\dfrac{\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\frac{1}{1+\left(\frac{\Omega_R}{4\omega}\right)^2}+\frac{\Omega_R}{2}\frac{-\frac{\Omega_R}{4\omega}}{1+\left(\frac{\Omega_R}{4\omega}\right)^2}}{B}=0 \\ B_{22}=\dfrac{i\beta A_{12}-i\alpha A_{22}}{B}=i\dfrac{\frac{\Omega_R}{2}\frac{1+\left(\frac{\Omega_R}{4\omega}\right)^2}{1+\left(\frac{\Omega_R}{4\omega}\right)^2}}{B}=\dfrac{i\Omega_R}{2B} \end{array}\right\}$$

Therefore, the solution is

$$\mathbf{x}(t)=\begin{bmatrix} C_1(t) \\ C_2(t)\end{bmatrix}=\begin{bmatrix} 1+i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega^2}\sin(2\omega t) & \frac{\Omega_R}{4\omega}(-e^{-i2\omega t}) \\ \frac{\Omega_R}{4\omega}e^{i2\omega t} & 1-i\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega^2}\sin(2\omega t)\end{bmatrix}\begin{bmatrix} z_1(t) \\ z_2(t)\end{bmatrix}\Rightarrow$$

$$\boxed{\begin{array}{l} C_1(t)=\left[1+i\left(\dfrac{\Omega_R}{2}\right)^2\dfrac{1}{2\omega^2}\sin(2\omega t)\right]z_1(t)-\dfrac{\Omega_R}{4\omega}e^{-i2\omega t}z_2(t) \\ C_2(t)=\dfrac{\Omega_R}{4\omega}e^{i2\omega t}z_1(t)+\left[1-i\left(\dfrac{\Omega_R}{2}\right)^2\dfrac{1}{2\omega^2}\sin(2\omega t)\right]z_2(t) \end{array}}, \tag{6.87}$$

with

$$\left\{\begin{array}{l} z_1(t)=A_{12}\cos(Bt)+B_{12}\sin(Bt) \\ z_2(t)=A_{22}\cos(Bt)+B_{22}\sin(Bt)\end{array}\right\}\text{ and }\left\{\begin{array}{l} A_{12}=\dfrac{1}{1+\left(\frac{\Omega_R}{4\omega}\right)^2} \\ A_{22}=\dfrac{-\frac{\Omega_R}{4\omega}}{1+\left(\frac{\Omega_R}{4\omega}\right)^2} \\ \mathrm{B}_{12}=0 \\ \mathrm{B}_{22}=\dfrac{i\Omega_R}{2B}\end{array}\right\}.$$

2. Let the initial conditions be $C_1(0)=0, C_2(0)=1$.

Solution for $\Delta \neq 0, 1^{\text{st}}$ order AM

Using Eqs. (6.59) for $\mathbf{x}(0)=\begin{bmatrix}0\\1\end{bmatrix}$, we have

$$\mathbf{x}(0)=\begin{bmatrix} y_{10} \\ y_{20}\end{bmatrix}+\frac{\Omega_R}{2}\begin{bmatrix} 0 & \frac{1}{\Delta}-\frac{1}{\Sigma} \\ \frac{1}{\Sigma}-\frac{1}{\Delta} & 0\end{bmatrix}\begin{bmatrix} y_{10} \\ y_{20}\end{bmatrix}\Rightarrow\left\{\begin{array}{l} 0=y_{10}+\dfrac{\Omega_R}{2}\left(\dfrac{1}{\Delta}-\dfrac{1}{\Sigma}\right)y_{20} \\ 1=y_{20}+\dfrac{\Omega_R}{2}\left(\dfrac{1}{\Sigma}-\dfrac{1}{\Delta}\right)y_{10}\end{array}\right\}\Rightarrow$$

$$\left\{\begin{array}{l} 0=y_{10}+\dfrac{2A}{\Omega_R}y_{20}\Rightarrow y_{10}=-\dfrac{2A}{\Omega_R}y_{20} \\ 1=y_{20}-\dfrac{2A}{\Omega_R}y_{10}\end{array}\right\}\Rightarrow 1=y_{20}+\left(\frac{2A}{\Omega_R}\right)^2 y_{20}\Rightarrow$$

$$\boxed{y_{20}=\frac{1}{1+\left(\frac{2A}{\Omega_R}\right)^2}}\,,\quad\boxed{y_{10}=\frac{-\frac{2A}{\Omega_R}}{1+\left(\frac{2A}{\Omega_R}\right)^2}}\,,\tag{6.88}$$

where

$$A=\left(\frac{\Omega_R}{2}\right)^2\frac{2\Omega}{\omega^2-\Omega^2}\tag{6.89}$$

Therefore, the solution is

$$\mathbf{x}(t)=\begin{bmatrix}C_1(t)\\C_2(t)\end{bmatrix}=\begin{bmatrix}1 & \frac{i\Omega_R}{2}\left(\frac{e^{+i\Delta t}}{i\Delta}-\frac{e^{-i\Sigma t}}{i\Sigma}\right)\\ \frac{i\Omega_R}{2}\left(-\frac{e^{-i\Delta t}}{i\Delta}+\frac{e^{+i\Sigma t}}{i\Sigma}\right) & 1\end{bmatrix}\begin{bmatrix}\frac{-\frac{2A}{\Omega_R}}{1+\left(\frac{2A}{\Omega_R}\right)^2}\\ \frac{1}{1+\left(\frac{2A}{\Omega_R}\right)^2}\end{bmatrix}\Rightarrow$$

$$\boxed{\begin{aligned}C_1(t)&=\frac{1}{1+\left(\frac{2A}{\Omega_R}\right)^2}\left[-\frac{2A}{\Omega_R}+\frac{\Omega_R}{2}\left(\frac{e^{i\Delta t}}{\Delta}-\frac{e^{-i\Sigma t}}{\Sigma}\right)\right]\\ C_2(t)&=\frac{1}{1+\left(\frac{2A}{\Omega_R}\right)^2}\left[1-A\left(-\frac{e^{-i\Delta t}}{\Delta}+\frac{e^{i\Sigma t}}{\Sigma}\right)\right]\end{aligned}}\,.\tag{6.90}$$

Solution for $\Delta \neq 0$, 2^{nd} order AM

Using Eqs. (6.60) for $\mathbf{x}(0)=\begin{bmatrix}0\\1\end{bmatrix}$, we have

$$\mathbf{x}(0)=\begin{bmatrix}z_{10}\\z_{20}\end{bmatrix}+\frac{\Omega_R}{2}\left\{\begin{bmatrix}0 & \frac{1}{\Delta}-\frac{1}{\Sigma}\\ \frac{1}{\Sigma}-\frac{1}{\Delta} & 0\end{bmatrix}\right\}\begin{bmatrix}z_{10}\\z_{20}\end{bmatrix}+i\left(\frac{\Omega_R}{2}\right)^2\left\{\frac{1}{i2\omega\Delta}\begin{bmatrix}1&0\\0&1\end{bmatrix}+\frac{1}{i2\omega\Sigma}\begin{bmatrix}1&0\\0&1\end{bmatrix}\right\}\begin{bmatrix}z_{10}\\z_{20}\end{bmatrix}\Rightarrow$$

$$\left\{\begin{aligned}0&=z_{10}+\frac{\Omega_R}{2}\left(\frac{1}{\Delta}-\frac{1}{\Sigma}\right)z_{20}+\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\left(\frac{1}{\Delta}+\frac{1}{\Sigma}\right)z_{10}\Rightarrow-\frac{2A}{\Omega_R}z_{20}=\left(1+\frac{A}{2\Omega}\right)z_{10}\\ 1&=z_{20}+\frac{\Omega_R}{2}\left(\frac{1}{\Sigma}-\frac{1}{\Delta}\right)z_{10}+\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\left(\frac{1}{\Delta}+\frac{1}{\Sigma}\right)z_{20}\Rightarrow 1=\left(1+\frac{A}{2\Omega}\right)z_{20}-\frac{2A}{\Omega_R}z_{10}\end{aligned}\right\}\Rightarrow$$

$$\left\{\begin{aligned}z_{10}&=\frac{-\frac{2A}{\Omega_R}}{\left(1+\frac{A}{2\Omega}\right)}z_{20}\\ 1&=\left(1+\frac{A}{2\Omega}\right)z_{20}+\frac{\left(\frac{2A}{\Omega_R}\right)^2}{\left(1+\frac{A}{2\Omega}\right)}z_{20}\end{aligned}\right\}\Rightarrow\left\{\begin{aligned}&\boxed{z_{10}=\frac{-\frac{2A}{\Omega_R}}{\left(1+\frac{A}{2\Omega}\right)^2+\left(\frac{2A}{\Omega_R}\right)^2}}\\ &\boxed{z_{20}=\frac{1+\frac{A}{2\Omega}}{\left(1+\frac{A}{2\Omega}\right)^2+\left(\frac{2A}{\Omega_R}\right)^2}}\end{aligned}\right\}$$

Therefore, the solution is

$$\mathbf{x}(t) = \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \begin{bmatrix} 1 + \left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega}\left(\frac{e^{-i2\omega t}}{\Delta} + \frac{e^{i2\omega t}}{\Sigma}\right) & \frac{\Omega_R}{2}\left(\frac{e^{i\Delta t}}{\Delta} - \frac{e^{-i\Sigma t}}{\Sigma}\right) \\ \frac{\Omega_R}{2}\left(-\frac{e^{-i\Delta t}}{\Delta} + \frac{e^{+i\Sigma t}}{\Sigma}\right) & 1 + \left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega}\left(\frac{e^{i2\omega t}}{\Delta} + \frac{e^{-i2\omega t}}{\Sigma}\right) \end{bmatrix} \begin{bmatrix} z_{10}e^{-iAt} \\ z_{20}e^{iAt} \end{bmatrix} \Rightarrow$$

$$\boxed{\begin{array}{l} C_1(t) = \left[1 + \left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega}\left(\frac{e^{-i2\omega t}}{\Delta} + \frac{e^{i2\omega t}}{\Sigma}\right)\right] z_{10}e^{-iAt} + \left[\frac{\Omega_R}{2}\left(\frac{e^{i\Delta t}}{\Delta} - \frac{e^{-i\Sigma t}}{\Sigma}\right)\right] z_{20}e^{iAt} \\ C_2(t) = \left[\frac{\Omega_R}{2}\left(-\frac{e^{-i\Delta t}}{\Delta} + \frac{e^{+i\Sigma t}}{\Sigma}\right)\right] z_{10}e^{-iAt} + \left[1 + \left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega}\left(\frac{e^{i2\omega t}}{\Delta} + \frac{e^{-i2\omega t}}{\Sigma}\right)\right] z_{20}e^{iAt} \end{array}}. \tag{6.91}$$

Solution for $\Delta = 0$, 1st order AM

Using Eqs. (6.80) for $\mathbf{x}(0) = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$, we have

$$\mathbf{x}(0) = \begin{bmatrix} A_{11} \\ A_{21} \end{bmatrix} + \frac{\Omega_R}{4\omega}\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} A_{11} \\ A_{21} \end{bmatrix} \Rightarrow \left\{\begin{array}{l} 0 = A_{11} - \frac{\Omega_R}{4\omega}A_{21} \Rightarrow A_{11} = \frac{\Omega_R}{4\omega}A_{21} \\ 1 = A_{21} + \frac{\Omega_R}{4\omega}A_{11} \end{array}\right\} \Rightarrow$$

$$\left\{\begin{array}{l} A_{11} = \frac{\Omega_R}{4\omega}A_{21} \\ 1 = A_{21} + \left(\frac{\Omega_R}{4\omega}\right)^2 A_{21} \end{array}\right\} \Rightarrow \boxed{A_{11} = \frac{\frac{\Omega_R}{4\omega}}{1 + \left(\frac{\Omega_R}{4\omega}\right)^2}}, \boxed{A_{21} = \frac{1}{1 + \left(\frac{\Omega_R}{4\omega}\right)^2}}$$

Furthermore, through Eq. (6.67), we know that

$$\left\{\begin{array}{l} y_1(0) = \frac{\Omega_R}{2}B_{11} = i\frac{\Omega_R}{2}y_2(0) \\ y_2(0) = \frac{\Omega_R}{2}B_{21} = i\frac{\Omega_R}{2}y_1(0) \end{array}\right\} \Rightarrow \left\{\begin{array}{l} B_{11} = iA_{21} = \frac{i}{1 + \left(\frac{\Omega_R}{4\omega}\right)^2} \\ B_{21} = iA_{11} = \frac{i\frac{\Omega_R}{4\omega}}{1 + \left(\frac{\Omega_R}{4\omega}\right)^2} \end{array}\right\}$$

Therefore, the solution is

$$x(t) = \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} + \frac{\Omega_R}{4\omega}\begin{bmatrix} 0 & -e^{-i2\omega t} \\ e^{i2\omega t} & 0 \end{bmatrix}\begin{bmatrix} y_1 \\ y_2 \end{bmatrix} \Rightarrow$$

$$\boxed{\begin{array}{l} C_1(t) = A_{11}\cos\left(\frac{\Omega_R}{2}t\right) + iA_{21}\sin\left(\frac{\Omega_R}{2}t\right) - \frac{\Omega_R}{4\omega}e^{-i2\omega t}\left[A_{21}\cos\left(\frac{\Omega_R}{2}t\right) + iA_{11}\sin\left(\frac{\Omega_R}{2}t\right)\right] \\ C_2(t) = A_{21}\cos\left(\frac{\Omega_R}{2}t\right) + iA_{11}\sin\left(\frac{\Omega_R}{2}t\right) + \frac{\Omega_R}{4\omega}e^{i2\omega t}\left[A_{11}\cos\left(\frac{\Omega_R}{2}t\right) + iA_{21}\sin\left(\frac{\Omega_R}{2}t\right)\right] \end{array}}. \tag{6.92}$$

Solution for $\Delta = 0$, 2nd order AM

Using Eqs. (6.81) for $\mathbf{x}(0) = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$, we have

$$\mathbf{x}(0) = \begin{bmatrix} A_{12} \\ A_{22} \end{bmatrix} + \frac{\Omega_R}{4\omega} \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} A_{12} \\ A_{22} \end{bmatrix} \Rightarrow \left\{ \begin{matrix} 0 = A_{12} - \dfrac{\Omega_R}{4\omega} A_{22} \Rightarrow A_{12} = \dfrac{\Omega_R}{4\omega} A_{22} \\ 1 = A_{22} + \dfrac{\Omega_R}{4\omega} A_{12} \end{matrix} \right\} \Rightarrow$$

$$\left\{ \begin{matrix} A_{12} = \dfrac{\Omega_R}{4\omega} A_{22} \\ 1 = A_{22} + \left(\dfrac{\Omega_R}{4\omega}\right)^2 A_{22} \end{matrix} \right\} \Rightarrow \boxed{A_{12} = \frac{\frac{\Omega_R}{4\omega}}{1 + \left(\frac{\Omega_R}{4\omega}\right)^2}}, \boxed{A_{22} = \frac{1}{1 + \left(\frac{\Omega_R}{4\omega}\right)^2}}$$

Furthermore, through Eq. (6.78), we know that

$$\left\{ \begin{matrix} \dot{z}_1(0) = B \cdot B_{12} = i\alpha z_1(0) + i\beta z_2(0) \\ \dot{z}_2(0) = B \cdot B_{22} = i\beta z_1(0) - i\alpha z_2(0) \end{matrix} \right\} \Rightarrow$$

$$\left\{ \begin{matrix} B_{12} = \dfrac{i\alpha A_{12} + i\beta A_{22}}{B} = i\dfrac{\frac{\Omega_R}{2} \frac{1+\left(\frac{\Omega_R}{4\omega}\right)^2}{1+\left(\frac{\Omega_R}{4\omega}\right)^2}}{B} = \dfrac{i\Omega_R}{2B} \\ B_{22} = \dfrac{i\beta A_{12} - i\alpha A_{22}}{B} = i\dfrac{\frac{\Omega_R}{2} \frac{\frac{\Omega_R}{4\omega}}{1+\left(\frac{\Omega_R}{4\omega}\right)^2} - \left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega} \frac{1}{1+\left(\frac{\Omega_R}{4\omega}\right)^2}}{B} = 0 \end{matrix} \right\}$$

Therefore, the solution is

$$\mathbf{x}(t) = \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \begin{bmatrix} 1 + i\left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega^2} \sin(2\omega t) & \frac{\Omega_R}{4\omega}(-e^{-i2\omega t}) \\ \frac{\Omega_R}{4\omega} e^{i2\omega t} & 1 - i\left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega^2} \sin(2\omega t) \end{bmatrix} \begin{bmatrix} z_1(t) \\ z_2(t) \end{bmatrix} \Rightarrow$$

$$\boxed{\begin{matrix} C_1(t) = \left[1 + i\left(\dfrac{\Omega_R}{2}\right)^2 \dfrac{1}{2\omega^2} \sin(2\omega t)\right] z_1(t) - \dfrac{\Omega_R}{4\omega} e^{-i2\omega t} z_2(t) \\ C_2(t) = \dfrac{\Omega_R}{4\omega} e^{i2\omega t} z_1(t) + \left[1 - i\left(\dfrac{\Omega_R}{2}\right)^2 \dfrac{1}{2\omega^2} \sin(2\omega t)\right] z_2(t) \end{matrix}}, \tag{6.93}$$

with

$$\left\{ \begin{matrix} z_1 = A_{12}\cos(Bt) + B_{12}\sin(Bt) \\ z_2 = A_{22}\cos(Bt) + B_{22}\sin(Bt) \end{matrix} \right\} \text{ and } \left\{ \begin{matrix} A_{12} = \dfrac{-\frac{\Omega_R}{4\omega}}{1 + \left(\frac{\Omega_R}{4\omega}\right)^2} \\ A_{22} = \dfrac{1}{1 + \left(\frac{\Omega_R}{4\omega}\right)^2} \\ \mathrm{B}_{12} = \dfrac{i\Omega_R}{2B} \\ \mathrm{B}_{22} = 0 \end{matrix} \right\}.$$

3. Let the initial conditions be $C_1(0) = \frac{1}{\sqrt{2}}e^{i\theta}, C_2(0) = \frac{1}{\sqrt{2}}e^{i\phi}$, with probability $|C_1(0)|^2 = |C_2(0)|^2 = \frac{1}{2}$.

Solution for $\Delta \neq 0, 1^{\text{st}}$ order AM

Using Eqs. (6.59) for $\mathbf{x}(0) = \begin{bmatrix} \frac{1}{\sqrt{2}}e^{i\theta} \\ \frac{1}{\sqrt{2}}e^{i\phi} \end{bmatrix}$, we have

$$\mathbf{x}(0) = \begin{bmatrix} y_{10} \\ y_{20} \end{bmatrix} + \frac{\Omega_R}{2}\begin{bmatrix} 0 & \frac{1}{\Delta} - \frac{1}{\Sigma} \\ \frac{1}{\Sigma} - \frac{1}{\Delta} & 0 \end{bmatrix}\begin{bmatrix} y_{10} \\ y_{20} \end{bmatrix} \Rightarrow \left\{ \begin{aligned} \frac{1}{\sqrt{2}}e^{i\theta} &= y_{10} + \frac{\Omega_R}{2}\left(\frac{1}{\Delta} - \frac{1}{\Sigma}\right)y_{20} \\ \frac{1}{\sqrt{2}}e^{i\phi} &= y_{20} + \frac{\Omega_R}{2}\left(\frac{1}{\Sigma} - \frac{1}{\Delta}\right)y_{10} \end{aligned} \right\} \Rightarrow$$

$$\left\{ \begin{aligned} \frac{1}{\sqrt{2}}e^{i\theta} &= y_{10} + \frac{2A}{\Omega_R}y_{20} \\ \frac{1}{\sqrt{2}}e^{i\phi} &= -\frac{2A}{\Omega_R}y_{10} + y_{20} \end{aligned} \right\} \Rightarrow \left\{ \begin{aligned} \frac{1}{\sqrt{2}}\frac{2A}{\Omega_R}e^{i\theta} &= \frac{2A}{\Omega_R}y_{10} + \left(\frac{2A}{\Omega_R}\right)^2 y_{20} \\ \frac{1}{\sqrt{2}}e^{i\phi} &= -\frac{2A}{\Omega_R}y_{10} + y_{20} \end{aligned} \right\} \overset{(+)}{\Rightarrow}$$

$$\frac{1}{\sqrt{2}}\frac{2A}{\Omega_R}e^{i\theta} + \frac{1}{\sqrt{2}}e^{i\phi} = y_{20} + \left(\frac{2A}{\Omega_R}\right)^2 y_{20} \Rightarrow \boxed{y_{20} = \frac{\frac{2A}{\Omega_R}e^{i\theta} + e^{i\phi}}{\sqrt{2}\left(1 + \left(\frac{2A}{\Omega_R}\right)^2\right)}}$$

$$\left\{ \begin{aligned} \frac{1}{\sqrt{2}}e^{i\theta} &= y_{10} + \frac{2A}{\Omega_R}y_{20} \\ \frac{1}{\sqrt{2}}e^{i\phi} &= -\frac{2A}{\Omega_R}y_{10} + y_{20} \end{aligned} \right\} \Rightarrow \left\{ \begin{aligned} \frac{1}{\sqrt{2}}e^{i\theta} &= y_{10} + \frac{2A}{\Omega_R}y_{20} \\ \frac{1}{\sqrt{2}}\left(-\frac{2A}{\Omega_R}\right)e^{i\phi} &= \left(\frac{2A}{\Omega_R}\right)^2 y_{10} + \left(-\frac{2A}{\Omega_R}\right)y_{20} \end{aligned} \right\} \overset{(+)}{\Rightarrow}$$

$$\frac{1}{\sqrt{2}}e^{i\theta} - \frac{1}{\sqrt{2}}\frac{2A}{\Omega_R}e^{i\phi} = y_{10} + \left(\frac{2A}{\Omega_R}\right)^2 y_{10} \Rightarrow \boxed{y_{10} = \frac{e^{i\theta} - \frac{2A}{\Omega_R}e^{i\phi}}{\sqrt{2}\left(1 + \left(\frac{2A}{\Omega_R}\right)^2\right)}},$$

where

$$A = \left(\frac{\Omega_R}{2}\right)^2 \frac{2\Omega}{\omega^2 - \Omega^2} \tag{6.94}$$

Therefore, the solution is

$$\mathbf{x}(t) = \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \begin{bmatrix} 1 & \frac{i\Omega_R}{2}\left(\frac{e^{+i\Delta t}}{i\Delta} - \frac{e^{-i\Sigma t}}{i\Sigma}\right) \\ \frac{i\Omega_R}{2}\left(-\frac{e^{-i\Delta t}}{i\Delta} + \frac{e^{+i\Sigma t}}{i\Sigma}\right) & 1 \end{bmatrix}\begin{bmatrix} \frac{e^{i\theta} - \frac{2A}{\Omega_R}e^{i\phi}}{\sqrt{2}\left(1 + \left(\frac{2A}{\Omega_R}\right)^2\right)} \\ \frac{\frac{2A}{\Omega_R}e^{i\theta} + e^{i\phi}}{\sqrt{2}\left(1 + \left(\frac{2A}{\Omega_R}\right)^2\right)} \end{bmatrix} \Rightarrow$$

$$\boxed{\begin{aligned}
C_1(t) &= \frac{1}{\sqrt{2}\left(1+\left(\frac{2A}{\Omega_R}\right)^2\right)}\left[\left(e^{i\theta}-\frac{2A}{\Omega_R}e^{i\phi}\right)+\frac{\Omega_R}{2}\left(\frac{e^{i\Delta t}}{\Delta}-\frac{e^{-i\Sigma t}}{\Sigma}\right)\left(\frac{2A}{\Omega_R}e^{i\theta}+e^{i\phi}\right)\right]\\
C_2(t) &= \frac{1}{\sqrt{2}\left(1+\left(\frac{2A}{\Omega_R}\right)^2\right)}\left[\frac{\Omega_R}{2}\left(-\frac{e^{-i\Delta t}}{\Delta}+\frac{e^{i\Sigma t}}{\Sigma}\right)\left(e^{i\theta}-\frac{2A}{\Omega_R}e^{i\phi}\right)+\left(\frac{2A}{\Omega_R}e^{i\theta}+e^{i\phi}\right)\right]
\end{aligned}}. \tag{6.95}$$

Solution for $\Delta \neq 0, 2^{\text{nd}}$ order AM

Using Eqs. (6.60) for $\mathbf{x}(0)=\begin{bmatrix}\frac{1}{\sqrt{2}}e^{i\theta}\\ \frac{1}{\sqrt{2}}e^{i\phi}\end{bmatrix}$, we have

$$\mathbf{x}(0)=\begin{bmatrix}z_{10}\\ z_{20}\end{bmatrix}+\frac{\Omega_R}{2}\left\{\begin{bmatrix}0 & \frac{1}{\Delta}-\frac{1}{\Sigma}\\ \frac{1}{\Sigma}-\frac{1}{\Delta} & 0\end{bmatrix}\right\}\begin{bmatrix}z_{10}\\ z_{20}\end{bmatrix}+i\left(\frac{\Omega_R}{2}\right)^2\left\{\frac{1}{i2\omega\Delta}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}+\frac{1}{i2\omega\Sigma}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}\right\}\begin{bmatrix}z_{10}\\ z_{20}\end{bmatrix}\Rightarrow$$

$$\left\{\begin{aligned}
\frac{1}{\sqrt{2}}e^{i\theta} &= z_{10}+\frac{\Omega_R}{2}\left(\frac{1}{\Delta}-\frac{1}{\Sigma}\right)z_{20}+\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\left(\frac{1}{\Delta}+\frac{1}{\Sigma}\right)z_{10}\\
\frac{1}{\sqrt{2}}e^{i\phi} &= z_{20}+\frac{\Omega_R}{2}\left(\frac{1}{\Sigma}-\frac{1}{\Delta}\right)z_{10}+\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\left(\frac{1}{\Delta}+\frac{1}{\Sigma}\right)z_{20}
\end{aligned}\right\}\Rightarrow$$

$$\left\{\begin{aligned}
\frac{1}{\sqrt{2}}e^{i\theta} &= \left(1+\frac{A}{2\Omega}\right)z_{10}+\frac{2A}{\Omega_R}z_{20}\\
\frac{1}{\sqrt{2}}e^{i\phi} &= -\frac{2A}{\Omega_R}z_{10}+\left(1+\frac{A}{2\Omega}\right)z_{20}
\end{aligned}\right\}\Rightarrow$$

$$\left\{\begin{aligned}
\frac{1}{\sqrt{2}}\frac{2A}{\Omega_R}e^{i\theta} &= \frac{2A}{\Omega_R}\left(1+\frac{A}{2\Omega}\right)z_{10}+\left(\frac{2A}{\Omega_R}\right)^2 z_{20}\\
\frac{1}{\sqrt{2}}\left(1+\frac{A}{2\Omega}\right)e^{i\phi} &= -\frac{2A}{\Omega_R}\left(1+\frac{A}{2\Omega}\right)z_{10}+\left(1+\frac{A}{2\Omega}\right)^2 z_{20}
\end{aligned}\right\}\overset{(+)}{\Rightarrow}$$

$$\frac{1}{\sqrt{2}}\frac{2A}{\Omega_R}e^{i\theta}+\frac{1}{\sqrt{2}}\left(1+\frac{A}{2\Omega}\right)e^{i\phi}=\left[\left(\frac{2A}{\Omega_R}\right)^2+\left(1+\frac{A}{2\Omega}\right)^2\right]z_{20}\Rightarrow$$

$$\boxed{z_{20}=\frac{\frac{2A}{\Omega_R}e^{i\theta}+\left(1+\frac{A}{2\Omega}\right)e^{i\phi}}{\sqrt{2}\left[\left(\frac{2A}{\Omega_R}\right)^2+\left(1+\frac{A}{2\Omega}\right)^2\right]}}$$

$$\left\{\begin{aligned}
\frac{1}{\sqrt{2}}e^{i\theta} &= \left(1+\frac{A}{2\Omega}\right)z_{10}+\frac{2A}{\Omega_R}z_{20}\\
\frac{1}{\sqrt{2}}e^{i\phi} &= -\frac{2A}{\Omega_R}z_{10}+\left(1+\frac{A}{2\Omega}\right)z_{20}
\end{aligned}\right\}\Rightarrow$$

$$\left\{\begin{aligned}
\frac{1}{\sqrt{2}}\left(1+\frac{A}{2\Omega}\right)e^{i\theta} &= \left(1+\frac{A}{2\Omega}\right)^2 z_{10}+\left(1+\frac{A}{2\Omega}\right)\frac{2A}{\Omega_R}z_{20}\\
\frac{1}{\sqrt{2}}\left(-\frac{2A}{\Omega_R}\right)e^{i\phi} &= \left(\frac{2A}{\Omega_R}\right)^2 z_{10}+\left(1+\frac{A}{2\Omega}\right)\left(-\frac{2A}{\Omega_R}\right)z_{20}
\end{aligned}\right\}\overset{(+)}{\Rightarrow}$$

$$\frac{1}{\sqrt{2}}\left(1+\frac{A}{2\Omega}\right)e^{i\theta}-\frac{1}{\sqrt{2}}\frac{2A}{\Omega_R}e^{i\phi}=\left[\left(\frac{2A}{\Omega_R}\right)^2+\left(1+\frac{A}{2\Omega}\right)^2\right]z_{10}\Rightarrow$$

$$\boxed{z_{10}=\frac{\left(1+\frac{A}{2\Omega}\right)e^{i\theta}-\frac{2A}{\Omega_R}e^{i\phi}}{\sqrt{2}\left[\left(\frac{2A}{\Omega_R}\right)^2+\left(1+\frac{A}{2\Omega}\right)^2\right]}}$$

Therefore, the solution is

$$\mathbf{x}(t)=\begin{bmatrix}C_1(t)\\C_2(t)\end{bmatrix}=\begin{bmatrix}1+\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\left(\frac{e^{-i2\omega t}}{\Delta}+\frac{e^{i2\omega t}}{\Sigma}\right) & \frac{\Omega_R}{2}\left(\frac{e^{i\Delta t}}{\Delta}-\frac{e^{-i\Sigma t}}{\Sigma}\right)\\ \frac{\Omega_R}{2}\left(-\frac{e^{-i\Delta t}}{\Delta}+\frac{e^{+i\Sigma t}}{\Sigma}\right) & 1+\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\left(\frac{e^{i2\omega t}}{\Delta}+\frac{e^{-i2\omega t}}{\Sigma}\right)\end{bmatrix}\begin{bmatrix}z_{10}e^{-iAt}\\z_{20}e^{iAt}\end{bmatrix}\Rightarrow$$

$$\boxed{\begin{aligned}C_1(t)&=\left[1+\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\left(\frac{e^{-i2\omega t}}{\Delta}+\frac{e^{i2\omega t}}{\Sigma}\right)\right]z_{10}e^{-iAt}+\left[\frac{\Omega_R}{2}\left(\frac{e^{i\Delta t}}{\Delta}-\frac{e^{-i\Sigma t}}{\Sigma}\right)\right]z_{20}e^{iAt}\\C_2(t)&=\left[\frac{\Omega_R}{2}\left(-\frac{e^{-i\Delta t}}{\Delta}+\frac{e^{+i\Sigma t}}{\Sigma}\right)\right]z_{10}e^{-iAt}+\left[1+\left(\frac{\Omega_R}{2}\right)^2\frac{1}{2\omega}\left(\frac{e^{i2\omega t}}{\Delta}+\frac{e^{-i2\omega t}}{\Sigma}\right)\right]z_{20}e^{iAt}\end{aligned}}. \tag{6.96}$$

$\boxed{\text{Solution for } \Delta=0, 1^{\text{st}} \text{ order AM}}$

Using Eqs. (6.80) for $\mathbf{x}(0)=\begin{bmatrix}\frac{1}{\sqrt{2}}e^{i\theta}\\\frac{1}{\sqrt{2}}e^{i\phi}\end{bmatrix}$, we have

$$\mathbf{x}(0)=\begin{bmatrix}A_{11}\\A_{21}\end{bmatrix}+\frac{\Omega_R}{4\omega}\begin{bmatrix}0&-1\\1&0\end{bmatrix}\begin{bmatrix}A_{11}\\A_{21}\end{bmatrix}\Rightarrow$$

$$\left\{\begin{array}{l}\frac{1}{\sqrt{2}}e^{i\theta}=A_{11}-\frac{\Omega_R}{4\omega}A_{21}\\ \frac{1}{\sqrt{2}}e^{i\phi}=A_{21}+\frac{\Omega_R}{4\omega}A_{11}\end{array}\right\}\Rightarrow\left\{\begin{array}{l}\frac{1}{\sqrt{2}}e^{i\theta}=A_{11}-\frac{\Omega_R}{4\omega}A_{21}\\ \frac{1}{\sqrt{2}}\frac{\Omega_R}{4\omega}e^{i\phi}=\frac{\Omega_R}{4\omega}A_{21}+\left(\frac{\Omega_R}{4\omega}\right)^2A_{11}\end{array}\right\}\overset{(+)}{\Rightarrow}$$

$$\frac{1}{\sqrt{2}}e^{i\theta}+\frac{1}{\sqrt{2}}\frac{\Omega_R}{4\omega}e^{i\phi}=\left(1+\left(\frac{\Omega_R}{4\omega}\right)^2\right)A_{11}\Rightarrow\boxed{A_{11}=\frac{e^{i\theta}+\frac{\Omega_R}{4\omega}e^{i\phi}}{\sqrt{2}\left(1+\left(\frac{\Omega_R}{4\omega}\right)^2\right)}}$$

$$\left\{\begin{array}{l}\frac{1}{\sqrt{2}}e^{i\theta}=A_{11}-\frac{\Omega_R}{4\omega}A_{21}\\ \frac{1}{\sqrt{2}}e^{i\phi}=A_{21}+\frac{\Omega_R}{4\omega}A_{11}\end{array}\right\}\Rightarrow\left\{\begin{array}{l}\frac{1}{\sqrt{2}}\left(-\frac{\Omega_R}{4\omega}\right)e^{i\theta}=\left(-\frac{\Omega_R}{4\omega}\right)A_{11}+\left(\frac{\Omega_R}{4\omega}\right)^2A_{21}\\ \frac{1}{\sqrt{2}}e^{i\phi}=A_{21}+\frac{\Omega_R}{4\omega}A_{11}\end{array}\right\}\overset{(+)}{\Rightarrow}$$

$$\frac{1}{\sqrt{2}}\left(-\frac{\Omega_R}{4\omega}\right)e^{i\theta}+\frac{1}{\sqrt{2}}e^{i\phi}=\left(1+\left(\frac{\Omega_R}{4\omega}\right)^2\right)A_{21}\Rightarrow\boxed{A_{21}=\frac{-\frac{\Omega_R}{4\omega}e^{i\theta}+e^{i\phi}}{\sqrt{2}\left(1+\left(\frac{\Omega_R}{4\omega}\right)^2\right)}}$$

Furthermore, through Eq. (6.67), we know that

$$\left\{\begin{aligned} \dot{y}_1(0) &= \frac{\Omega_R}{2}B_{11} = i\frac{\Omega_R}{2}y_2(0) \\ \dot{y}_2(0) &= \frac{\Omega_R}{2}B_{21} = i\frac{\Omega_R}{2}y_1(0) \end{aligned}\right\} \Rightarrow \left\{\begin{aligned} B_{11} &= iA_{21} = i\frac{-\frac{\Omega_R}{4\omega}e^{i\theta} + e^{i\phi}}{\sqrt{2}\left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)} \\ B_{21} &= iA_{11} = i\frac{e^{i\theta} + \frac{\Omega_R}{4\omega}e^{i\phi}}{\sqrt{2}\left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)} \end{aligned}\right\}$$

Therefore, the solution is

$$\mathbf{x}(t) = \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} + \frac{\Omega_R}{4\omega}\begin{bmatrix} 0 & -e^{-i2\omega t} \\ e^{i2\omega t} & 0 \end{bmatrix}\begin{bmatrix} y_1 \\ y_2 \end{bmatrix} \Rightarrow$$

$$\boxed{\begin{aligned} C_1(t) &= A_{11}\cos\left(\frac{\Omega_R}{2}t\right) + iA_{21}\sin\left(\frac{\Omega_R}{2}t\right) - \frac{\Omega_R}{4\omega}e^{-i2\omega t}\left[A_{21}\cos\left(\frac{\Omega_R}{2}t\right) + iA_{11}\sin\left(\frac{\Omega_R}{2}t\right)\right] \\ C_2(t) &= A_{21}\cos\left(\frac{\Omega_R}{2}t\right) + iA_{11}\sin\left(\frac{\Omega_R}{2}t\right) + \frac{\Omega_R}{4\omega}e^{i2\omega t}\left[A_{11}\cos\left(\frac{\Omega_R}{2}t\right) + iA_{21}\sin\left(\frac{\Omega_R}{2}t\right)\right] \end{aligned}}. \tag{6.97}$$

Solution for $\Delta = 0, 2^{\text{nd}}$ order AM

Using Eqs. (6.81) for $\mathbf{x}(0) = \begin{bmatrix} \frac{1}{\sqrt{2}}e^{i\theta} \\ \frac{1}{\sqrt{2}}e^{i\phi} \end{bmatrix}$, we have

$$\mathbf{x}(0) = \begin{bmatrix} A_{12} \\ A_{22} \end{bmatrix} + \frac{\Omega_R}{4\omega}\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} A_{12} \\ A_{22} \end{bmatrix} \Rightarrow$$

$$\left\{\begin{aligned} \frac{1}{\sqrt{2}}e^{i\theta} &= A_{12} - \frac{\Omega_R}{4\omega}A_{22} \\ \frac{1}{\sqrt{2}}e^{i\phi} &= A_{22} + \frac{\Omega_R}{4\omega}A_{12} \end{aligned}\right\} \Rightarrow \left\{\begin{aligned} \frac{1}{\sqrt{2}}e^{i\theta} &= A_{12} - \frac{\Omega_R}{4\omega}A_{22} \\ \frac{1}{\sqrt{2}}\frac{\Omega_R}{4\omega}e^{i\phi} &= \frac{\Omega_R}{4\omega}A_{22} + \left(\frac{\Omega_R}{4\omega}\right)^2 A_{12} \end{aligned}\right\} \overset{(+)}{\Rightarrow}$$

$$\frac{1}{\sqrt{2}}e^{i\theta} + \frac{1}{\sqrt{2}}\frac{\Omega_R}{4\omega}e^{i\phi} = \left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)A_{12} \Rightarrow \boxed{A_{12} = \frac{e^{i\theta} + \frac{\Omega_R}{4\omega}e^{i\phi}}{\sqrt{2}\left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)}}$$

$$\left\{\begin{aligned} \frac{1}{\sqrt{2}}e^{i\theta} &= A_{12} - \frac{\Omega_R}{4\omega}A_{22} \\ \frac{1}{\sqrt{2}}e^{i\phi} &= A_{22} + \frac{\Omega_R}{4\omega}A_{12} \end{aligned}\right\} \Rightarrow \left\{\begin{aligned} \frac{1}{\sqrt{2}}\left(-\frac{\Omega_R}{4\omega}\right)e^{i\theta} &= \left(-\frac{\Omega_R}{4\omega}\right)A_{12} + \left(\frac{\Omega_R}{4\omega}\right)^2 A_{22} \\ \frac{1}{\sqrt{2}}e^{i\phi} &= A_{22} + \frac{\Omega_R}{4\omega}A_{12} \end{aligned}\right\} \overset{(+)}{\Rightarrow}$$

$$\frac{1}{\sqrt{2}}\left(-\frac{\Omega_R}{4\omega}\right)e^{i\theta} + \frac{1}{\sqrt{2}}e^{i\phi} = \left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)A_{22} \Rightarrow \boxed{A_{22} = \frac{-\frac{\Omega_R}{4\omega}e^{i\theta} + e^{i\phi}}{\sqrt{2}\left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)}}$$

Furthermore, through Eq. (6.78), we know that

$$\left\{\begin{aligned} \dot{z}_1(0) &= B\cdot B_{12} = i\alpha z_1(0) + i\beta z_2(0) \\ \dot{z}_2(0) &= B\cdot B_{22} = i\beta z_1(0) - i\alpha z_2(0) \end{aligned}\right\} \Rightarrow$$

$$\left\{\begin{aligned}
B_{12} &= \frac{i\alpha A_{12} + i\beta A_{22}}{B} = i\frac{\left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega}\left(e^{i\theta} + \frac{\Omega_R}{4\omega}e^{i\phi}\right) + \frac{\Omega_R}{2}\left(-\frac{\Omega_R}{4\omega}e^{i\theta} + e^{i\phi}\right)}{\sqrt{2}B\left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)} = \\
&= i\frac{\cancelto{0}{\left(\left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega} - \frac{\Omega_R}{2}\frac{\Omega_R}{4\omega}\right)}e^{i\theta} + \left(\left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega}\frac{\Omega_R}{4\omega} + \frac{\Omega_R}{2}\right)e^{i\phi}}{\sqrt{2}B\left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)} = i\frac{\frac{\Omega_R}{2}\cancel{\left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)}e^{i\phi}}{\sqrt{2}B\cancel{\left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)}} = i\frac{\Omega_R e^{i\phi}}{2\sqrt{2}B} \\
B_{22} &= \frac{i\beta A_{12} - i\alpha A_{22}}{B} = i\frac{\frac{\Omega_R}{2}\left(e^{i\theta} + \frac{\Omega_R}{4\omega}e^{i\phi}\right) - \left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega}\left(-\frac{\Omega_R}{4\omega}e^{i\theta} + e^{i\phi}\right)}{\sqrt{2}B\left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)} = \\
&= i\frac{\left(\frac{\Omega_R}{2} + \left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega}\frac{\Omega_R}{4\omega}\right)e^{i\theta} + \cancelto{0}{\left(\frac{\Omega_R}{2}\frac{\Omega_R}{4\omega} - \left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega}\right)}e^{i\phi}}{\sqrt{2}B\left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)} = i\frac{\frac{\Omega_R}{2}\cancel{\left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)}e^{i\theta}}{\sqrt{2}B\cancel{\left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)}} = i\frac{\Omega_R e^{i\theta}}{2\sqrt{2}B}
\end{aligned}\right\}$$

Therefore, the solution is

$$\mathbf{x}(t) = \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \begin{bmatrix} 1 + i\left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega^2}\sin(2\omega t) & \frac{\Omega_R}{4\omega}\left(-e^{-i2\omega t}\right) \\ \frac{\Omega_R}{4\omega}e^{i2\omega t} & 1 - i\left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega^2}\sin(2\omega t) \end{bmatrix} \begin{bmatrix} z_1(t) \\ z_2(t) \end{bmatrix} \Rightarrow$$

$$\boxed{\begin{aligned} C_1(t) &= \left[1 + i\left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega^2}\sin(2\omega t)\right] z_1(t) - \frac{\Omega_R}{4\omega}e^{-i2\omega t}z_2(t) \\ C_2(t) &= \frac{\Omega_R}{4\omega}e^{i2\omega t}z_1(t) + \left[1 - i\left(\frac{\Omega_R}{2}\right)^2 \frac{1}{2\omega^2}\sin(2\omega t)\right] z_2(t) \end{aligned}}, \tag{6.98}$$

with

$$\left\{\begin{aligned} z_1 &= A_{12}\cos(Bt) + B_{12}\sin(Bt) \\ z_2 &= A_{22}\cos(Bt) + B_{22}\sin(Bt) \end{aligned}\right\} \text{ and } \left\{\begin{aligned} A_{12} &= \frac{e^{i\theta} + \frac{\Omega_R}{4\omega}e^{i\phi}}{\sqrt{2}\left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)} \\ A_{22} &= \frac{-\frac{\Omega_R}{4\omega}e^{i\theta} + e^{i\phi}}{\sqrt{2}\left(1 + \left(\frac{\Omega_R}{4\omega}\right)^2\right)} \\ \mathrm{B}_{12} &= i\frac{\Omega_R e^{i\phi}}{2\sqrt{2}B} \\ \mathrm{B}_{22} &= i\frac{\Omega_R e^{i\theta}}{2\sqrt{2}B} \end{aligned}\right\}.$$

6.3 Results with NRWA, RWA, first and second order AM.

In the following, we compare results for NRWA, RWA, first- and second-order AM, and focus the limits of the approximate methods (RWA, AM). In all figures, the horizontal axes represent the dimensionless quantity $\frac{\Omega_{\mathrm{R}}t}{2\pi}$, i.e, time t divided by $T_{\mathrm{RWA},0}$, and the vertical axes represent the probability at the lower level, P_1. For non-resonance ($\Delta \neq 0$), we have defined three types of small quantities ϵ, i.e., $\frac{\Omega_{\mathrm{R}}}{\Delta}$, $\frac{\Omega_{\mathrm{R}}}{\Sigma}$ and $\frac{\Omega_{\mathrm{R}}}{\omega}$. Unavoidably, when Δ becomes smaller, at some point, $\frac{\Omega_{\mathrm{R}}}{\Delta}$ gets so large that non-resonant AM is not successful anymore and resonance must be treated via a different path, using just one type of ϵ, i.e., $\frac{\Omega_{\mathrm{R}}}{\omega}$. In general, the accuracy of second-order AM has a range between the outcomes, $\frac{\Omega_{\mathrm{R}}}{\Delta} \cdot \frac{\Omega_{\mathrm{R}}}{\omega} = \frac{\Omega_{\mathrm{R}}^2}{\Delta\omega}$ and $\frac{\Omega_{\mathrm{R}}}{\Sigma} \cdot \frac{\Omega_{\mathrm{R}}}{\omega} = \frac{\Omega_{\mathrm{R}}^2}{\Sigma\omega}$, due to the fact that the above terms appear in the final equations [see Eqs. (6.60)] and they are the last terms that we do not ignore. First-order AM is frequently far from the numerical solution. We include it in the figures below for comparison, and to demonstrate the real reason why we should use second-order AM.

The values of ϵ were chosen with the purpose of introducing cases where AM approaches success. Hence, the values are down to the order of magnitude 0.01. For smaller values, AM is successful. Furthermore, very small values of ϵ mean very small perturbation, i.e., these are trivial cases.

6.3.1 Results for electron initial placement at the lower level.

Let the initial conditions be $C_1(0) = 1, C_2(0) = 0$, i.e., we initially (at $t = 0$) place the electron at the lower level.

6.3.1.1 Non-resonance.

In Fig. 6.1 we modify $\epsilon_2 = \frac{\Omega_{\mathrm{R}}}{\Sigma}$, keeping $\epsilon_1 = \frac{\Omega_{\mathrm{R}}}{\Delta} = -0.5$ ($\epsilon_1 = 0.5$) on the left (right) column. For $\epsilon_1 > 0$, as ϵ_2 gets smaller, RWA becomes identical to NRWA. Second-order AM is very close to NRWA in all cases. For $\epsilon_1 < 0$, as ϵ_2 gets smaller, second-order AM and RWA become identical to NRWA. The different behavior of AM for negative and positive ϵ_1 stems from $\epsilon_3 = \frac{\Omega_{\mathrm{R}}}{\omega}$ being different: for $\epsilon_1 > 0, \epsilon_3$ is smaller than for $\epsilon_1 < 0$. In Fig. 6.2 we modify $\epsilon_1 = \frac{\Omega_{\mathrm{R}}}{\Delta}$ and keep $\epsilon_2 = \frac{\Omega_{\mathrm{R}}}{\Sigma} = 0.01$. On left (right) column $\epsilon_1 < 0$ ($\epsilon_1 > 0$). RWA gets identical to NRWA, but not with second order AM. As ϵ_1 gets smaller, AM gradually approaches NRWA. Oscillations diminish as ϵ_1 becomes smaller. Oscillations at the same row but in different columns are a little different due to the different value of ϵ_3. In Figs. 6.1, 6.2, the two panels of the same line seem similar, because $\epsilon_3 = \frac{\Omega_{\mathrm{R}}}{\omega}$ are almost identical, except for the first line in Fig. 6.1. For example, in Fig. 6.1, the two panels of the last line have $\epsilon_1 = -0.5, \epsilon_2 = 0.01, \epsilon_3 = \frac{1}{49}$ and $\epsilon_1 = 0.5$, $\epsilon_2 = 0.01, \epsilon_3 = \frac{1}{51}$, respectively, while the two panels of the first line have $\epsilon_1 = -0.5, \epsilon_2 = 0.4, \epsilon_3 = 4$ and $\epsilon_1 = 0.5, \epsilon_2 = 0.4, \epsilon_3 = \frac{4}{9}$, respectively. Hence, second-order AM is identical to NRWA when ϵ_1, ϵ_2 and ϵ_3 are sufficiently small.

6.3.1.2 Resonance.

In Fig. 6.3 we illustrate P_1 vs. $\frac{\Omega_{\mathrm{R}}t}{2\pi}$, modifying $\epsilon = \frac{\Omega_{\mathrm{R}}}{\omega}$. As ϵ gets smaller, AM is identical to NRWA. Additionally, since we are in resonance, oscillations are particularly strong, of the order of one.

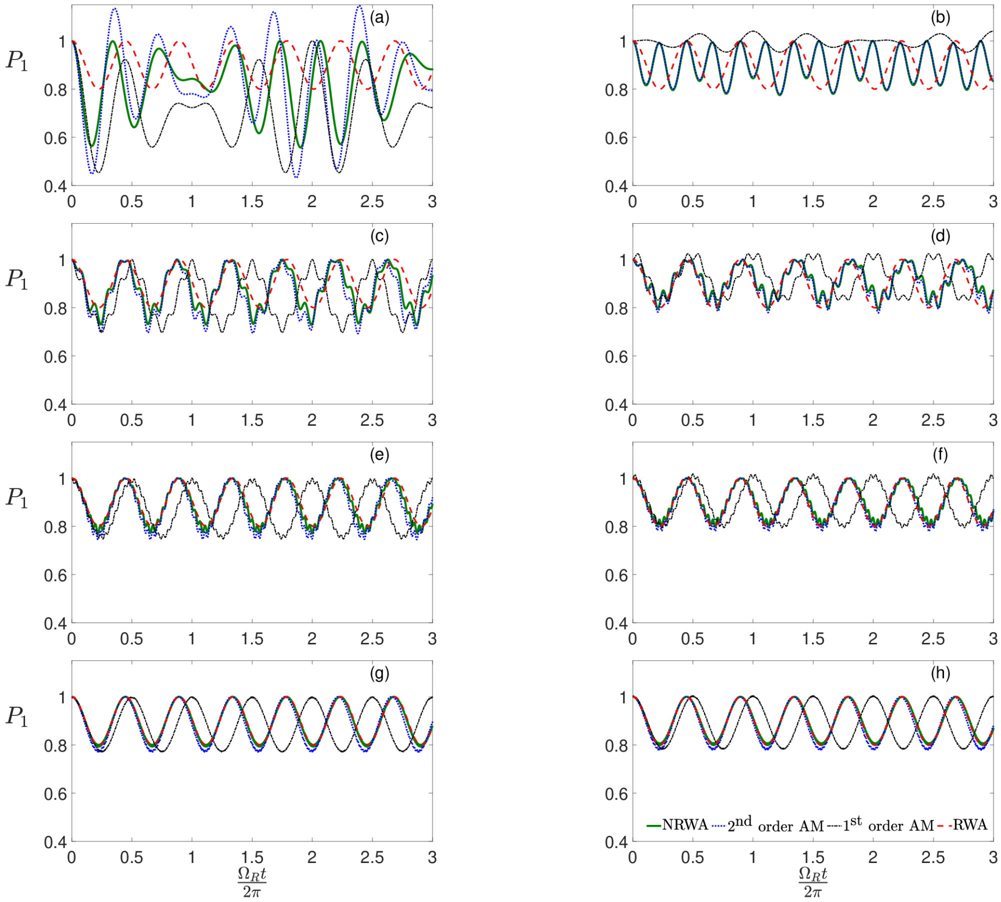

Figure 6.1: $\Delta \neq 0$. P_1 vs. $\frac{\Omega_{\rm R} t}{2\pi}$ for $\epsilon_1 = \frac{\Omega_{\rm R}}{\Delta} = -0.5$ (left column) and $\epsilon_1 = \frac{\Omega_{\rm R}}{\Delta} = 0.5$ (right column), varying $\epsilon_2 = \frac{\Omega_{\rm R}}{\Sigma}$. (a), (b) $\epsilon_2 = 0.4$. (c), (d) $\epsilon_2 = 0.1$. (e), (f) $\epsilon_2 = 0.04$. (g), (h) $\epsilon_2 = 0.01$. Lines correspond to NRWA (continuous —), RWA (dashed −−), second-order AM (dotted ⋯), first-order AM (dash-dotted ·−).

6.3.2 Results for initial electron placement at both levels with equal probability, but with phase difference.

Let the initial conditions be $C_1(0) = \frac{1}{\sqrt{2}} e^{i\theta}$, $C_2(0) = \frac{1}{\sqrt{2}} e^{i\phi}$, i.e., we initially (at $t = 0$) place half electron at each level, but with a phase difference $\theta - \phi$.

6.3.2.1 Non-resonance.

In Fig. 6.4 we vary $\epsilon_2 = \frac{\Omega_{\rm R}}{\Sigma}$, keeping $\epsilon_1 = \frac{\Omega_{\rm R}}{\Delta} = -0.5$ ($\epsilon_1 = 0.5$) on the left (right) column, with $\theta - \phi = \frac{\pi}{3}$. Although the initial probabilities at the two levels are equal, phase difference of the initial wave functions leads to strong oscillations, a clear coherent phenomenon. Decreasing ϵ_2, second-order AM approaches NRWA.

In Fig. 6.5 we modify $\epsilon_1 = \frac{\Omega_{\rm R}}{\Delta}$, keeping $\epsilon_2 = \frac{\Omega_{\rm R}}{\Sigma} = 0.01$ with $\theta - \phi = \frac{\pi}{3}$. We observe strong oscillations, depending of course on the magnitude of ϵ_1, although the initial probabilities are equal, a pure coherent phenomenon, due to the initial phase difference of the wave functions. Decreasing $|\epsilon_1|$, second order AM approaches NRWA. The discussion on the effect of the relative magnitude of $\epsilon_1, \epsilon_2, \epsilon_3$, applies here, too.

In Fig. 6.6 we keep $\epsilon_1 = 0.5$ and $\epsilon_1 = 0.01$, varying the initial phase difference of the wave functions,

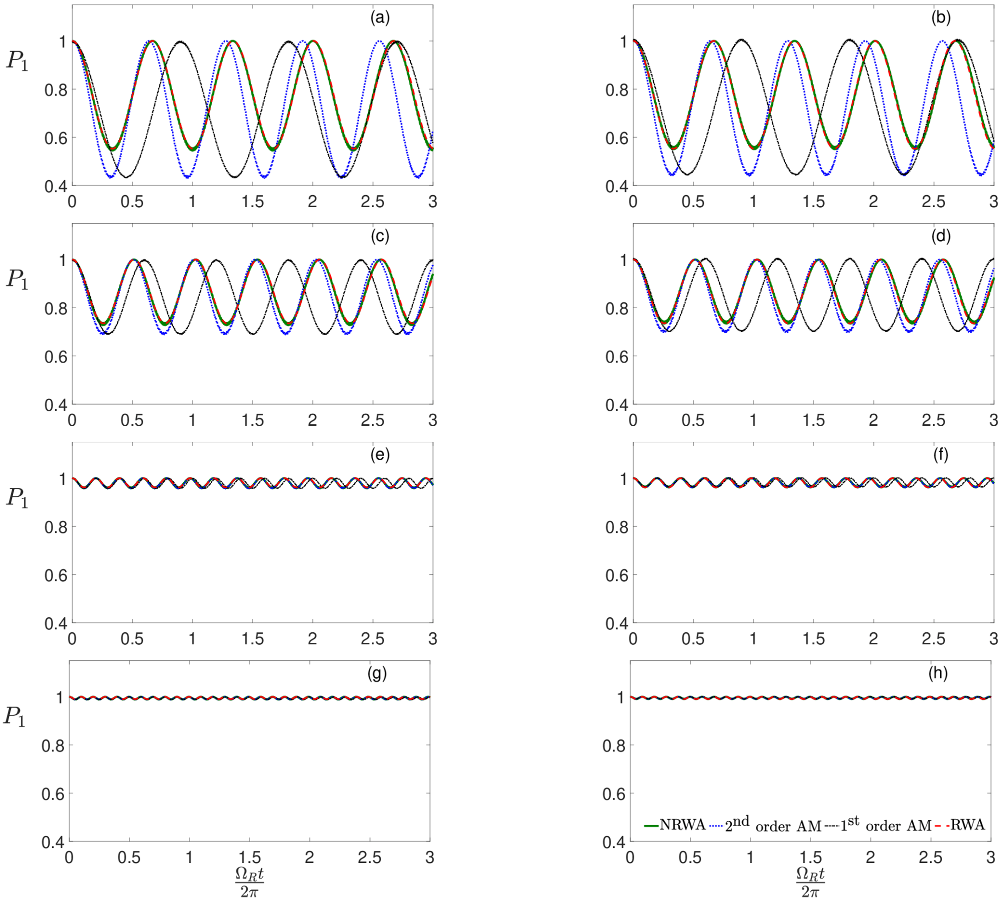

Figure 6.2: $\Delta \neq 0$. P_1 vs. $\frac{\Omega_\mathrm{R} t}{2\pi}$, for $\epsilon_2 = \frac{\Omega_\mathrm{R}}{\Sigma} = 0.01$, varying $\epsilon_1 = \frac{\Omega_\mathrm{R}}{\Delta}$. (a) $\epsilon_1 = -0.9$. (b) $\epsilon_1 = 0.9$. (c) $\epsilon_1 = -0.6$. (d) $\epsilon_1 = 0.6$. (e) $\epsilon_1 = -0.2$. (f) $\epsilon_1 = 0.2$. (g) $\epsilon_1 = -0.1$. (h) $\epsilon_1 = 0.1$. Lines correspond to NRWA (continuous —), RWA (dashed – –), second order AM (dotted ···), first order AM (dash-dotted ·–).

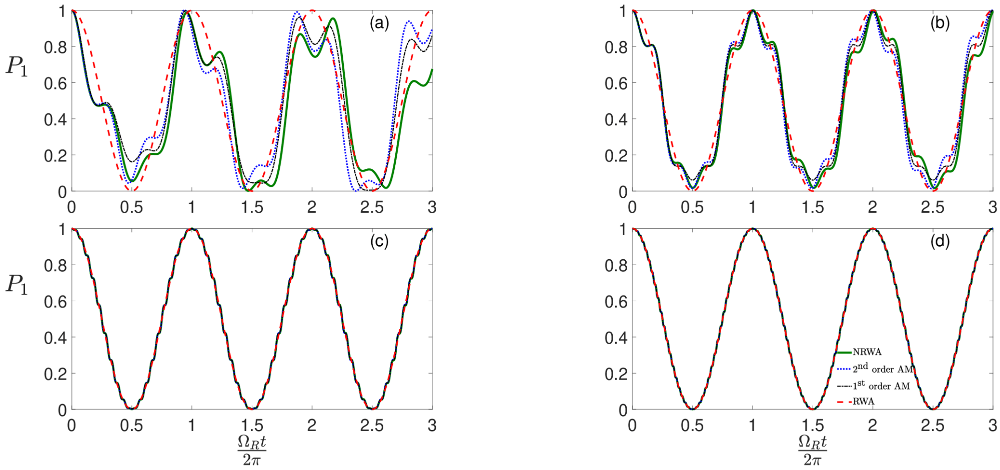

Figure 6.3: $\Delta = 0$. P_1 vs. $\frac{\Omega_\mathrm{R} t}{2\pi}$, varying $\epsilon = \frac{\Omega_\mathrm{R}}{\omega}$. (a) $\epsilon = 0.9$. (b) $\epsilon = 0.5$. (c) $\epsilon = 0.1$. (d) $\epsilon = 0.05$. Lines correspond to NRWA (continuous —), RWA (dashed – –), second order AM (dotted ···), first order AM (dash-dotted ·–).

$\theta - \phi$. We observe another aspect of coherence, a vertical and horizontal displacement of the oscillations.

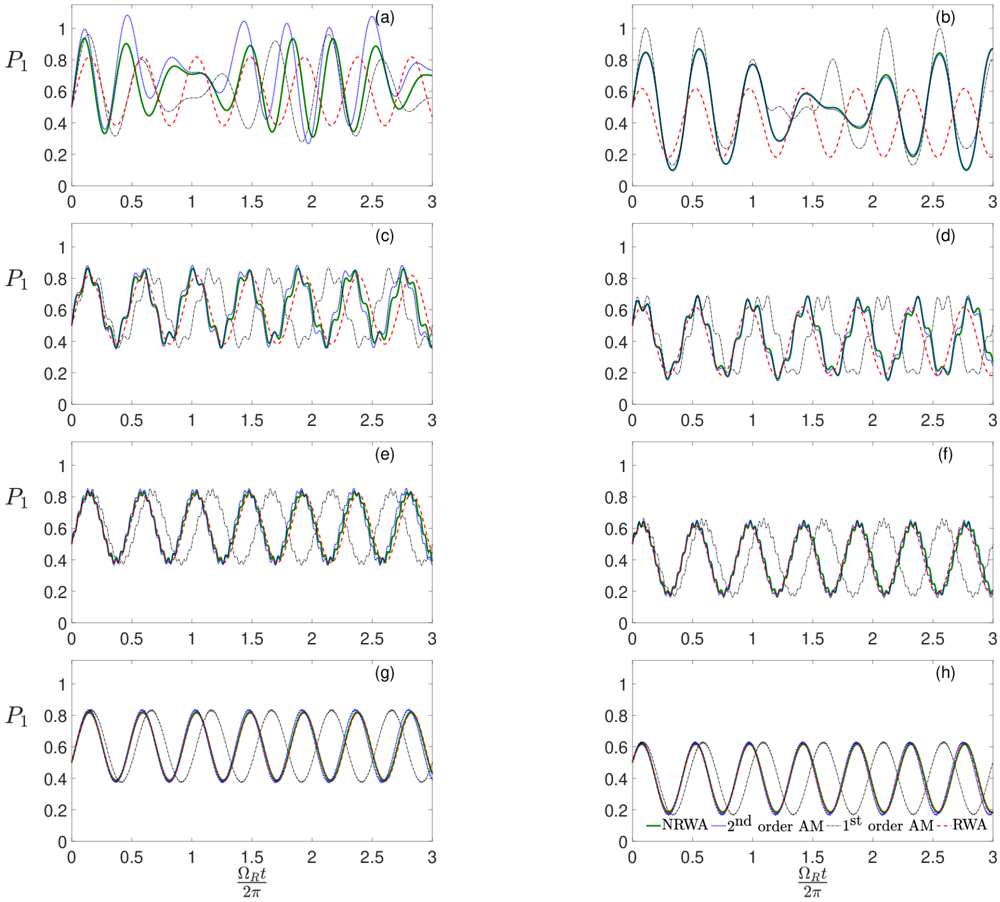

Figure 6.4: $\Delta \neq 0$. P_1 vs. $\frac{\Omega_\mathrm{R} t}{2\pi}$ for $\epsilon_1 = \frac{\Omega_\mathrm{R}}{\Delta} = -0.5$ (left column) and $\epsilon_1 = \frac{\Omega_\mathrm{R}}{\Delta} = 0.5$ (right column), varying $\epsilon_2 = \frac{\Omega_\mathrm{R}}{\Sigma}$ with $\theta - \phi = \frac{\pi}{3}$. (a), (b) $\epsilon_2 = 0.4$. (c), (d) $\epsilon_2 = 0.1$. (e), (f) $\epsilon_2 = 0.04$. (g), (h) $\epsilon_2 = 0.01$. Lines correspond to NRWA (continuous —), RWA (dashed −−), second order AM (dotted ···), first order AM (dash-dotted ·−).

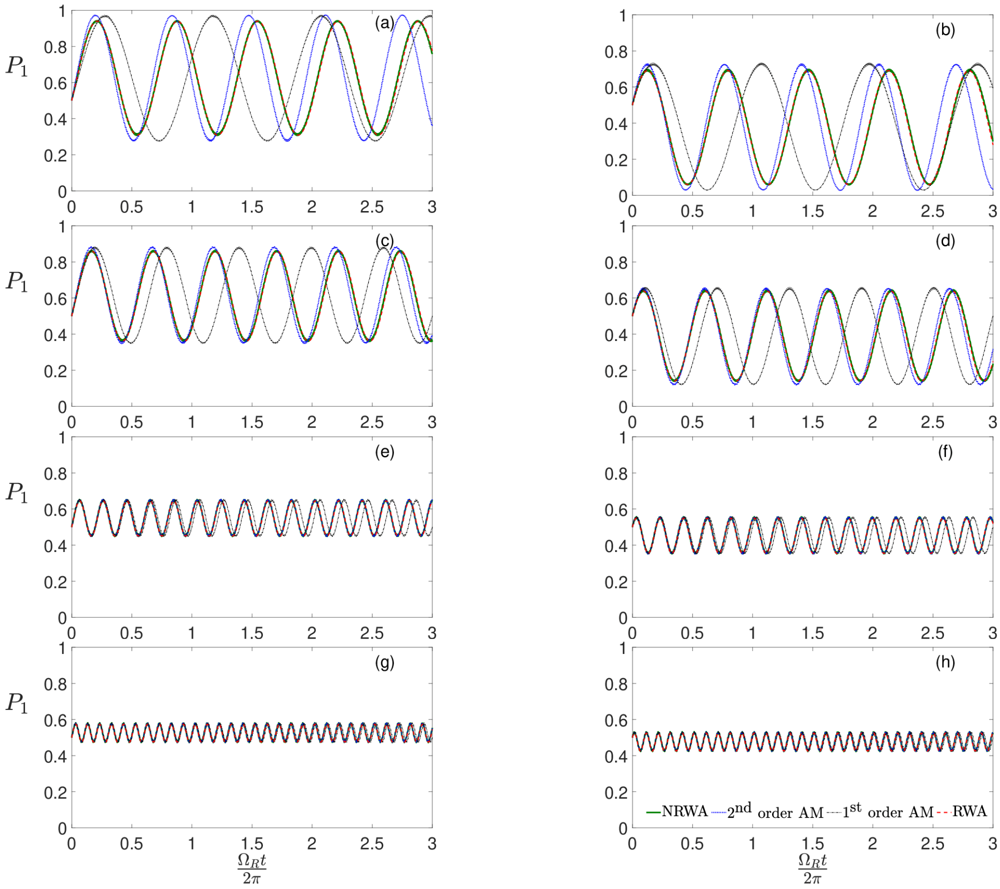

Figure 6.5: $\Delta \neq 0$. P_1 vs. $\frac{\Omega_\mathrm{R} t}{2\pi}$, for $\epsilon_2 = \frac{\Omega_\mathrm{R}}{\Sigma} = 0.01$, varying $\epsilon_1 = \frac{\Omega_\mathrm{R}}{\Delta}$ with $\theta - \phi = \frac{\pi}{3}$. (a) $\epsilon_1 = -0.9$. (b) $\epsilon_1 = 0.9$. (c) $\epsilon_1 = -0.6$. (d) $\epsilon_1 = 0.6$. (e) $\epsilon_1 = -0.2$. (f) $\epsilon_1 = 0.2$. (g) $\epsilon_1 = -0.1$. (h) $\epsilon_1 = 0.1$. Lines correspond to NRWA (continuous —), RWA (dashed – –), second order AM (dotted ···), first order AM (dash-dotted ·–).

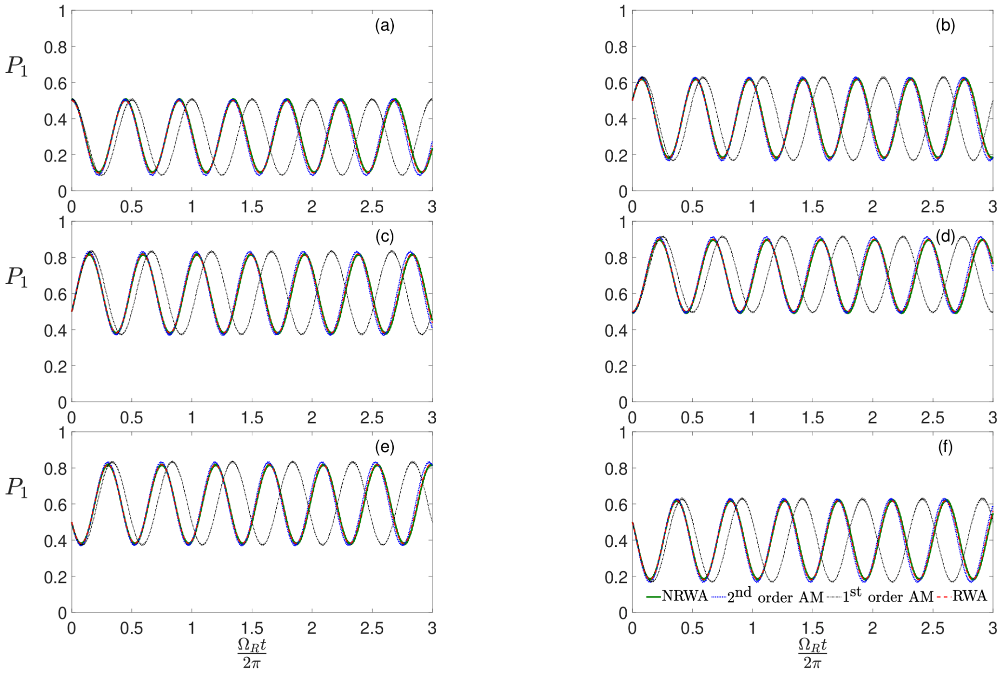

Figure 6.6: $\Delta \neq 0$. P_1 vs. $\frac{\Omega_\mathrm{R} t}{2\pi}$ for $\epsilon_1 = \frac{\Omega_\mathrm{R}}{\Delta} = 0.5$ and $\epsilon_2 = \frac{\Omega_\mathrm{R}}{\Sigma} = 0.01$, varying $\theta - \phi$. (a) $\theta - \phi = 0$. (b) $\theta - \phi = \frac{\pi}{3}$. (c) $\theta - \phi = \frac{2\pi}{3}$. (d) $\theta - \phi = \pi$. (e) $\theta - \phi = \frac{4\pi}{3}$. (f) $\theta - \phi = \frac{5\pi}{3}$. Lines correspond to NRWA (continuous —), RWA (dashed – –), second order AM (dotted ···), first order AM (dash-dotted ·–).

6.3.2.2 Resonance.

In Fig. 6.7 we modify $\epsilon = \frac{\Omega_R}{\omega}$, for initial phase difference, $\theta - \phi = \frac{\pi}{3}$. As ϵ gets smaller, AM becomes identical to NRWA.

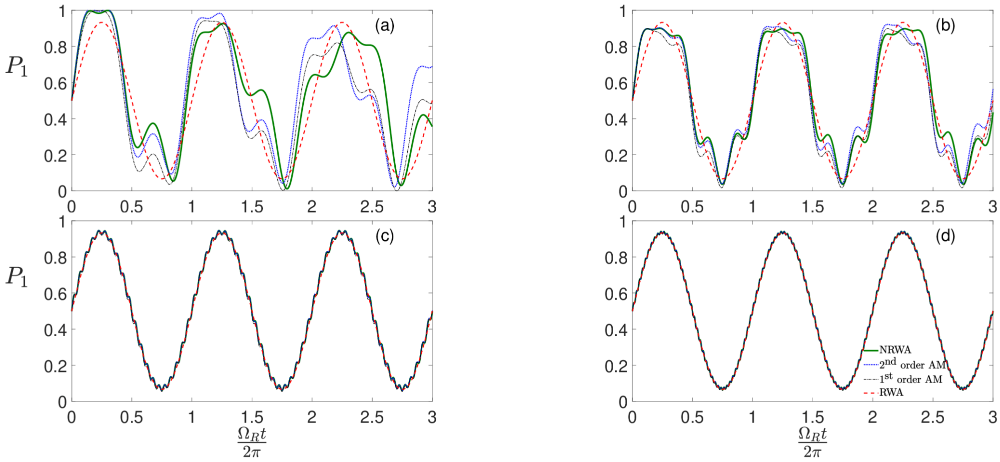

Figure 6.7: $\Delta = 0$. P_1 vs. $\frac{\Omega_R t}{2\pi}$, varying $\epsilon = \frac{\Omega_R}{\omega}$ with $\theta - \phi = \frac{\pi}{3}$. (a) $\epsilon = 0.9$. (b) $\epsilon = 0.5$. (c) $\epsilon = 0.1$. (d) $\epsilon = 0.05$. Lines correspond to NRWA (continuous —), RWA (dashed −−), second order AM (dotted ···), first order AM (dash-dotted ·−).

In Fig. 6.8 we keep $\epsilon = 0.1$, varying the initial phase difference, $\theta - \phi$. We observe that the amplitude of the oscillations can be readily manipulated this way.

6.3.3 Non-resonant AM vs. resonant AM.

The reader might wonder why we have introduced two different versions of the AM, one for non-resonance and another for resonance. We have already explained the reason above: When Δ becomes very small, $\frac{\Omega_R}{\Delta}$ gets very large, so that non-resonant AM is not successful anymore. Therefore, in resonance, the AM has to be manipulated in a different way.

Here we give a few examples. In Fig. 6.9, we vary $\epsilon_1 = \frac{\Omega_R}{\Delta}$ and keep $\epsilon_2 = \frac{\Omega_R}{\Sigma} = 0.01$. We observe that for $\epsilon_1 < 1$, the second order AM for non-resonance is closer to the numerical solution (NRWA) than the second-order AM for resonance. However, for $\epsilon_1 > 1$, Δ is so small that the second-order AM for resonance comes closer to NRWA than the second-order AM for non-resonance.

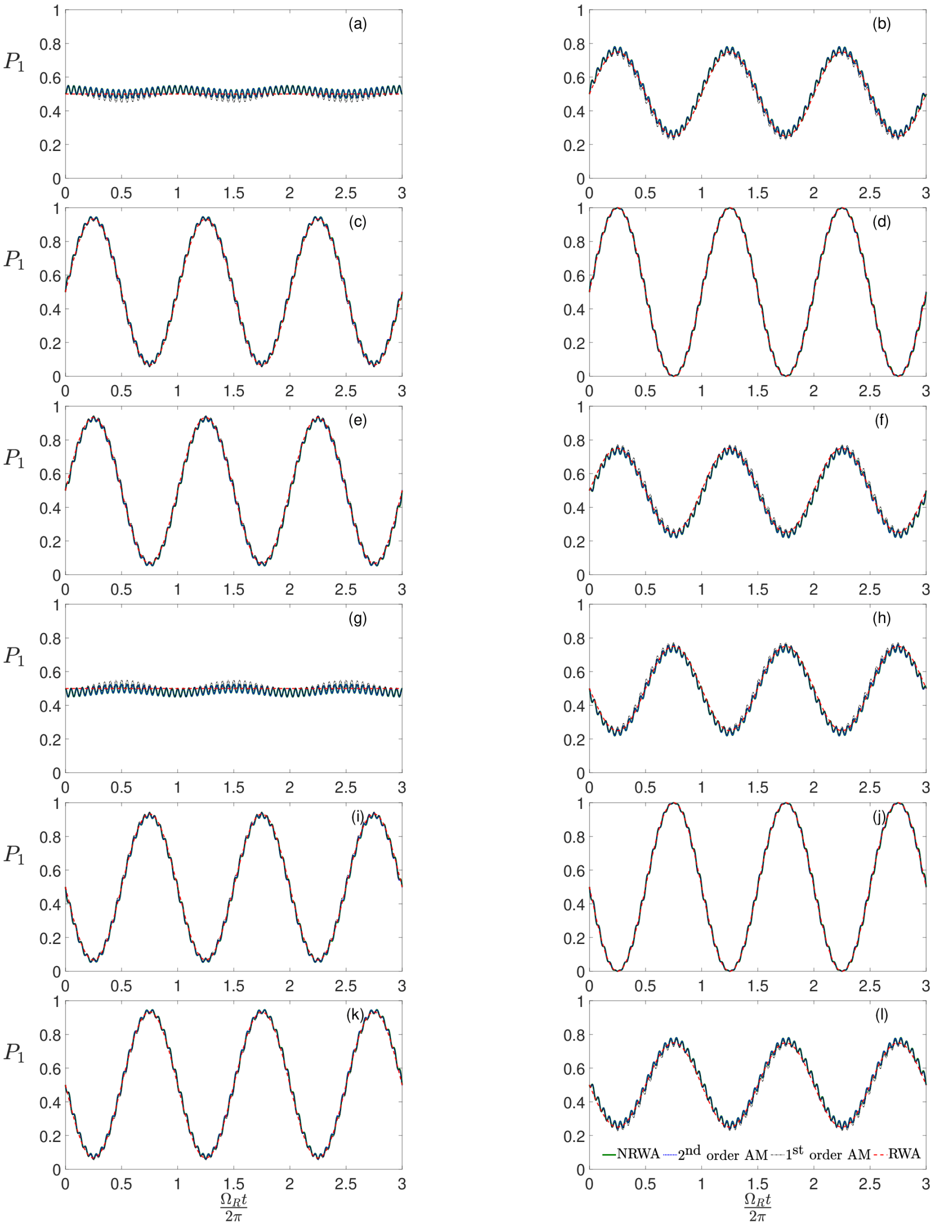

Figure 6.8: $\Delta = 0$. P_1 vs. $\frac{\Omega_{\mathrm{R}} t}{2\pi}$, $\epsilon = \frac{\Omega_{\mathrm{R}}}{\omega} = 0.1$, varying $\theta - \phi$. (a) $\theta - \phi = 0$. (b) $\theta - \phi = \frac{\pi}{6}$. (c) $\theta - \phi = \frac{\pi}{3}$. (d) $\theta - \phi = \frac{\pi}{2}$. (e) $\theta - \phi = \frac{2\pi}{3}$. (f) $\theta - \phi = \frac{5\pi}{6}$. (g) $\theta - \phi = \pi$. (h) $\theta - \phi = \frac{7\pi}{6}$. (i) $\theta - \phi = \frac{4\pi}{3}$. (j) $\theta - \phi = \frac{3\pi}{2}$. (k) $\theta - \phi = \frac{5\pi}{3}$. (l) $\theta - \phi = \frac{11\pi}{6}$. Lines refer to NRWA (continuous —), RWA (dashed – –), second order AM (dotted ···), first order AM (dash-dotted ·–).

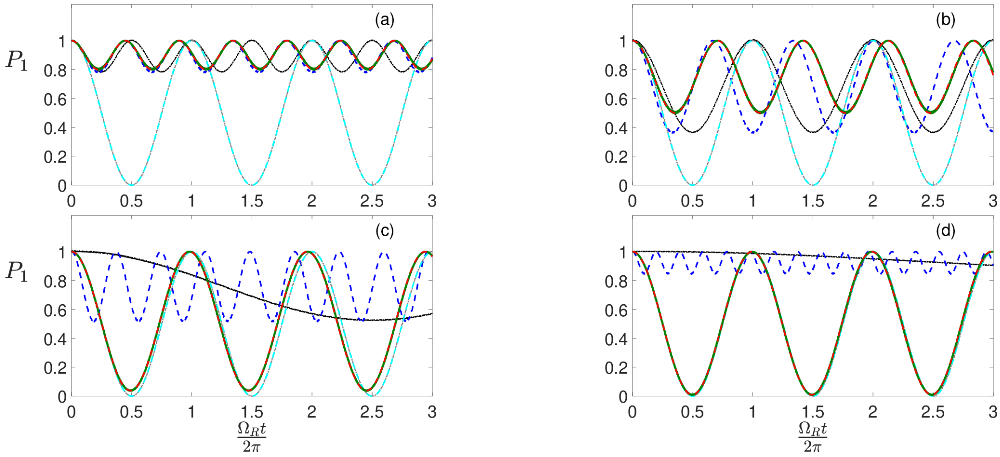

Figure 6.9: $\Delta \neq 0$. P_1 vs. $\frac{\Omega_{\mathrm{R}} t}{2\pi}$, keeping $\epsilon_2 = \frac{\Omega_{\mathrm{R}}}{\Sigma} = 0.01$ and varying $\epsilon_1 = \frac{\Omega_{\mathrm{R}}}{\Delta}$. (a) $\epsilon_1 = 0.5$. (b) $\epsilon_1 = 1$. (c) $\epsilon = 5$. (d) $\epsilon_1 = 10$. Lines correspond to NRWA (continuous —), RWA (dashed −−), non-resonance second order AM (dashed −−), non-resonance first order AM (dash-dotted ·−), resonance second order AM (dashed −−), resonance first order AM (dash-dotted ·−).

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CHAPTER 7

ALLOWED AND FORBIDDEN OPTICAL TRANSITIONS

In this Chapter:

We discuss the so-called allowed and forbidden optical transitions, within the dipole approximation. We refer to historical atomic models (Rutherford, Bohr) and finally to the atomic orbitals model. We focus on hydrogen atom as a didactic example. We discuss the shape and symmetry of atomic orbitals and we calculate the dipole moment matrix elements. We explain the so-called allowed and forbidden transitions within the dipole approximation. We include the relevant selection rules.
Prerequisite knowledge: Basic knowledge of Quantum Physics.

7.1 Allowed and forbidden optical transitions within the dipole approximation.

We remind the reader of the steps we have taken so far within the dipole approximation, which are mentioned in Section 5.3, considering the hydrogen atom as an example. $\vec{R}$ is the position of the nucleus (N) and $\vec{r}_H$ is the position of the electron (E) with respect to the origin of the coordinate system O, while $\vec{r}$ is the position of E with respect to N, i.e., $\vec{r} = \overrightarrow{\mathrm{NE}}$.

$$\left.\begin{aligned} \vec{\mathscr{E}} &= \vec{\mathscr{E}}_a \exp\left[i(\vec{k}\cdot\vec{r}_H - \omega t + \phi)\right] \\ \vec{r}_H &\simeq \vec{R} \end{aligned}\right\} \Rightarrow \text{(homogeneous, time-dependent } \vec{\mathscr{E}}\text{)} \Rightarrow$$

$$\left.\begin{aligned} \vec{\mathscr{E}} = \vec{\mathscr{E}}_0 \exp(-i\omega t) = \vec{\mathscr{E}}(t) \\ \left.\begin{aligned} \vec{\mathscr{E}} &= -\vec{\nabla} V \\ dV &= \vec{\nabla} V \cdot d\vec{r} \end{aligned}\right\} dV = -\vec{\mathscr{E}}\cdot d\vec{r} \end{aligned}\right\} \cdots \Rightarrow \underset{\text{potential}}{V} = -\vec{\mathscr{E}}\cdot\vec{r} \Rightarrow$$

$$\boxed{\underset{\text{of electron}}{\overset{\text{potential energy}}{U}} = e\vec{\mathscr{E}}\cdot\vec{r} = -\vec{\mathscr{P}}\cdot\vec{\mathscr{E}}} \qquad (\clubsuit)$$

Constantinos Simserides (2023). «Quantum Optics».
Kallipos, Open Academic Editions. https://dx.doi.org/10.57713/kallipos-186

i.e., Eq. 5.35. The matrix element of the potential energy of the perturbation,

$$U_{\mathscr{E}k'k}(t) = \int d^3r\, \Phi^*_{k'}(\vec{r})\, U_{\mathscr{E}}(\vec{r}, t)\Phi_k(\vec{r}),$$

can be written, given Eq. (♣), as

$$U_{\mathscr{E}k'k}(t) = -\vec{\mathscr{E}} \cdot \underbrace{\int d^3r\, \Phi^*_{k'}(\vec{r})\vec{\mathscr{P}}\Phi_k(\vec{r})}_{\vec{\mathscr{P}}_{k'k}} = -\vec{\mathscr{E}} \cdot \vec{\mathscr{P}}_{k'k},$$

where $\vec{\mathscr{P}}_{k'k}$ is the matrix element of the dipole moment or as

$$U_{\mathscr{E}k'k}(t) = e\vec{\mathscr{E}} \cdot \underbrace{\int d^3r\, \Phi^*_{k'}(\vec{r})\,\vec{r}\,\Phi_k(\vec{r})}_{\vec{r}_{k'k}} = e\vec{\mathscr{E}} \cdot \vec{r}_{k'k},$$

where $\vec{r}_{k'k}$ is the matrix element of the position of the negative charge with respect to the positive one, e.g. of the electron's position with respect to the nucleus. Of course, $\vec{\mathscr{P}}_{k'k} = -e\,\vec{r}_{k'k}$. Finally, we can see that everything is reduced to the symmetry of the eigenfunctions of the unperturbed problem, since which of these are even or odd determines whether the matrix element $\vec{r}_{k'k}$ becomes zero or not, given that the function $\vec{r}$ is evidently odd.

If $\vec{r}_{k'k}$ becomes zero, then $U_{\mathscr{E}k'k}(t)$ becomes zero, as well. If $U_{\mathscr{E}k'k}(t) = 0$, then the perturbation does not couple states k' and k; hence, if the electron was at k, it will not transition to k' and vice versa. Therefore, if $\vec{r}_{k'k} = 0 \Leftrightarrow U_{\mathscr{E}k'k}(t) = 0$, we say that the transition $k' \longleftrightarrow k$ is "forbidden". We note that the above hold within the dipole approximation, within which the wavelength is very much smaller than the dimensions of the system. In other cases these rules about "allowed" and "forbidden" transitions do not hold. Finally, the larger the magnitude of $\vec{r}_{k'k}$, hence of $U_{\mathscr{E}k'k}(t)$ is, the stronger the "allowed" transitions are.

7.2 Atomic models.

The discovery of the electron in 1897 by J. J. Thomson [1], led scientists to realize that atoms are composed of charged particles. In 1902, G. N. Lewis developed the model of the **cubical atom** (it was published later [2]), according to which electrons are placed on the corners of cubes. In 1904, again J. J. Thomson formulated the so-called **plum pudding model** [3], within which atoms are made up of a positively charged volume inside which there are tiny, negatively charged, electrons. In the same year, H. Nagaoka [4] proposed an alternative model, the **Saturnian model**, according to which atoms are composed of a large, positively charged, center, surrounded by a number of electrons revolving around it, just like the rings of Saturn. 1911 was marked by the discovery of the atomic nucleus by E. Rutherford [5]. This discovery lead again to the formulation of a planetary model, within which atoms are revolving around a small, dense, positively charged nucleus. Many phenomena related to electrons in atoms and solids could not be explained though the classical theory. These insurmountable difficulties led to the development of the old quantum theory (1900-1925) and subsequently of quantum mechanics (> 1925).

7.2.1 Rutherford's model.

Experiments by Rutherford [5] led to the conclusion that electrons revolve around a tiny, dense, positively charged, nucleus. Rutherford's atomic model is an idiotypic, classical, "solar" or "planetary" system.

Rutherford's model (1911) is based on classical physics. The electron is in a circular orbit around the nucleus, and the the centripetal force is the electrostatic attraction between the nucleus and the electron. That is,

$$F_{\text{electric}} = F_{\text{centripetal}} \quad \Rightarrow \quad \frac{m_e v^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2} \quad \Rightarrow \tag{7.1}$$

$$v = \sqrt{\frac{Ze^2}{m_e 4\pi\epsilon_0 r}} \quad \overset{v=2\pi\nu r}{\Longrightarrow} \quad \nu = \sqrt{\frac{Ze^2}{m_e 16\pi^3\epsilon_0 r^3}}, \tag{7.2}$$

where m_e, e, v, ν is the electron mass, charge, (linear) velocity, and frequency, respectively, r is the electron-nucleus distance, and Z is the atomic number of the nucleus. Let us note that today we know that the atomic center of mass essentially coincides with the center of the nucleus, sinnce the later is much smaller (of the order of fm) than the whole atom (of the order of Å), i.e., it is 10^5 times smaller, while the masses of the nuclear particles are $m_{\text{p}} \approx 1836 m_{\text{e}}$ and $m_{\text{n}} \approx 1839 m_{\text{e}}$. p, n, e stand for proton, neutron, electron, respectively. The reduced mass in the hydrogen atom is $\mu = \frac{m_{\text{e}} m_{\text{p}}}{m_{\text{e}} + m_{\text{p}}} \approx m_{\text{e}}$. Therefore, the kinetic energy of the electron is

$$E_{\text{K}} = \frac{1}{2} m_e v^2 = \frac{Ze^2}{8\pi\epsilon_0 r}. \tag{7.3}$$

Hence, given that its potential energy is

$$E_{\text{P}} = -\frac{Ze^2}{4\pi\epsilon_0 r}, \tag{7.4}$$

its total energy is given by the formula

$$E_{\text{T}} = E_{\text{K}} + E_{\text{P}} = \frac{Ze^2}{8\pi\epsilon_0 r} - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{Ze^2}{8\pi\epsilon_0 r}. \tag{7.5}$$

Contradictions of the Rutherford's model

1. According to the Rutherford's model, since the electron is revolving around the nucleus, it will have a centripetal acceleration. However, in classical electrodynamics, accelerating particles emit electromagnetic waves. The power, P, emitted by an accelerating, non-relativistic ($v \ll c$), point charge is given by the Larmor equation as

$$P = \frac{q^2 a^2}{6\pi\epsilon_0 c^3}, \tag{7.6}$$

   where q is the particle's charge (in our case, $q = -e$) and a the magnitude of its acceleration (in our case, centripetal). [We denote decrease by ↓ and increase by ↑.] Therefore, since the electron loses energy as it accelerates, Eq. 7.5 yields

$$E_{\text{T}} \downarrow \quad \Rightarrow \quad |E_{\text{T}}| \uparrow \quad \Rightarrow \quad r \downarrow \quad \Rightarrow \quad v \uparrow \quad \text{και} \quad \nu \uparrow. \tag{7.7}$$

   Thus, the electron loses energy by following a spiral orbit of increasingly smaller radius r and larger velocity v and frequency ν, until it eventually collapses in the nucleus. Therefore, Rutherford's model is a *fatally flawed* model.

2. According to Eq. 7.5, the electron-nucleus distance and the velocity (hence, the frequency) can change in a continuous manner. This is in contradiction with experimental data, which, already by the end of the 19th, suggested that atoms emit light in discrete, not in continuous, frequencies. See Fig. 7.2 and Table 7.1.

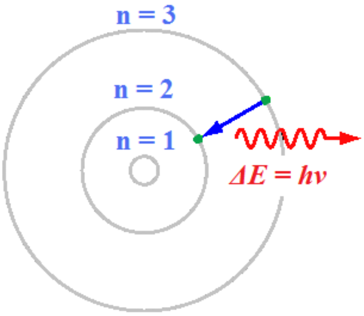


Figure 7.1: The Bohr's model (1913) [6] is an evolved version of the Rutherford's model (1911) [5] and belongs to the old quantum theory. The electron revolves only in specific, allowed, circular orbits characterized by a quantum number $n = 1, 2, 3, \ldots$. When it moves from an initial state to another final state, it emits or absorbs electromagnetic radiation $h\nu$.

7.2.2 Bohr's model.

The Bohr's model (1913) [6] is an evolved version of the Rutherford's model (1911) [5] and belongs to the old quantum theory. See Fig. 7.1. It is based on the following assumptions:

1. Electrons move in circular orbits around the nucleus. The centripetal force comes from the electrostatic attraction between the nucleus and the electron and obeys to the laws of classical mechanics, expressed by Eqs. (7.1), (7.2), (7.3), (7.4), (7.5) (mentioned previously in the context of Rutherford's model) for F_{electric}, $F_{\text{centripetal}}$, E_{K}, E_{P}, E_{T}, υ, ν.

2. However, instead of the infinite orbits that would be possible within classical mechanics, within the Bohr's model the electron can only move in circular orbits in which the magnitude ($|\vec{L}| := L$) of the angular momentum, $\vec{L} = \vec{r} \times \vec{p}$, is a natural multiple of the constant known today as "the Planck constant", i.e.,
$$\vec{L} = \vec{r} \times \vec{p} \Rightarrow L = rp = m_e \upsilon r = n\hbar, \ \forall n = 1, 2, 3, \ldots .$$
In other words, Bohr introduced the hypothesis that the angular momentum is quantized, i.e., it comes in discrete values. The positive integer number n is today called the principal quantum number.

3. In these allowed stationary orbits, the electron does not radiate, i.e., the Larmor equation 7.6 does not hold. In these orbits, which lie in specific distances from the nucleus, the electrons have a specific, constant energy.

4. EM radiation is emitted or absorbed only when the electron moves to another allowed orbit and the frequency of the emitted or absorbed radiation follows the relationship $h\nu = |E_i - E_f|$, where $E_{i(f)}$ is the energy corresponding to the initial (final) orbit.

Since the angular momentum is quantized, it follows that

$$m_e \upsilon r = n\hbar, \tag{7.8}$$

therefore Eq. (7.2) yields

$$r = r_n = \frac{4\pi\epsilon_0 \hbar^2}{Z m_e e^2} n^2. \tag{7.9}$$

The quantity $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \simeq 0.529\cdot 10^{-10}$ m is called the *Bohr radius*. Thus, in the hydrogen atom $(Z = 1)$, $r_1 = a_0, r_2 = 4a_0, r_3 = 9a_0$, and so forth.

Given, Eq. 7.9, Eq. 7.5 for the total energy becomes

$$E_T = E_n = -\frac{Ze^2}{8\pi\epsilon_0 r_n} = -\frac{Z^2 m_e e^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2}. \tag{7.10}$$

The quantity $R_E = \frac{m_e e^4}{32\pi^2\epsilon_0^2\hbar^2} \simeq 13.6$ eV is called *the Rydberg energy*. Thus, in the hydrogen atom $(Z = 1)$, $\mathrm{E}_1 \simeq -13.6$ eV, $E_2 \simeq -3.4$ eV, $E_3 \simeq -1.5$ eV, and so forth. Compactly, in the hydrogen atom,

$$E_n = -\frac{R_E}{n^2} \simeq -\frac{13.6}{n^2}\ \mathrm{eV}. \tag{7.11}$$

From the above, it follows that the photon energy is

$$h\nu = \left|E_f - E_i\right| \Rightarrow h\frac{c}{\lambda} = \left|-\frac{R_E}{n_f} + \frac{R_E}{n_i}\right| \Rightarrow \frac{1}{\lambda} = \frac{R_E}{hc}\left|\frac{1}{n_i} - \frac{1}{n_f}\right|, \tag{7.12}$$

where $R := \frac{R_E}{hc} \approx 1.097\ 10^7 \mathrm{m}^{-1}$ is the Rydberg constant. In other words, the experimental Rydberg formula occurs. Success! To sum up, Bohr's atomic model:

- Managed to explain the experimental Rydberg formula for the hydrogen atom

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \tag{7.13}$$

where $n_i, n_f \in \mathbb{N}^*$, with $n_f < n_i$. This formula predicts the wavelengths at which the hydrogen atom emits EM radiation. The emission spectral lines of atomic hydrogen are presented in Figure 7.2 and are grouped in the so-called Lyman, Balmer, Paschen, etc, series, depending on the values of n_f and n_i, which are presented in Table 7.1.

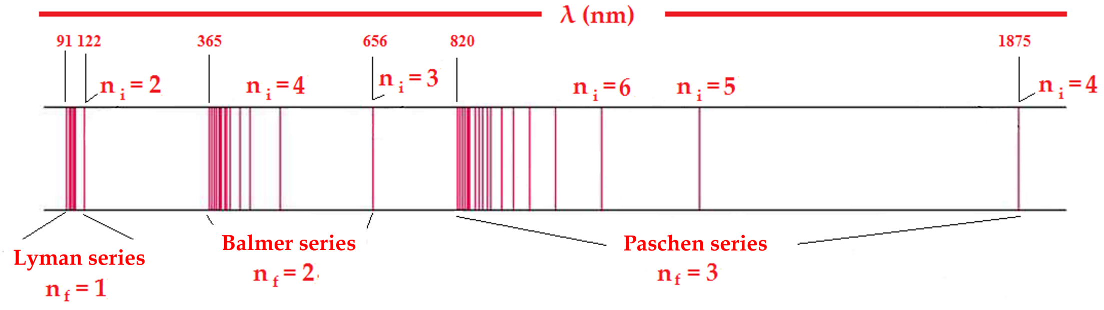


Figure 7.2: Emission spectral lines of the hydrogen atom.

- Can also be applied to hydrogen-like atoms, such as He^+, Li^{2+}, Be^{3+}, etc, through the form

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right). \tag{7.14}$$

- Can also be applied to describe distant electrons in multi-electron atoms, the effective nuclear charge of which can be considered $\approx e > 0$, since all nuclear charges apart from one are screened by the rest electrons.

Table 7.1: Hydrogen spectral series.

n_f	n_i	**Name**	**Converge towards**	
1	$2 \to \infty$	Lyman series	91.13 nm	(UV)
2	$3 \to \infty$	Balmer series	364.51 nm	(~Visible)
3	$4 \to \infty$	Paschen series	820.14 nm	(IR)
4	$5 \to \infty$	Brackett series	1458.03 nm	(FIR)
5	$6 \to \infty$	Pfund series	2278.17 nm	(FIR)
6	$7 \to \infty$	Humphreys series	3280.56 nm	(FIR)

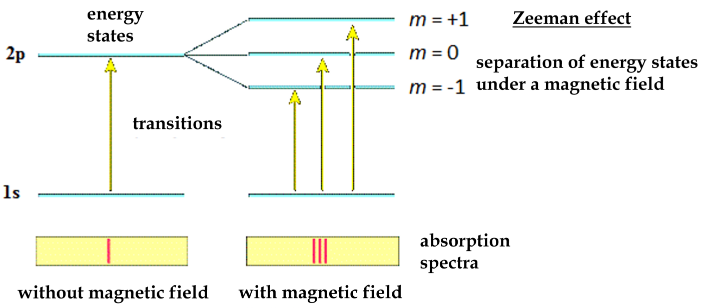


Figure 7.3: Zeeman effect: separation of the energy states of a subshell due to the presence of an external magnetic field.

On the other hand, Bohr's model also displays serious disadvantages [7].

- It can only be applied to H, single-electron ions such as He^+, Li^{+2}, Be^{+3}, ... and outer electrons. It is not sufficient to even explain the He atom.
- It cannot explain why some spectral lines are more intense than others, i.e., why some transitions between energy levels are more probable to occur that others.
- It cannot explain why many spectral lines are multiple, i.e. they are composed of distinct lines with a very small wavelength difference. In other words, it cannot describe the fine structure of atomic spectra.
- It cannot explain why, when a magnetic field is applied, the multiple lines are separated (Zeeman effect). See Figure 7.3.
- It does not provide an understanding of how the atoms interact to form molecules, solids, and other clusters. In other words, it cannot be applied in Chemistry and Condensed Matter Physics.

Even though there where several efforts to improve the Bohr's modes, e.g., by Wilson [8] and Sommerfeld [9], the above contradictions could only be solved in the context of modern quantum mechanics, which was developed after 1925. Below, we discuss the atomic orbitals model, which belongs to modern quantum mechanics.

7.3 Schrödinger equation in spherical coordinates

The Schrödinger equation in spherical coordinates is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{2m}{\hbar^2}\left(E-U(\vec{r})\right)\psi=0, \tag{7.15}$$

where

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}=\nabla^2\psi(r,\theta,\phi), \tag{7.16}$$

is the Laplacian in spherical coordinates. In the hydrogen atom

$$U(\vec{r})=-\frac{e^2}{4\pi\epsilon_0 r}. \tag{7.17}$$

Let us try to solve the problem by separating variables, i.e., by trying solutions of the form

$$\psi(r,\theta,\phi)=R(r)\,\Theta(\theta)\,\Phi(\phi). \tag{7.18}$$

Thus,

$$\frac{\Theta\Phi}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right)+\frac{R\Phi}{r^2\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)+\frac{R\Theta}{r^2\sin^2\theta}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}+\frac{2m}{\hbar^2}\left(E-U(\vec{r})\right)R\Theta\Phi=0. \tag{7.19}$$

If $R\Theta\Phi=0$, then the previous equation is trivially satisfied, whereas if $R\Theta\Phi\neq 0$, then we can divide by $R\Theta\Phi$, so that

$$\frac{1}{R}\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right)+\frac{1}{\Theta}\frac{1}{r^2\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)+\frac{1}{\Phi}\frac{1}{r^2\sin^2\theta}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}+\frac{2m}{\hbar^2}\left(E-U(\vec{r})\right)=0. \tag{7.20}$$

We multiply by $r^2\sin^2\theta$ to obtain

$$\frac{\sin^2\theta}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right)+\frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)+\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}+\frac{2mr^2\sin^2\theta}{\hbar^2}\left(E-U(\vec{r})\right)=0. \tag{7.21}$$

The third addend of the above equation is a function of ϕ only. We move it to the right-hand size and we use Eq. (7.17), so that

$$\frac{\sin^2\theta}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right)+\frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)+\frac{2mr^2\sin^2\theta}{\hbar^2}\left(E+\frac{e^2}{4\pi\epsilon_0 r}\right)=-\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}. \tag{7.22}$$

The left-hand side, A, is a function of r and θ, while the right-hand side, Δ, is a function of ϕ. For the left-hand side to be equal to the right-hand side $\forall\, r,\theta,\phi$, it must hold that $\mathrm{A}=\Delta=$ constant. Let us call this constant, without justification at this point, m_ℓ^2, i.e., $\mathrm{A}=\Delta:=m_\ell^2$.

Thus, it occurs that

$$\boxed{-\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}=m_\ell^2} \tag{7.23}$$

which is an equation with respect to ϕ, as well as

$$\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right)+\frac{2mr^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\epsilon_0 r}\right)=\frac{m_\ell^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right), \tag{7.24}$$

the left-hand side of which, A', depends only on r and the right-hand side, Δ', only on θ. For the left-hand side to be equal to the right-hand side $\forall\, r, \theta$, it must hold that $\mathrm{A}' = \Delta' =$ constant. Let us call this constant, without justification at this point $\ell(\ell+1)$, i.e., $\mathrm{A}' = \Delta' := \ell(\ell+1)$. Hence, moving on, we obtain the equation

$$\boxed{\frac{m_\ell^2}{\sin^2\theta} - \frac{1}{\Theta \sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta \frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) = \ell(\ell+1)} \tag{7.25}$$

which is a function of θ only, and the equation

$$\boxed{\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \frac{2mr^2}{\hbar^2}\left(E + \frac{e^2}{4\pi\epsilon_0 r}\right) = \ell(\ell+1)} \tag{7.26}$$

which is a function of r only. Eq. (7.26) is the only one containing the potential energy. It is going to give us E, that is the energy eigenvalues or the “allowed energies”.

Let us solve Eq. (7.23) first, by trying solutions of the form

$$\Phi(\phi) = A\, e^{im_\ell\phi}, \tag{7.27}$$

so that

$$\Phi'(\phi) = Aim_\ell\, e^{im_\ell\phi}, \tag{7.28}$$

and

$$\Phi''(\phi) = -Am_\ell^2\, e^{im_\ell\phi}. \tag{7.29}$$

Thus, it can easily be shown that Eq. (7.23) is satisfied. Moreover, since it must hold that

$$\Phi(\phi+2\pi) = \Phi(\phi) \Rightarrow e^{im_\ell(\phi+2\pi)} = e^{im_\ell\phi} \Rightarrow e^{im_\ell 2\pi} = 1 = e^{i2\pi m}, m \in \mathscr{Z} \Rightarrow m_\ell = m \in \mathscr{Z}. \tag{7.30}$$

Concisely,

$$\Phi_{m_\ell}(\phi) = A\, e^{im_\ell\phi}, \quad m_\ell \in \mathscr{Z}. \tag{7.31}$$

m_ℓ is called the magnetic quantum number, for reasons that will not be explained yet. Additionally, normalizing over the interval $[0, 2\pi]$, we obtain

$$\int_0^{2\pi} \left|A\, e^{im_\ell\phi}\right|^2 = 1 \Rightarrow |A|^2 = \frac{1}{2\pi}, \tag{7.32}$$

hence it would be convenient to choose $\mathrm{A} = \frac{1}{\sqrt{2\pi}}$, i.e.,

$$\boxed{\Phi_{m_\ell}(\phi) = \frac{1}{\sqrt{2\pi}}\, e^{im_\ell\phi}, \quad m_\ell \in \mathscr{Z}} \tag{7.33}$$

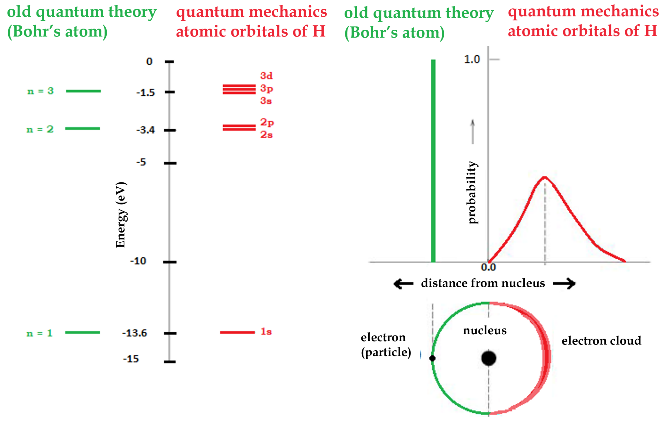
Regarding Eq. (7.25), we mention (without proof) that it has solutions when

$$m_\ell = 0, \pm1, \pm2, \ldots, \pm\ell. \tag{7.34}$$

ℓ is called the secondary quantum number or angular momentum quantum number. Therefore, we can denote the solutions to Eq. (7.25) as $\Theta_{\ell m_\ell}(\theta)$.

Regarding Eq. (7.26), we mention (without proof) that it has solutions when $E > 0$ or when

$$E_n = -\frac{R_E}{n^2} = -\frac{m_e e^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2}, \tag{7.35}$$



Comparison of energies

Comparison of positions

Figure 7.4: Comparison of energies and positions, at the ground state, between the Bohr's model and the atomic orbitals model.

and, at the same time, $\ell = 0, 1, 2, \ldots, n-1$. States with $E = E_n$ are called bound states. It is worth-noting that these energies are the same with the ones of the simplistic Bohr's model. n is called the principal quantum number. Thus, we can denote the solutions to Eq. (7.26) as $R_{n\ell}(r)$. We also note that we can bring Eq. (7.26) to the form

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \frac{2m}{\hbar^2}\left(E + \frac{e^2}{4\pi\epsilon_0 r} - \frac{\hbar^2\ell(\ell+1)}{2mr^2}\right)R = 0. \tag{7.36}$$

If we remember that the energy of a particle moving inside a central potential (such as $U(\vec{r}) = -\frac{e^2}{4\pi\epsilon_0 r}$) contains the rotational term

$$E_{rot} = \frac{L^2}{2mr^2}, \tag{7.37}$$

it follows that the magnitude of the angular momentum L is given by

$$L = \hbar\sqrt{\ell(\ell+1)},\ \ell = 0, 1, 2, \ldots, n-1. \tag{7.38}$$

In other words, the angular momentum is quantized. This is why the number ℓ is called this way.

To wrap this up, the solutions to the Schrödinger equation for the hydrogen atom have the general form

$$\Psi_{n\ell m_\ell} = \mathcal{N} R_{n\ell}(r)\Theta_{\ell m_\ell}(\theta)\Phi_{m_\ell}(\phi), \tag{7.39}$$

or

$$\Psi_{n\ell m_\ell} = \mathcal{N} R_{n\ell}(r) Y_{\ell m_\ell}(\theta, \phi), \tag{7.40}$$

where the product $\Theta_{\ell m_\ell}\Phi_{m_\ell}$ is represented by the spherical harmonics, $Y_{\ell m_\ell}$.

7.3.1 Atomic orbitals model.

According to the atomic orbitals model, the state of the electrons inside an atom is determined by the solutions to the Schrödinger equation, which gives its allowed energy levels, $E_{n\ell m}$, and its eigenfunctions (atomic orbitals), $\Psi_{n\ell m}(\vec{r})$. For the hydrogen atom, this procedure was described above, and it leads to $E_{n\ell m_\ell} = E_n$. In multi-electron atoms, $E_{n\ell m_\ell} = E_{n\ell}$. However, as we will see below, the degeneracy with respect to m_ℓ is lifted under a magnetic field. Generally, the electronic states are dependent on the following quantum numbers:

- $n = 1, 2, 3, \ldots$ is the **principal quantum number**, which defines the shell and determines the **average distance** between the electron and the nucleus (contrary to Bohr's atomic model, in which it determined the **radius of the circular motion**).

- $\ell = 0, 1, 2, \ldots, n-1$ is the **secondary quantum number** or angular momentum quantum number, which determines the subshell and the shape of the probability density to find the electron somewhere in space. For example, for $n = 1$, there is one subshell with $\ell = 0$. For $n = 2$, there are two subshells with $\ell = 0, 1$, and so forth. The number ℓ determines the form of the probability density to find the electron somewhere in space. Subshells with $l = 0$ are called s orbitals, with $\ell = 1$ p orbitals, with $\ell = 2$ d orbitals, and so forth. s orbitals display shperical symmetry, p orbitals are bilobed with directionality, and so forth.

- $m = -\ell, -\ell+1, \ldots, \ell-1, \ell$ is the **magnetic quantum number**. It takes $2\ell + 1$ different values. This number is the total number of energy states within a subshell. For example, for $\ell = 3$, $m = 0, \pm 1, \pm 2, \pm 3$. Hence, there 7 energy states within in an f-subshell. In the absence of magnetic fields, the energy states of a subshell are degenerate, i.e., $E_{n\ell m} = E_{nl}$. This degeneracy is lifted under a magnetic field (Zeeman effect, see Figure 7.3). Consider a magnetic field, $\vec{B}$, along the z-direction. The magnitude of the electronic angular momentum is

$$L = \hbar\sqrt{\ell(\ell+1)}, \tag{7.41}$$

while the z-component of the electronic angular momentum is

$$L_z = \hbar m_\ell,\ m_\ell = 0, \pm 1, \pm 2, \ldots, \pm \ell. \tag{7.42}$$

However, since $|m_\ell| \leq \ell \Rightarrow m_\ell^2 \leq \ell^2 < \ell(\ell+1) \Rightarrow \hbar^2 m_\ell^2 < \hbar^2 \ell(\ell+1) \Rightarrow |L_z|^2 < |L|^2$. This means that that the angular momentum $\vec{L}$ cannot be directed exactly parallel or antiparallel to $\vec{B}$. The components L_x, L_y are not well defined, however, due to symmetry reasons, $\langle L_x \rangle = \langle L_y \rangle = 0$. Therefore, we can imagine $\vec{L}$ as if it were rotating around the z-axis (Larmor precession). See Figure 7.5, e.g. for $\ell = 2$, $m_\ell = -2, -1, 0, 1, 2$. We note that the magnetic field only provides an experimentally well-defined direction. This analysis holds for any given direction. To sum up, the magnitude of the angular momentum $L = \hbar\sqrt{\ell(\ell+1)}$ as well as one of its components (whichever we choose), e.g. $L_z = \bar{m}_\ell$, are quantized quantities. The rest components are not well defined. If they were, i.e., if the angular momentum could be fully determined, e.g.. $\vec{L} = L_z\hat{z}$, it would hold that

$$\vec{L} = \vec{r} \times \vec{p} \Rightarrow \vec{r} \cdot \vec{L} = \vec{r} \cdot \vec{r} \times \vec{p} = \vec{p} \cdot \vec{r} \times \vec{r} = \vec{p} \cdot \vec{0} = \vec{0} \Rightarrow \vec{r} \perp \vec{L}. \tag{7.43}$$

In other words $\vec{r}$ would lie on xy-plane, which in turn means that the z-component of the electron would be fully determined, i.e., $\Delta z = 0$. This is **absurd**, since it contradicts the Heisenberg's uncertainty principle, according to which $\Delta z \Delta p_z \geq \frac{\hbar}{2}$. Thus, since only L, L_z are well-defined and $|L| < |L_z|$, the electron can never be confined to a plane.

Under a magnetic field $\vec{B}$, there is a potential energy term added to the Hamiltonian which has the form

$$U = -\vec{\mu}\vec{B}, \tag{7.44}$$

where $\vec{\mu}$ is the magnetic moment of the system. For a magnetic field along the z-direction and ignoring spin-related effects, we obtain

$$U = -\frac{-e}{2m_e}\vec{L}\vec{B} = \frac{e}{2m_e}L_z B = \frac{e\hbar}{2m_e}m_\ell B = \mu_b m_\ell B, \tag{7.45}$$

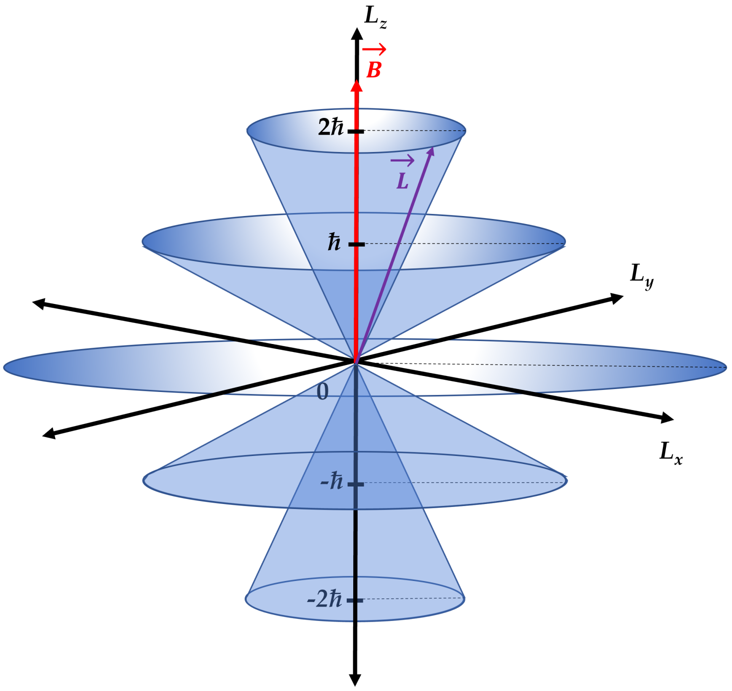


Figure 7.5: The cones represent the possible directions of the angular momentum, e.g., for $\ell = 2$ $(m_\ell = -2, -1, 0, 1, 2)$. For a magnetic field along the z-direction, the angular momentum cannot directed exactly parallel or antiparallel to the field. The x- and y- components of the angular momentum are not well defined.

where the quantity $\mu_B \approx 9.274 \cdot 10^{-24}$ J/T $\approx 5.788 \cdot 10^{-5}$ eV/T is called the **Bohr's magneton**. Therefore, under a magnetic field, the energy depends not only on the quantum number n, but also on m_ℓ. This is the reason why this number is called the magnetic quantum number. Under a magnetic field, the $2\ell + 1$ degenerate energy states are separated. Therefore, under a magnetic field, the spectral emission lines are separated. This is the **normal Zeeman effect** (see Figure 7.3).

- There is also the **spin quantum number**, m_s, which for electrons takes the values $m_s = \pm 1/2$. Similar to the angular momentum, the magnitude of the spin of a particle is

$$S = \hbar\sqrt{s(s+1)}, \tag{7.46}$$

while its z-component is z

$$S_z = \hbar m_s,\ m_s = 0, \pm 1, \pm 2, \dots, \pm s. \tag{7.47}$$

The quantum number s takes positive integer values when the particle is a boson or positive half-integer values when the particle is a fermion. Electrons are fermions with spin $s = \frac{1}{2}$ (half-integer). Therefore, $m_s = \pm\frac{1}{2}$. Similar to the angular momentum, for a magnetic field along the z-axis, the spin cannot be directed exactly parallel or antiparallel to the field. The x- and y- components of the spin are not well-defined. Therefore we can imagine $\vec{S}$ as if it were rotating around the z-axis. See Figure 7.6.

Under a magnetic field $\vec{B}$, there is a potential energy term added to the Hamiltonian which has the form

$$U = -\vec{\mu}\vec{B}, \tag{7.48}$$

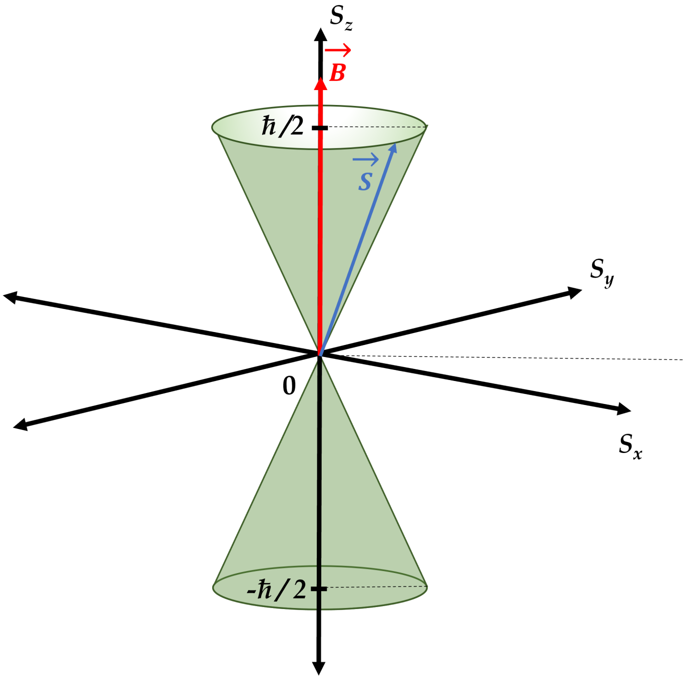


Figure 7.6: The cones represent the possible directions of the electron spin. For a magnetic field along the z-direction, the spin cannot directed exactly parallel or antiparallel to the field. The x- and y- components of the spin are not well defined.

where $\vec{\mu}$ is the magnetic moment of the system. For a magnetic field along the z-direction

$$U = -\vec{\mu}\vec{B} = -\frac{-e}{2m_e}(\vec{L} + g\vec{S})\vec{B} = \frac{e}{2m_e}(L_z + gS_z)B = \frac{e\hbar}{2m_e}m_\ell B = \mu_b(m_\ell + gm_s)B, \quad (7.49)$$

where the constant $g \approx 2$ is called the Landé factor. Therefore, under a magnetic field, the energy depends not only on the quantum number n, but also on m_ℓ, m_s. Hence, under a magnetic field, the $2\ell + 1$ degenerate energy states of angular momentum and the 2 spin-states are separated. This is called the **anomalous Zeeman effect**. For degenerate spin, every state of each subshell can be occupied by up to 2 electrons (with $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$), due to the Pauli's exclusion principle, according to which two fermions cannot occupy the same quantum state. We note that, apart from the Zeeman effect, there are other corrections to the eigenenergies of hydrogen, such as the **fine structure**, which occurs from relativistic corrections to the Schrödinger equation and the **hyperfine structure**, which occurs if we take into account interactions with the spin of the atomic nucleus. These corrections are several orders of magnitude smaller.

In Table 7.2 the structure of the first four energy shells within the atomic orbitals model is presented. Taking into account the Pauli's exclusion principle, since in an s ($\ell = 0$) subshell there is 1 state ($m_\ell = 0$), this subshell can by occupied by 2 electrons at most, one with spin up ($m_s = +\frac{1}{2}$) and one with spin down ($m_s = -\frac{1}{2}$). Similarly, in a p ($\ell = 1$) subshell there are 3 states ($m_\ell = 0, \pm1$), hence it can by occupied by up to 6 electrons. In a d ($\ell = 2$) subshell there are 5 states ($m_\ell = 0, \pm1, \pm2$), hence it can by occupied by up to 10 electrons. In an f ($\ell = 3$) subshell there are 7 states ($m_\ell = 0, \pm1, \pm2, \pm3$), hence it can by occupied by up to 14 electrons.

In Figure 7.7, an approximative schematic representation of the relative energies of various shells and subshells is presented. We observe that:

Table 7.2: Structure of the first four energy shells within the atomic orbitals model.

Shell (n)	**Subshell** (ℓ)	**States** (m_ℓ)	**Maximum** $\#e^-$ **in shell**	**Maximum** $\#e^-$ **in subshell**
1 (K)	0 (1s)	0	2	2
2 (L)	0 (2s)	0	2	8
	1 (2p)	$0, \pm1$	6	
3 (M)	0 (3s)	0	2	18
	1 (3p)	$0, \pm1$	6	
	2 (3d)	$0, \pm1, \pm2$	10	
4 (N)	0 (4s)	0	2	32
	1 (4p)	$0, \pm1$	6	
	2 (4d)	$0, \pm1, \pm2$	10	
	3 (4f)	$0, \pm1, \pm2, \pm3$	14	

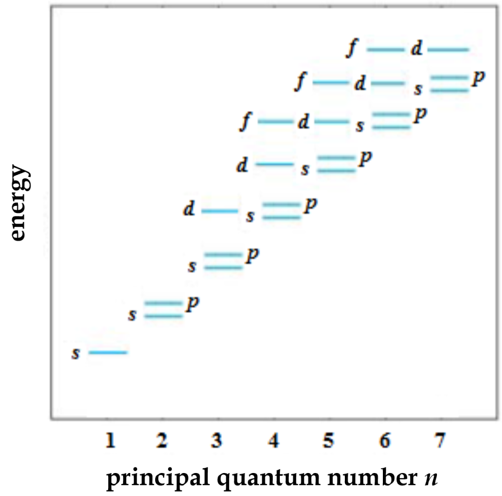


Figure 7.7: Approximative schematic of the relative energies of shells and subshells.

- The more inner the shell (i.e., the less the value of the principal quantum number n), the less the energy of the subshell of the same form, e.g., $E_{1s} < E_{2s} < E_{3s} < E_{4s}, \dots, E_{2p} < E_{3p} < E_{4p} \dots$, κ.ο.κ.
- For any given shell, i.e. for a given n, the energy of the subshell increases with the value of ℓ, e.g. $E_{3s} < E_{3p} < E_{3d}$.
- It is possible that a subshell with a smaller n (“a more inner shell”) has a larger energy than a subshell of another form with larger n (“a more outer shell”), e.g. $E_{3d} > E_{4s}$. In other words, shells can be overlapping with each other. This effect is mainly observed for large values of n and especially between f and d orbitals.

We characterized this representation as approximative, since, e.g., the $3d$ and $4s$ orbitals are very close to each other energetically, and their specific arrangement depends on:

- the specific atom, i.e., the number of protons, neutrons, and electrons.
- the repulsion between electrons that occupy orbitals. For example the combinations $3d^1\ 4s^2$ or $3d^2 4s^1$ are more favorable, since d and s orbital have different distributions of the electron cloud, hence the repulsion between them is different,

- the Pauli's exclusion principle, etc.

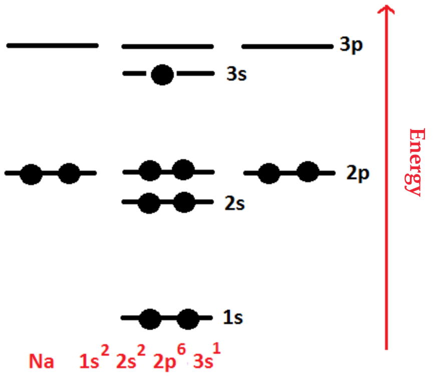


Figure 7.8: Ground state configuration of the Sodium atom (Na).

Of course, not all of the possible energy states of an atom are occupied by electrons. The way in which the energy states of an atom are occupied by electrons is called the **electron configuration**. In most atoms, electrons fill the states with the lowest energy, with two electrons with opposite spins occupying each state. The ground state (i.e., the one with lowest energy) electron configuration of the Sodium atom is schematically presented in Figure 7.8. Of course, there are many ways to excite electrons in atoms so that electronic configurations with larger energies occur. The conventional notation is that the number of electrons in each subshell is marked by an exponent next to the subshell symbol. For example, for Sodium: Na $1s^2 2s^2 2p^6 3s^1$, which means that, out of its 11 electrons, 2 belong to the $1s$ subshell, 2 to the $2s$ subshell, 6 to the $2p$ subshell, and 1 to the $3s$ subshell.

The electrons that occupy the outer shell (i.e., the highest energetically shell which is partially or fully occupied) are called **valence electrons**. For example, in Sodium there is one valence electron, the one that belongs in shell 3, and specifically in subshell $3s$. These electrons are very important, since they participate to bonding between atoms to form atomic and molecular clusters. Furthermore, many physical and chemical properties mainly depend on the valence electrons.

We say that an atom has a **stable electronic configuration** when the s and$p$ subshells of the outer shell (or, for He, only the s subshell) are filled. Therefore, the occupied outer shell has $2 + 6 = 8$ electrons (or, for He, 2 electrons). The elements He, Ne, Ar, Kr, Xe, Rn have a stable electronic configurations. These elements are called noble gases or inert gases and have essentially no chemical reactivity. Some atoms with no fully occupied valence shells can obtain a stable electronic configuration by adding or losing electrons, i.e. by forming ions, or by sharing their valence electrons with other atoms. This is a general tendency, not a strict rule. Some exceptions are, e.g., BF_3 and PCl_5. The electronic configuration of noble gases is presented in Table 7.3.

Finally, it should be noticed that we cannot know *a priori* the relationship between the energies of the subshells of two different atoms. For example, the electronic configuration of Na is $[\mathrm{Ne}]3s^1$, with ionization energy 5.1391 eV, i.e., $\mathrm{E}_{3\square\square}^{\mathrm{Na}} = -5.1391$ eV, while the electronic configuration of Cl is $[\mathrm{Ne}]3s^2 3p^5$, with ionization energy 12.9676 eV, i.e., $\mathrm{E}_{3p}^{\mathrm{Cl}} = -12.9676$ eV . In other words, $\mathrm{E}_{3\square\square}^{\mathrm{Na}} > \mathrm{E}_{3p}^{\mathrm{Cl}}$. This is why chlorine is said to be more electronegative than sodium.

Table 7.3: Electronic configuration of noble gases.

Noble gas	**Electronic configuration**	**Number of electrons in shells**
Helium (He)	$1s^2$	2
Neon (Ne)	$[\mathrm{He}]2s^2 2p^6$	$2, 8$
Argon (Ar)	$[\mathrm{Ne}]3s^2 3p^6$	$2, 8, 8$
Krypton (Kr)	$[\mathrm{Ar}]3d^{10} 4s^2 4p^6$	$2, 8, 18, 8$
Xenon (Xe)	$[\mathrm{Kr}]5s^2 4d^{10} 5p^6$	$2, 8, 18, 18, 8$
Radon (Rn)	$[\mathrm{Xe}]4f^{14} 5d^{10} 6s^2 6p^6$	$2, 8, 18, 32, 18, 8$

7.4 Hydrogen Atom: Form of atomic orbitals.

In Fig. 7.9 we show the spherical coordinates (r, θ, φ) as they are commonly used in physics: the distance r from the axes origin O, the polar angle θ, and the azimuthal angle φ. The unit vectors $\hat{e}_r, \hat{e}_\theta, \hat{e}_\varphi$ are also depicted.

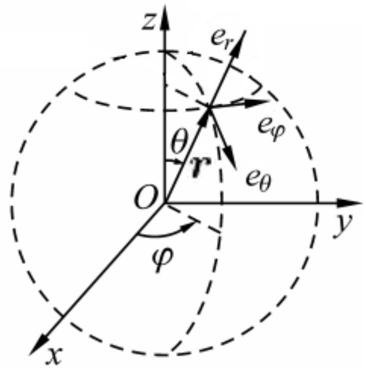


Figure 7.9: The spherical coordinates (r, θ, φ): the distance r from the axes origin O, the polar angle θ, and the azimuthal angle φ. The unit vectors $\hat{e}_r, \hat{e}_\theta, \hat{e}_\varphi$ are also depicted.

We remind that the unit vectors $\hat{e}_r, \hat{e}_\theta, \hat{e}_\varphi$ of the spherical coordinate system can be transformed to the unit vectors of the Cartesian coordinate system $(\hat{e}_x, \hat{e}_y, \hat{e}_z)$ and vice versa according to the relationships

$$\begin{bmatrix} \hat{e}_r \\ \hat{e}_\theta \\ \hat{e}_\varphi \end{bmatrix} = \begin{bmatrix} \sin\theta\cos\varphi & \sin\theta\sin\varphi & \cos\theta \\ \cos\theta\cos\varphi & \cos\theta\sin\varphi & -\sin\theta \\ -\sin\varphi & \cos\varphi & 0 \end{bmatrix} \begin{bmatrix} \hat{e}_x \\ \hat{e}_y \\ \hat{e}_z \end{bmatrix}, \quad \begin{bmatrix} \hat{e}_x \\ \hat{e}_y \\ \hat{e}_z \end{bmatrix} = \begin{bmatrix} \sin\theta\cos\varphi & \cos\theta\cos\varphi & -\sin\phi \\ \sin\theta\sin\varphi & \cos\theta\sin\varphi & \cos\varphi \\ \cos\theta & -\sin\theta & 0 \end{bmatrix} \begin{bmatrix} \hat{e}_r \\ \hat{e}_\theta \\ \hat{e}_\varphi \end{bmatrix}. \tag{7.50}$$

In spherical coordinates, the eigenfunctions of hydrogen have the form

$$\Psi_{n\ell m}(r, \theta, \varphi) = R_{n\ell}(r)\Theta_{\ell m}(\theta)\Phi_m(\varphi).$$

These are the $\Phi_k(\vec{r})$ of the general notation we have been using so far, where $k = \{n, \ell, m\}$ is the collective quantum number. To be more specific, below we list the atomic orbitals $1s, 2s, 2p, 3s, 3p, 3d$ [10].

$$\Psi_{100}(r, \theta, \varphi) = \left(\pi a_0^3\right)^{-\frac{1}{2}} e^{-\frac{r}{a_0}} \qquad \Psi_{100} := 1s$$

$$\Psi_{200}(r, \theta, \varphi) = \left(32\,\pi a_0^3\right)^{-\frac{1}{2}} \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \qquad \Psi_{200} := 2s$$

$$\Psi_{210}(r, \theta, \varphi) = \left(32\,\pi a_0^3\right)^{-\frac{1}{2}} \frac{r}{a_0} \cos\theta\, e^{-\frac{r}{2a_0}} \qquad \Psi_{210} := 2p_z$$

$$\Psi_{21\pm1}(r,\theta,\varphi) = \left(64\,\pi a_0^3\right)^{-\frac{1}{2}} \frac{r}{a_0} \sin\theta\, e^{\pm i\varphi} e^{-\frac{r}{2a_0}} \qquad (\Psi_{21+1}+\Psi_{21-1})/\sqrt{2} := 2p_x$$

$$(\Psi_{21+1}-\Psi_{21-1})/(i\sqrt{2}) := 2p_y$$

$$\Psi_{300}(r,\theta,\varphi) = \left(19683\,\pi a_0^3\right)^{-\frac{1}{2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-\frac{r}{3a_0}} \qquad \Psi_{300} := 3s$$

$$\Psi_{310}(r,\theta,\varphi) = \left(6561\,\pi a_0^3/2\right)^{-\frac{1}{2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-\frac{r}{3a_0}} \cos\theta \qquad \Psi_{310} := 3p_z$$

$$\Psi_{31\pm1}(r,\theta,\varphi) = \left(6561\,\pi a_0^3\right)^{-\frac{1}{2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-\frac{r}{3a_0}} \sin\theta\, e^{\pm i\varphi} \qquad (\Psi_{31+1}+\Psi_{31-1})/\sqrt{2} := 3p_x$$

$$(\Psi_{31+1}-\Psi_{31-1})/(i\sqrt{2}) := 3p_y$$

$$\Psi_{320}(r,\theta,\varphi) = \left(39366\,\pi a_0^3\right)^{-\frac{1}{2}} \left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{3a_0}} \left(3\cos^2\theta - 1\right) \qquad \Psi_{320} := 3d_{z^2}$$

$$\Psi_{32\pm1}(r,\theta,\varphi) = \left(6561\,\pi a_0^3\right)^{-\frac{1}{2}} \left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{3a_0}} \sin\theta\, \cos\theta\, e^{\pm i\varphi} \qquad (\Psi_{32+1}+\Psi_{32-1})/\sqrt{2} := 3d_{xz}$$

$$(\Psi_{32+1}-\Psi_{32-1})/(i\sqrt{2}) := 3d_{yz}$$

$$\Psi_{32\pm2}(r,\theta,\varphi) = \left(26244\,\pi a_0^3\right)^{-\frac{1}{2}} \left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{3a_0}} \sin^2\theta\, e^{\pm 2i\varphi} \qquad (\Psi_{32+2}+\Psi_{32-2})/\sqrt{2} := 3d_{x^2-y^2}$$

$$(\Psi_{32+2}-\Psi_{32-2})/(i\sqrt{2}) := 3d_{xy}$$

Of course, the eigenfunctions can be multiplied by a factor e^{ia}, where a is an arbitrary phase, still remaining eigenfunctions. As discussed above, the respective eigenenergies are $E_k = \hbar\Omega_k = -\frac{R_E}{n^2} = E_n$, i.e., there is degeneracy with respect to ℓ, m. $R_E = 13.6$ eV is the Rydberg of energy and a_0 is the Bohr radius. The first five atomic orbitals, i.e., $1s, 2s, 2p_x, 2p_y, 2p_z$, are depicted in Figure 7.10, the five $3d$ orbitals in Figure 7.11, while all the atomic orbitals of hydrogen-like wavefunctions up to $7s$ are presented in Figure 7.12.

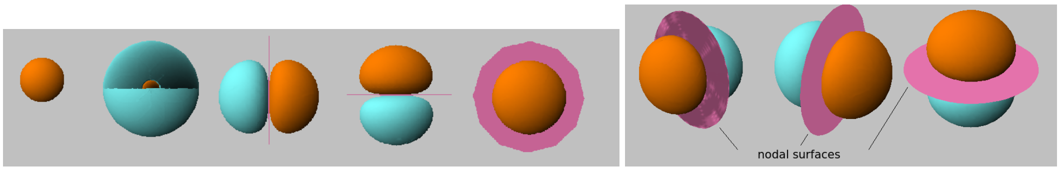


Figure 7.10: The first five atomic orbitals, i.e., $1s, 2s, 2p_x, 2p_y, 2p_z$ [11]. The colors (orange, azure) correspond to different signs; e.g., if the orange region is positive, then the azure region is negative. We set the factor $e^{ia} = 1$. On the right we show the nodal surfaces of $2p$ with detail.

7.5 Nodal surfaces.

In Figure 7.12 we can observe that, apart from $1s$, all orbitals have at least one **nodal surface**. A nodal surface is a surface on which the wavefunction becomes zero; hence, the probability to find the electron there becomes zero, as well. There are two types of nodal surfaces:

- Spherical nodal surfaces, which are called **radial nodes**, since they are fully described by their radius. The number of radial nodes in an orbital is determined by the quantum numbers n and ℓ; in

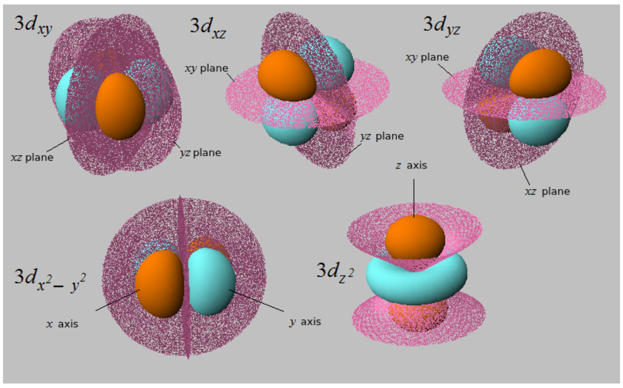


Figure 7.11: The five $3d$ orbitals [11]. The colors (orange, azure) correspond to different signs; e.g., if the orange region is positive, then the azure region is negative. We set the factor $e^{ia} = 1$.

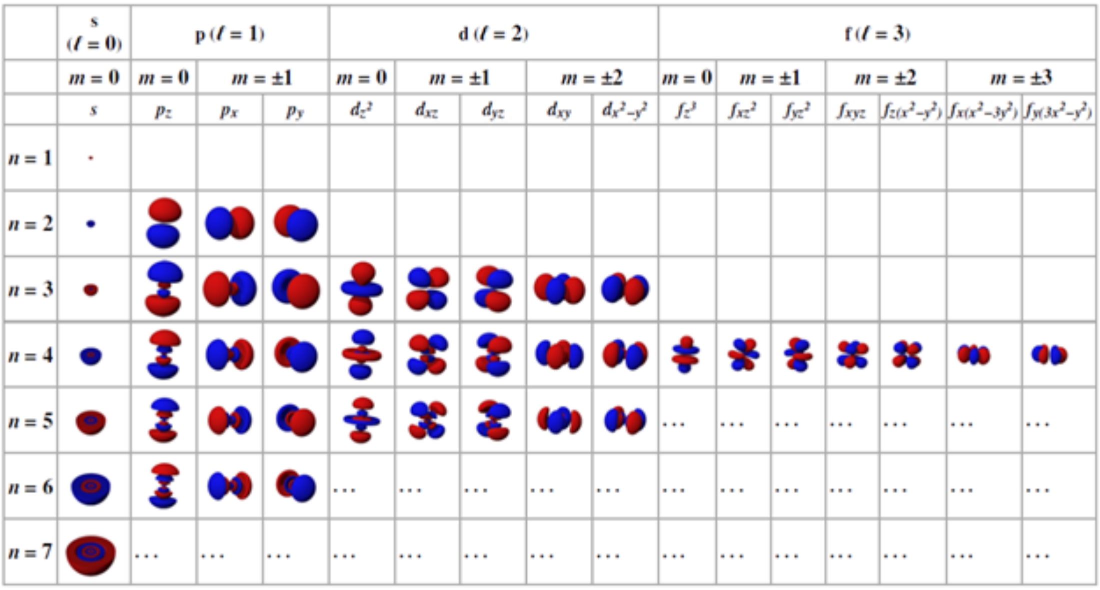


Figure 7.12: All the atomic orbitals of hydrogen-like wavefunctions up to $7s$. The colors correspond to different signs; e.g., if the red region is positive, then the blue region is negative. We set the factor $e^{ia} = 1$. Image from wikipedia [12].

specific, it is $n - \ell - 1$. Radial nodes can be determined by obtaining these distances r at which the wavefunction becomes zero. Thus, $1s$ orbitals have no radial nodes,, $2s$ have one, $2p$ have none, $3s$ have two, $3p$ have one, and so forth.

- Planar or conical surfaces, which are called **angular nodes**, since they are fully described by the angle they form with one of the three axes. The number of angular nodes in an orbital is determined by the quantum number ℓ; in fact, it is equal to ℓ. Angular nodes can be determined by obtaining these angles θ, ϕ at which the wavefunction becomes zero. Thus, s orbitals have no angular nodes, p have one, d have two, f have three, and so forth. The angular nodes are the ones that essentially determine the outer orbital shape.

Based on the above, the total number of nodal surfaces, both radial and angular, is $n - \ell - 1 + \ell = n - 1$.

7.6 Parity, allowed and forbidden transitions, selection rules.

The fact that we know the analytical form of the wavefunctions of hydrogen allows us to use it as an example in order to study its allowed and forbidden transitions within the dipole approximation. We remind that, within this approximation, the potential energy of the perturbation is

$$U_{\mathscr{E}k'k}(t) = e\vec{\mathscr{E}} \cdot \underbrace{\int d^3r\, \Phi^*_{k'}(\vec{r})\, \vec{r}\, \Phi_k(\vec{r})}_{\vec{r}_{k'k}}.$$

If $\vec{r}_{k'k}$ becomes zero, then $U_{\mathscr{E}k'k}(t)$ also becomes zero, hence states k' and k are not coupled. Therefore, the electron cannot move from state k to k' and vice versa. Thus, everything is reduced to the parity of the hydrogen wavefunctions, since $\vec{r}$ is of course an odd function. If two eigenfunctions $\Phi_k(\vec{r}) = \Psi_{n\ell m_\ell}(r,\theta,\phi)$ and $\Phi_{k'}(\vec{r}) = \Psi_{n'\ell' m'_\ell}(r,\theta,\phi)$ have the same parity, then the integrand is an odd function, hence the spatial integral becomes zero by identity. In this case, we say that this transition is "forbidden". On the contrary, if the two eigenfunctions have different parities, then the integrand is an even funtion and the spatial integral is not zero by identity. In this case, we say that this transition is "allowed". Of couse, in the latter case, the value of the integral is different for different pairs $\Psi_{n\ell m_\ell}(r,\theta,\phi)$ and $\Psi_{n'\ell' m'_\ell}(r,\theta,\phi)$. In other words, not all transitions have the same strength. In the case of hydrogen, the symmetry of the eigenfunctions results in transitions with $\Delta\ell = \pm 1$, $\Delta m_\ell = 0, \pm 1$ being "allowed". These are the so-called **selection rules**. We will address all the above on more detail below, using the hydrogen atom as an example/exercise. Additional relevant exercises can be found in Appendix A.

7.7 Hydrogen Atom: Calculation of the dipole moment matrix elements. Allowed and forbidden transitions. Selection rules.

Consider the eigenfunctions of the hydrogen atom

$$\Psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r)\Theta_{\ell m}(\theta)\Phi_m(\varphi) = \Phi_k(\vec{r})$$

where $k = \{n,\ell,m\}$ is the collective quantum number. $n = 1,2,3,\ldots$ is the **principal quantum number**, $\ell = 0,1,2,\ldots,n-1$ is the **angular momentum quantum number**, and $m = -\ell,-\ell+1,\ldots,\ell-1,\ell$ is the **magnetic quantum number**. Specifically, consider the eigenfunctions

$$\Psi_{100}(r,\theta,\varphi) = \left(\pi a_0^3\right)^{-\frac{1}{2}} e^{-\frac{r}{a_0}} \qquad \Psi_{100} := 1s$$

$$\Psi_{200}(r,\theta,\varphi) = \left(32\,\pi a_0^3\right)^{-\frac{1}{2}} \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \qquad \Psi_{200} := 2s$$

$$\Psi_{210}(r,\theta,\varphi) = \left(32\,\pi a_0^3\right)^{-\frac{1}{2}} \frac{r}{a_0} \cos\theta\, e^{-\frac{r}{2a_0}} \qquad \Psi_{210} := 2p_z$$

$$\Psi_{21\pm1}(r,\theta,\varphi) = \left(64\,\pi a_0^3\right)^{-\frac{1}{2}} \frac{r}{a_0} \sin\theta\, e^{\pm i\varphi} e^{-\frac{r}{2a_0}} \qquad (\Psi_{21+1} + \Psi_{21-1})/\sqrt{2} := 2p_x$$

$$(\Psi_{21+1} - \Psi_{21-1})/(i\sqrt{2}) := 2p_y$$

$$\Psi_{300}(r,\theta,\varphi) = \left(19683\,\pi a_0^3\right)^{-\frac{1}{2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-\frac{r}{3a_0}} \qquad \Psi_{300} := 3s$$

The corresponding eigenenergies are $E_k = \hbar\Omega_k = -\dfrac{R_E}{n^2} = E_n$, thus there is degeneracy with respect to ℓ, m. $R_E = 13.6$ eV is the Rydberg energy and a_0 is the Bohr radius.

1. Check whether the above given eigenfunctions are normalized.
2. Check whether they are even or odd.
3. Determine whether the integrals

$$\vec{r}_{k_1 k_2} := \int\limits_{\text{everywhere}} dV \Phi^*_{k_1}(\vec{r})\, \vec{r}\, \Phi_{k_2}(\vec{r})$$

   i.e., the matrix elements of the electron's position with respect to the nucleus, become zero or not. These integrals are proportional to the matrix elements of the dipole moment $\vec{\mathscr{P}} = -e\vec{r}$, i.e.,

$$\vec{\mathscr{P}}_{k_1 k_2} := \int\limits_{\text{everywhere}} dV \Phi^*_{k_1}(\vec{r})\, (-e)\vec{r}\, \Phi_{k_2}(\vec{r})$$

   We remind that if $\vec{r}_{k_1 k_2} = \vec{0}$, then the optical transition $k_1 \leftrightarrow k_2$ is "forbidden".
4. Predict which of the transitions between the above given eigenstates are allowed, and check whether the "selection rules" $\Delta\ell = \pm 1, \Delta m = 0, \pm 1$ hold.
5. Check whether the above given $\Phi_k(\vec{r})$ are orthogonal.
6. Calculate the dipole moment matrix elements $\vec{\mathscr{P}}_{100\,210}$ and $\vec{\mathscr{P}}_{100\,21\pm 1}$.
7. Compare the strengths of the optical transitions $1s \longleftrightarrow 2p_z$ and $1s \longleftrightarrow 2p_x$.

Consider the following as given:

A. $\int\limits_0^\infty e^{-\gamma r}\, r^n\, dr = \gamma^{-(n+1)} n!$ where $n = 1, 2, 3, \ldots$ and $\gamma > 0$.

B. In spherical coordinates (r, θ, φ), inversion through the origin of the reference system, i.e., the operation $\vec{r} \longrightarrow \vec{r'} = -\vec{r}$, corresponds to the variable changes $r' = r$, $\theta' = \pi - \theta$, and $\varphi' = \varphi + \pi$.

C. The following expression for the position vector holds:
$\vec{r} = \frac{r}{2} \sin\theta [(\hat{e}_x - i\hat{e}_y)e^{i\varphi} + (\hat{e}_x + i\hat{e}_y)e^{-i\varphi}] + r\cos\theta\, \hat{e}_z$.

Answer

In what follows, we will use the **variable change** $q = \frac{r}{a_0}$ and the **notation**:

$\langle n'\ell'm'|n\ell m\rangle := \int d^3r\, \Psi^*_{n'\ell'm'}(\vec{r})\, \Psi_{n\ell m}(\vec{r})$ and $\langle n'\ell'm'|\vec{r}|n\ell m\rangle := \int d^3r\, \Psi^*_{n'\ell'm'}(\vec{r})\, \vec{r}\, \Psi_{n\ell m}(\vec{r})$.

1. For $\Psi_{100}(\vec{r})$ we have:

$$\langle 100|100\rangle : = \int d^3r\, \Psi^*_{100}(\vec{r})\, \Psi_{100}(\vec{r}) = \int\limits_0^\infty \int\limits_0^\pi \int\limits_0^{2\pi} r^2 \sin\theta\, dr d\theta d\varphi \frac{1}{\pi a_0^3} e^{-\frac{2r}{a_0}} =$$

$$= \frac{1}{\pi a_0^3} \int\limits_0^\infty dr\, r^2\, e^{-\frac{2r}{a_0}} \int\limits_0^\pi \sin\theta d\theta \int\limits_0^{2\pi} d\varphi = \frac{a_0^3}{\pi a_0^3} \int\limits_0^\infty dq q^2 e^{-2q} [-\cos\theta]_0^\pi 2\pi$$

$$= 2 \int\limits_0^\infty dq q^2 e^{-2q} [-\cos\pi + \cos 0] = 4 \int\limits_0^\infty dq q^2 e^{-2q} \overset{*}{\doteq} 4 \frac{2!}{2^{2+1}} = 1.$$

$*$ We used **A.**, for $\gamma = 2, n = 2$. In other words, $|100\rangle$ is normalized, as expected. Similarly, the normalization of the rest functions can be checked, by calculating $\langle 200|200\rangle$, $\langle 210|210\rangle$, $\langle 21\pm1|21\pm1\rangle$, $\langle 300|300\rangle$.

2. We can check the parity using **B.** We note that $\sin\theta' = \sin(\pi-\theta) = \sin\theta$, $\cos\theta' = \cos(\pi-\theta) = -\cos\theta$, while $e^{\pm i\varphi'} = e^{\pm i(\varphi+\pi)} = e^{\pm i\varphi}e^{\pm i\pi} = (-1)e^{\pm i\varphi}$. Thus,

$$\begin{array}{rlr}
\Psi_{100}(-\vec{r}) = \Psi_{100}(\vec{r}) & * & \text{even}\\
\Psi_{200}(-\vec{r}) = \Psi_{200}(\vec{r}) & * & \text{even}\\
\Psi_{300}(-\vec{r}) = \Psi_{300}(\vec{r}) & * & \text{even}\\
\Psi_{210}(-\vec{r}) = -\Psi_{210}(\vec{r}) & ** & \text{odd}\\
\Psi_{21\pm1}(-\vec{r}) = -\Psi_{21\pm1}(\vec{r}) & *** & \text{odd}
\end{array}$$

$*$ Since it depends only on r and the operation $\vec{r} \to \vec{r'} = -\vec{r}$ has no effect.
$**$ Since it depends not only on r, which is unaffected by the operation $\vec{r} \to \vec{r'} = -\vec{r}$, but also on $\cos\theta$, which will become $\cos\theta' = \cos(\pi-\theta) = -\cos\theta$.
$***$ It depends on r, which is unaffected by the operation $\vec{r} \to \vec{r'} = -\vec{r}$, on $\sin\theta$, which goes to $\sin\theta' = \sin(\pi-\theta) = \sin\theta$, i.e., which is unaffected as well, but also on $e^{\pm i\varphi'} = e^{\pm i(\varphi+\pi)} = e^{\pm i\varphi}e^{\pm i\pi} = (-1)e^{\pm i\varphi}$, i.e., it is odd due to φ.

In other words, we have shown that $1s, 2s, 3s$ are even, while $2p_z$ is odd. $2p_x$ and $2p_y$ are also odd, since they are derived by the sum or difference of the odd functions $\Psi_{21\pm1}$. Actually, it is "encyclopedic" knowledge that s-type functions are even and p-type functions are odd.

3.-4. In Table 7.4, the transitions within the fist two shells, i.e., for $n = 1, 2$, are briefly described. (E) means even and (O) means odd. We observe that the **selection rule** $\Delta\ell = \pm1, \Delta m = 0, \pm1$ holds, i.e., when these relations are satisfied, then the transition is allowed.

Table 7.4: Allowed (AL.)and forbidden (FORB.) optical transitions within the first two shells of the hydrogen atom, using the dipole approximation. The notation ★ means that, in the hydrogen atom, the initial and final states correspond to the same energy, i.e., they are degenerate, thus in fact such transitions do not exist. $2p_x$ and $2p_y$ are derived by the sum or difference of the odd functions $\Psi_{21\pm1}$.

$k_1 = \{n_1,\ell_1,m_1\}$		$k_2 = \{n_2,\ell_2,m_2\}$		$\Phi^*_{k_1}(\vec{r})$	$\Phi_{k_2}(\vec{r})$	$\Phi^*_{k_1}(\vec{r})\,\vec{r}\,\Phi_{k_2}(\vec{r})$	$\vec{r}_{k_1k_2}$	$\Delta\ell$	Δm
100	$1s$	200	$2s$	(E)	(E)	(O) FORB.	0	0	0
100	$1s$	210	$2p_z$	(E)	(O)	(E) AL.	$\neq 0$	1	0
100	$1s$	21 ± 1	$2p_x, 2p_y$	(E)	(O)	(E) AL.	$\neq 0$	1	±1
100	$1s$	300	$3s$	(E)	(E)	(O) FORB.	0	0	0
200	$2s$	210	$2p_z$	(E)	(O)	(E) AL. ★	$\neq 0$	1	0
200	$2s$	21 ± 1	$2p_x, 2p_y$	(E)	(O)	(E) AL. ★	$\neq 0$	1	±1
200	$2s$	300	$3s$	(E)	(E)	(O) FORB.	0	0	0
210	$2p_z$	21 ± 1	$2p_x, 2p_y$	(O)	(O)	(O) FORB.	0	0	±1
210	$2p_z$	300	$3s$	(O)	(E)	(E) AL.	$\neq 0$	-1	0
21 ± 1	$2p_x, 2p_y$	300	$3s$	(O)	(E)	(E) AL.	$\neq 0$	-1	∓1

5. Let us check for orthogonality the eigenfunctions Ψ_{100} and Ψ_{200}:

$$\langle 100|200\rangle := \int d^3r\, \overset{(E)}{\Psi^*_{100}}\, \overset{(E)}{\Psi_{200}} = \frac{1}{\pi a_0^3\sqrt{32}} \int_0^\infty\int_0^\pi\int_0^{2\pi} r^2 \sin\theta\, dr d\theta d\varphi\, e^{-\frac{r}{a_0}} \left(2-\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} =$$

$$= \frac{1}{4\pi a_0^3\sqrt{2}} 4\pi \int_0^\infty r^2 e^{-\frac{r}{a_0}} \left(2-\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}\, dr \underset{q=\frac{r}{a_0}}{\overset{\text{we set}}{=}} \frac{a_0^3}{a_0^3\sqrt{2}} \int_0^\infty q^2\cdot e^{-q}(2-q)e^{-\frac{q}{2}} dq$$

$$= \frac{2}{\sqrt{2}} \int_0^\infty e^{-\frac{3q}{2}} q^2 dq - \frac{1}{\sqrt{2}} \int_0^\infty e^{-\frac{3q}{2}} q^3 dq \overset{*}{=} \sqrt{2}\frac{2!}{\left(\frac{3}{2}\right)^{2+1}} - \frac{1}{\sqrt{2}}\frac{3!}{\left(\frac{3}{2}\right)^{3+1}} = 0$$

We used **A.**, for $\gamma = \frac{3}{2}$, $n = 2$ and for $\gamma = \frac{3}{2}$, $n = 3$. Thus, he have shown that $\langle 100|200\rangle = 0$, hence Ψ_{100} and Ψ_{200} are orthogonal, as expected. Similarly, the rest inner products between different eigenfunctions can be calculated, which actually become zero, as well.

Reminder: The spatial integral of an even function is not zero by identity. This does not mean that it cannot become zero, see, e.g., Figure 7.13. On the other hand, the spatial integral of an odd function is zero by identity, since, e.g.

$$\int_{-\infty}^{+\infty} dx\, f(x) = \underbrace{\int_{-\infty}^{0} dx\, f(x)}_{\text{we set } y=-x} + \int_{0}^{+\infty} dx\, f(x) = -\int_{+\infty}^{0} dy\, f(-y) + \int_{0}^{+\infty} dx\, f(x) = -\int_{0}^{+\infty} dy\, f(y) + \int_{0}^{+\infty} dx\, f(x) = 0$$

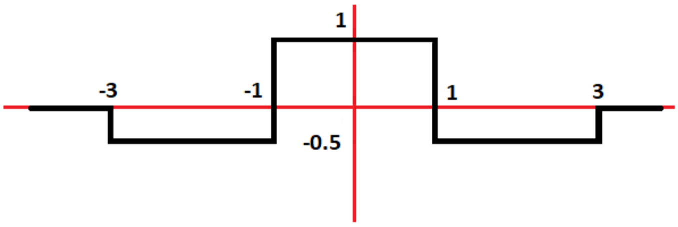


Figure 7.13: The spatial integral of an even function is not zero by identity but it can become zero, as is the case, e.g., with the depicted even function.

5. We know that $\vec{\mathscr{P}}_{k'k} = -e\vec{r}_{k'k}$, hence the calculation of $\vec{\mathscr{P}}_{100210}$ and $\vec{\mathscr{P}}_{10021\pm1}$ is reduced to the calculation of $\vec{r}_{100210}$ and $\vec{r}_{10021\pm1}$, respectively. For the first one:

$$\vec{r}_{100210} = \langle 100|\vec{r}|210\rangle = \int d^3r\, \Psi^*_{100}\, \vec{r}\, \Psi_{210}$$

$$= \frac{1}{\pi a_0^3\sqrt{32}} \int_0^\infty\int_0^\pi\int_0^{2\pi} r^2 \sin\theta\, dr d\theta d\varphi\, e^{-\frac{r}{a_0}} \underbrace{\vec{r}}_{\text{see } \Gamma.} \frac{r}{a_0} \cos\theta\, e^{-\frac{r}{2a_0}}$$

$$= \frac{1}{4\pi a_0^3\sqrt{2}} \int_0^\infty\int_0^\pi\int_0^{2\pi} r^2 \sin\theta\, dr d\theta d\varphi\, e^{-\frac{r}{a_0}} \left\{\frac{r}{2}\sin\theta\left[(\hat{e}_x - i\hat{e}_y)e^{i\varphi} + (\hat{e}_x + i\hat{e}_y)e^{-i\varphi}\right] + r\cos\theta\hat{e}_z\right\}.$$

$$\cdot \frac{r}{a_0} \cos\theta\, e^{-\frac{r}{2a_0}}$$

$$= \frac{1}{4\pi a_0^3\sqrt{2}} \underbrace{\int_0^\infty r^2\, dr\, e^{-\frac{r}{a_0}}\, r\, \frac{r}{a_0}\, e^{-\frac{r}{2a_0}}}_{I(r)} \left\{ \int_0^\pi\int_0^{2\pi} \sin^2\theta\, d\theta d\varphi \frac{1}{2}\left[(\hat{e}_x - i\hat{e}_y)e^{i\varphi} + (\hat{e}_x + i\hat{e}_y)e^{-i\varphi}\right] \cos\theta + \right.$$

$$\left. + \int_0^\pi\int_0^{2\pi} \sin\theta\, d\theta d\varphi\, \cos^2\theta\hat{e}_z \right\}.$$

We will now use **A.**, for $\gamma = \frac{3}{2}$ and $n = 4$.

$$I(r) = a_0^4 \int_0^\infty q^2\, dq\, e^{-q}\, q\, q\, e^{-\frac{q}{2}} = a_0^4 \int_0^\infty q^4\, dq\, e^{-\frac{3q}{2}} = a_0^4 \frac{4!}{\left(\frac{3}{2}\right)^{4+1}} = a_0^4 \frac{2\cdot 3\cdot 4}{3^5}\, 2^5 = a_0^4 \frac{2^8}{3^4}.$$

Also,

$$\int_0^{2\pi} e^{\pm i\varphi}\, d\varphi = \left[\frac{e^{\pm i\varphi}}{i}\right]_0^{2\pi} = 0,$$

$$\int_0^{2\pi} d\varphi \int_0^\pi \sin\theta\, \cos^2\theta\, d\theta\, \hat{e}_z = 2\pi\hat{e}_z \int_1^{-1} \frac{d(\cos^3\theta)}{3} \cdot (-1) = \frac{2\pi\hat{e}_z}{3} \int_{-} 1^1 dy = \frac{2\pi\hat{e}_z}{3} \big[y\big]_{-1}^1 = \frac{4\pi\hat{e}_z}{3},$$

$$\frac{d(\cos^3\theta)}{3} = 3\cos^2\theta(-1)\sin\theta \Rightarrow \quad \frac{d(\cos^3\theta)}{-3} = \cos^2\theta\sin\theta d\theta.$$

Thus,

$$\vec{r}_{100210} = \frac{1}{\cancel{4\pi} a_0^3\sqrt{2}}\, a_0^4 \cdot \frac{2^8}{3^4}\, \frac{\cancel{4\pi}\hat{e}_z}{3} = a_0\hat{e}_z \frac{2^{15/2}}{3^5} \Rightarrow \boxed{\vec{r}_{100210} = 100\vec{r}210 = \frac{2^{15/2}}{3^5}\, a_0\hat{e}_z} \Rightarrow$$

$$\boxed{\vec{\mathscr{P}}_{100210} = -\frac{2^{15/2}}{3^5} e a_0\hat{e}_z}, \qquad \boxed{|\vec{\mathscr{P}}_{100210}| = \frac{2^{15/2}}{3^5} e a_0}.$$

For the second one:

$$\vec{r}_{10021\pm1} = \langle 100|\vec{r}|21\pm1\rangle = \int d^3r\, \Psi^*_{100}\, \vec{r}\, \Psi_{21\pm1}$$

$$= \frac{1}{(\pi a_0^3)^{1/2}}\, \frac{1}{8(\pi a_0^3)^{1/2}} \int_0^\infty\int_0^\pi\int_0^{2\pi} r^2 \sin\theta\, dr d\theta d\varphi\, e^{-\frac{r}{a_0}} \left\{ \frac{r}{2} \sin\theta\left[(\hat{e}_x - i\hat{e}_y)e^{i\varphi} + (\hat{e}_x + i\hat{e}_y)e^{-i\varphi}\right] + \right.$$

$$\left. + r\cos\theta\hat{e}_z \right\} \frac{r}{a_0}\, \sin\theta\, e^{\pm i\varphi} e^{-\frac{r}{2a_0}}$$

$$= \frac{1}{8\pi a_0^3} \int_0^\infty dr\, r^2\, e^{-\frac{r}{a_0}}\, r\, \frac{r}{a_0}\, e^{-\frac{r}{2a_0}} \int_0^\pi\int_0^{2\pi} \sin^2\theta d\theta d\varphi \left\{ \frac{\sin\theta}{2}\left[(\hat{e}_x - i\hat{e}_y)e^{i\varphi} + (\hat{e}_x + i\hat{e}_y)e^{-i\varphi}\right] + \cos\theta\hat{e}_z \right\} e^{\pm i\varphi}$$

$$= \frac{a_0}{8\pi}\int_0^\infty dq\, q^4\, e^{-\frac{3q}{2}} \cdot \text{angular dependence} = \frac{a_0}{8\pi}\frac{4!}{\left(\frac{3}{2}\right)^{4+1}} \cdot \text{angular dependence}$$

$$= \frac{a_0}{\pi}\frac{2^5}{3^4} \cdot \text{angular dependence.}$$

But

$$\int_0^{2\pi} e^{\pm 2i\varphi}\, d\varphi = \left[\frac{e^{\pm 2i\varphi}}{\pm 2i}\right]_0^{2\pi} = 0 \quad \text{and} \quad \int_0^{2\pi} e^{\pm i\varphi}\, d\varphi = \left[\frac{e^{\pm i\varphi}}{\pm i}\right]_0^{2\pi} = 0,$$

$$\text{angular dependence} = \int_0^\pi d\theta \frac{\sin^3\theta}{2}\Big[2\pi(\hat{e}_x \pm i\hat{e}_y)\Big] = \pi\Big[\hat{e}_x \pm i\hat{e}_y\Big]\int_0^\pi d\theta \sin^3\theta = \frac{4\pi}{3}\Big[\hat{e}_x \pm i\hat{e}_y\Big],$$

$$\int_0^\pi d\theta \sin^3\theta = \left[\frac{\cos^3\theta}{3} - \cos\theta\right]_0^\pi = -\frac{1}{3} + 1 - \frac{1}{3} + 1 = \frac{4}{3},$$

$$\text{since} \quad \frac{d}{d\theta}\left(\frac{\cos^3\theta}{3} - \cos\theta\right) = -\cos^2\theta \cdot \sin\theta + \sin\theta = \sin\theta[1 - \cos^2\theta] = \sin^3\theta.$$

Thus,

$$\vec{r}_{10021\pm1} = \frac{a_0}{\cancel{\pi}} \cdot \frac{2^5}{3^4}\frac{4\cancel{\pi}}{3}(\hat{e}_x \pm i\hat{e}_y) \Rightarrow \boxed{\vec{r}_{10021\pm1} = a_0\frac{2^7}{3^5}(\hat{e}_x \pm i\hat{e}_y)}$$

$$\boxed{\vec{\mathscr{P}}_{10021\pm1} = -\frac{2^7}{3^5}(\hat{e}_x \pm i\hat{e}_y)ea_0}, \qquad \boxed{|\vec{\mathscr{P}}_{10021\pm1}| = \frac{2^{15/2}}{3^5}ea_0}.$$

7. From the previous question, it occurs that

$$\frac{|\vec{\mathscr{P}}_{100210}|}{|\vec{\mathscr{P}}_{10021\pm1}|} = 1.$$

Thus, these two transitions have the same strength.

More indicative calculations can be found at the end of this Chapter's exercises, in Appendix A.

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CHAPTER 8

QUANTUM MECHANICAL APPROACH I

In this Chapter:

We proceed to the full quantum mechanical approach of the photon - 2LS, 3LS, MLS interaction and to the quantization of the EM field, which is performed in a somehow heuristic manner. The main part here are the Rabi oscillations of the number of photons and of the probability of electron presence in the levels of a 2LS, which interacts with photons inside a cavity. Initially, we explain what the full quantum mechanical approach versus the semiclassical approach is: now we quantize the electromagnetic (EM) field, too. We discuss the relation between wavevectors, angular frequencies and phases of the electric and magnetic field and how a standing wave inside a cavity is created. We continue by describing the Hamiltonian of the EM field with photon creation and annihilation (or raising and lowering) operators, the Hamiltonian of the two-level system with spinors and electron creation and annihilation (or raising and lowering) operators [and generalize presenting the Hamiltonian of the three-level and multi-level system with spinors and electron creation and annihilation (or raising and lowering) operators]. Then, we discuss thoroughly the two-level system - EM field interaction Hamiltonian and calculate the mean (expectation) values of various quantities for the Jaynes-Cummings Hamiltonian, which is a simplified total Hamiltonian. With this Hamiltonian we study the Rabi oscillations, i.e., the time-dependent probabilities of the two levels occupation and of the number of photons in the cavity, for photon absorption and emission.

Prerequisite knowledge: Basic knowledge of Quantum Physics.

8.1 Fully quantum mechanical approach versus semiclassical approach.

In Chapters 5 and 6 we discussed the so-called Semiclassical Approach (two-level system: quantum mechanically - EM field: classically). To describe the EM field, we used *the language of vectors* $\vec{E}, \vec{B}$. We assumed that the amplitude of the electric field is constant. The EM radiation had to be dense enough so that the amplitude of the electric field is not significantly affected by photon absorption or emission.

In this Chapter, we move on to the Fully Quantum Mechanical Approach, i.e. we threat both the two-

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level system and the EM field quantum mechanically. We could say that we are trying to describe the EM field using the *language of the number of photons*. Therefore, we have to obtain an expression for the Hamiltonian of the EM field that allows the translation from the language that uses the vectors $\vec{E}$ and $\vec{B}$ to the language of the number of photons. This will be done in the example of an EM wave in a cavity, in Section **??**. Prior to this, in Section 8.2, we will examine the relationship between the wavevectors, angular frequencies and initial phases of the electric and magnetic fields. Then, in Section 8.4, we will remember the photon creation and annihilation operators, and, using these operators, we will quantize the Hamiltonian that describes the EM field, as well as the electric and magnetic fields separately. Thus, we will obtain a Hamiltonian for the EM field. Next, in Section 8.5, we will use spinors to describe two two-level system, and specifically the raising and lowering of an electron between its two energy levels. Thus, we will obtain a Hamiltonian for the two-level system. Afterwards, in Section 8.7, we will also construct the Hamiltonian describing the two-level system - EM field interaction. After all, we will be in position to define a Total Hamiltonian which describes the EM field, the two-level system and the interaction between them (Rabi and Jaynes-Cummings Hamiltonians). In Section 8.8, these Hamiltonians are summarized. In Section 8.9, we calculate the average (expected) values of quantities related to the Jaynes-Cummings Hamiltonian, which are useful for the description of photon absorption and emission. Finally, we present two applications of the Jaynes-Cummings Hamiltonian to the problems of photon absorption (Section 8.10) and photon emission (Section 8.11), arriving at the description of oscillations for the photon population and energy level occupations.

8.2 Relations between wavevectors, angular frequencies and initial phases of electric and magnetic fields.

Let us remember the Maxwell's equations in terms of total charge and total current, and specifically in their differential form

$$\vec{\nabla} \cdot \vec{E} = \frac{\rho}{\varepsilon_0} \quad \text{Gauss's law for electricity} \tag{8.1a}$$

$$\vec{\nabla} \cdot \vec{B} = 0 \quad \text{Gauss's law for magnetism} \tag{8.1b}$$

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad \text{Faraday's law} \tag{8.1c}$$

$$\vec{\nabla} \times \vec{B} = \mu_0 \vec{J} + \mu_0 \epsilon_0 \frac{\partial \vec{E}}{\partial t} \quad \text{Ampère's law and Maxwell's correction.} \tag{8.1d}$$

In vacuum, where $\rho = 0$ and $\vec{J} = \vec{0}$ οι Eqs. 8.1a, 8.1b, 8.1c, 8.1d become

$$\vec{\nabla} \cdot \vec{E} = 0 \tag{8.2a}$$

$$\vec{\nabla} \cdot \vec{B} = 0 \tag{8.2b}$$

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \tag{8.2c}$$

$$\vec{\nabla} \times \vec{B} = \mu_0 \epsilon_0 \frac{\partial \vec{E}}{\partial t}. \tag{8.2d}$$

The following identities hold:

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{\Delta}) = \vec{\nabla}(\vec{\nabla} \cdot \vec{\Delta}) - \nabla^2 \vec{\Delta} \tag{8.3}$$

$$\nabla^2 \vec{\Delta} := (\vec{\nabla} \cdot \vec{\nabla}) \vec{\Delta}. \tag{8.4}$$

Thus, Eq. 8.2 implies

$$\nabla^2\vec{E} = \epsilon_0\mu_0\frac{\partial^2\vec{E}}{\partial t^2} \tag{8.5}$$

Trying solutions of the form

$$\vec{E}(\vec{r},t) = \vec{E}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t+\delta)} \tag{8.6}$$

at Eq. 8.5, it follows that

$$|\vec{k}| := k = \frac{\omega}{c}. \tag{8.7}$$

Similarly, Eq. 8.2 implies

$$\nabla^2\vec{B} = \epsilon_0\mu_0\frac{\partial^2\vec{B}}{\partial t^2}. \tag{8.8}$$

Trying solutions of the form

$$\vec{B}(\vec{r},t) = \vec{B}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t+\delta')} \tag{8.9}$$

at Eq. 8.8, we again obtain Eq. 8.7. Since $\omega = 2\pi\nu, c = \lambda\nu$, Eq. 8.7 yields $k = \frac{2\pi}{\lambda}$. We notice that, given that we differentiate over x, y, z, t, the "initial phases" δ, δ' remain constant, i.e. they are not determined by the calculations made so far.

From the solutions 8.6 and 8.9, after some calculations, we conclude that the operator $\vec{\nabla}$ can be replaced by $i\vec{k}$, i.e. schematically

$$\boxed{\vec{\nabla} \to i\vec{k}}, \tag{8.10}$$

since, if we assume a field of the form

$$\vec{\Delta} = \vec{\Delta}_0\, e^{i(\vec{k}\cdot\vec{r}-\omega t+\delta)} := (\Delta_{0x}, \Delta_{0y}, \Delta_{0z})\, e^{\textcircled{d}}, \tag{8.11}$$

then

$$\begin{aligned}
&\vec{\nabla}\cdot\vec{\Delta} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)\cdot(\Delta_x, \Delta_y, \Delta_z) = \frac{\partial\Delta_x}{\partial x} + \frac{\partial\Delta_y}{\partial y} + \frac{\partial\Delta_z}{\partial z} = \\
&\Delta_{0x}\, e^{\textcircled{d}} ik_x + \Delta_{0y}\, e^{\textcircled{d}} ik_y + \Delta_{0z}\, e^{\textcircled{d}} ik_z = i(k_x, k_y, k_z)\cdot(\Delta_{0x}, \Delta_{0y}, \Delta_{0z})\, e^{\textcircled{d}} = i\vec{k}\cdot\vec{\Delta},
\end{aligned}$$

and also

$$\begin{aligned}
\vec{\nabla}\times\vec{\Delta} &= \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ \Delta_{0x}e^{\textcircled{d}} & \Delta_{0y}e^{\textcircled{d}} & \Delta_{0z}e^{\textcircled{d}} \end{vmatrix} \\
&= \hat{i}\left(\frac{\partial\Delta_{0z}e^{\textcircled{d}}}{\partial y} - \frac{\partial\Delta_{0y}e^{\textcircled{d}}}{\partial z}\right) - \hat{j}\left(\frac{\partial\Delta_{0z}e^{\textcircled{d}}}{\partial x} - \frac{\partial\Delta_{0x}e^{\textcircled{d}}}{\partial z}\right) + \hat{k}\left(\frac{\partial\Delta_{0x}e^{\textcircled{d}}}{\partial y} - \frac{\partial\Delta_{0y}e^{\textcircled{d}}}{\partial x}\right) \\
&= \hat{i}\left(ik_y\Delta_z - ik_z\Delta_y\right) - \hat{j}\left(ik_x\Delta_z - ik_z\Delta_x\right) + \hat{k}\left(ik_y\Delta_x - ik_x\Delta_y\right) \\
&= i\begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ k_x & k_y & k_z \\ \Delta_x & \Delta_y & \Delta_z \end{vmatrix} = i\vec{k}\times\vec{\Delta}.
\end{aligned}$$

Therefore,

Eqs. 8.2a, 8.6 ⇒ $$i\vec{k}\cdot\vec{E} = 0 \Rightarrow \vec{k}\cdot\vec{E} = 0 \qquad (8.12a)$$

Eqs. 8.2b, 8.9 ⇒ $$i\vec{k}\cdot\vec{B} = 0 \Rightarrow \vec{k}\cdot\vec{B} = 0 \qquad (8.12b)$$

Eqs. 8.2c, 8.6, 8.9 ⇒ $$i\vec{k}\times\vec{E} = i\omega\vec{B} \Rightarrow \vec{k}\times\vec{E} = \omega\vec{B} \qquad (8.12c)$$

Eqs. 8.2d, 8.6, 8.9 ⇒ $$i\vec{k}\times\vec{B} = \mu_0\epsilon_0(-i\omega)\vec{E} \Rightarrow \vec{k}\times\vec{B} = -\mu_0\epsilon_0\omega\vec{E} \qquad (8.12d)$$

It is a brief mind game to obtain the direction of the vectors $\vec{E}, \vec{B}, \vec{k}$ by Eqs. 8.12a, 8.12b, 8.12c, 8.12d; more precisely, it can be found that the inner product between $\vec{E}$ μɛ τo $\vec{B}$ has the same direction as $\vec{k}$, i.e.

$$\boxed{\vec{E}\times\vec{B} \uparrow\uparrow \vec{k}}. \qquad (8.13)$$

Actually, $\vec{E}, \vec{B}, \vec{k}$ obey to the directional and the perpendicularity relations depicted in Figure 8.1. The relationship of Eq. 8.13 can mathematically be shown using the identity

$$\vec{a}\times(\vec{b}\times\vec{c}) = (\vec{a}\cdot\vec{c})\vec{b} - (\vec{a}\cdot\vec{b})\vec{c}. \qquad (8.14)$$

For example, starting from Eq. 8.12c, we have $\vec{E}\times(\vec{k}\times\vec{E}) = \omega\vec{E}\times\vec{B} \Rightarrow (\vec{E}\cdot\vec{E})\vec{k} - (\vec{E}\cdot\vec{k})\vec{E} = \omega\vec{E}\times\vec{B}$.

Figure 8.1: $\vec{E}\times\vec{B} \uparrow\uparrow \vec{k}$.

But, given Eq. 8.12a, it follows that

$$\boxed{\vec{E}\times\vec{B} = \frac{|\vec{E}|^2}{\omega}\vec{k}}. \qquad (8.15)$$

Taking the above perpendicularity conditions for $\vec{E}, \vec{B}, \vec{k}$ into account, Eqs. 8.12c-8.12d imply that

$$\boxed{\frac{|\vec{E}|}{|\vec{B}|} = c}. \qquad (8.16)$$

Now, instead of Eqs. 8.6 and 8.9, let us try solutions of the form

$$\vec{E}(\vec{r},t) = \vec{E}_0 e^{i(\vec{k}_e\cdot\vec{r}-\omega_e t+\delta_e)} = \vec{E}_0 e^{\textcircled{e}} \qquad (8.17)$$

$$\vec{B}(\vec{r},t) = \vec{B}_0 e^{i(\vec{k}_b\cdot\vec{r}-\omega_b t+\delta_b)} = \vec{B}_0 e^{\textcircled{b}} \qquad (8.18)$$

to Eqs. 8.5 and 8.8. In other words, let us **assume** that $\vec{E}(\vec{r},t)$ and $\vec{B}(\vec{r},t)$ **do not necessarily have the same wave vectors,** $\vec{k}_e$ and $\vec{k}_b$, **angular frequencies,** ω_e and ω_b, and **"initial phases"**, δ_e and δ_b. Then,

Eqs. 8.2a, 8.17 ⇒ $$\vec{k}_e\cdot\vec{E} = 0 \qquad (8.19a)$$

Eqs. 8.2b, 8.18 ⇒ $$\vec{k}_b\cdot\vec{B} = 0 \qquad (8.19b)$$

Eqs. 8.2c, 8.17, 8.18 ⇒ $$\vec{k}_e\times\vec{E} = \omega_b\vec{B} \qquad (8.19c)$$

Eqs. 8.2d, 8.17, 8.18 ⇒ $$\vec{k}_b\times\vec{B} = -\mu_0\epsilon_0\omega_e\vec{E} \qquad (8.19d)$$

and no relationship between δ_e and δ_b occurs. From Eq. 8.19c, it follows that

$$\begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ k_{ex} & k_{ey} & k_{ez} \\ E_{0x}e^{\textcircled{e}} & E_{0y}e^{\textcircled{e}} & E_{0z}e^{\textcircled{e}} \end{vmatrix} = (\omega_b B_{0x}e^{\textcircled{b}}, \omega_b B_{0y}e^{\textcircled{b}}, \omega_b B_{0z}e^{\textcircled{b}}) \Rightarrow \tag{8.20a}$$

$$\left\{ \begin{array}{ccc} k_{ey}E_{0z}e^{\textcircled{e}} & -k_{ez}E_{0y}e^{\textcircled{e}} & = & \omega_b B_{0x}e^{\textcircled{b}} \\ k_{ez}E_{0x}e^{\textcircled{e}} & -k_{ex}E_{0z}e^{\textcircled{e}} & = & \omega_b B_{0y}e^{\textcircled{b}} \\ k_{ex}E_{0y}e^{\textcircled{e}} & -k_{ey}E_{0x}e^{\textcircled{e}} & = & \omega_b B_{0z}e^{\textcircled{b}} \end{array} \right\} \Rightarrow \tag{8.20b}$$

$$\left\{ \begin{array}{ccccc} \frac{k_{ey}E_{0z}-k_{ez}E_{0y}}{\omega_b B_{0x}} & = & e^{\textcircled{b}}e^{\textcircled{e}^*} & = & e^{i[(\vec{k}_b-\vec{k}_e)\cdot\vec{r}-(\omega_b-\omega_e)t+(\delta_b-\delta_e)]} \\ \frac{k_{ez}E_{0x}-k_{ex}E_{0z}}{\omega_b B_{0y}} & = & e^{\textcircled{b}}e^{\textcircled{e}^*} & = & \text{same} \\ \frac{k_{ex}E_{0y}-k_{ey}E_{0x}}{\omega_b B_{0z}} & = & e^{\textcircled{b}}e^{\textcircled{e}^*} & = & \text{same} \\ \text{constants} & & & & \text{functions of } \vec{r}, t \end{array} \right\} \tag{8.20c}$$

Assuming some specific time t, given that the left-hand sides are constants (i.e. independent of $\vec{r}$), then the right-hand sides must be constants, as well. Thus,

$$\vec{k}_b = \vec{k}_e. \tag{8.21}$$

If we assume some specific position $\vec{r}$, given that the left-hand sides are constants (i.e. independent of $\vec{r}$), then the right hand-sides must be constants, as well. Thus,

$$\omega_b = \omega_e. \tag{8.22}$$

Finally, from Eqs. 8.21-8.22 it follows that the right-hand sides will be equal to $e^{i(\delta_b-\delta_e)} = \cos(\delta_b - \delta_e) + i\sin(\delta_b - \delta_e)$. If the left-hand sides were real, then $\sin(\delta_b - \delta_e) = 0 \Rightarrow \delta_b - \delta_e = n\pi, n \in \mathscr{Z}$, hence there is a partial solution $\delta_b = \delta_e$. However, $\vec{E}_0, \vec{B}_0$ are generally complex, hence we arrive at the relations

$$\begin{array}{ccc} \frac{k_{ey}E_{0z}-k_{ez}E_{0y}}{\omega_b B_{0x}} & = & e^{i(\delta_b-\delta_e)} \\ \frac{k_{ez}E_{0x}-k_{ex}E_{0z}}{\omega_b B_{0y}} & = & e^{i(\delta_b-\delta_e)} \\ \frac{k_{ex}E_{0y}-k_{ey}E_{0x}}{\omega_b B_{0z}} & = & e^{i(\delta_b-\delta_e)} \end{array} \tag{8.23}$$

8.3 Standing EM wave in a cavity.

In this Section, we will construct an expression for the Hamiltonian of the EM field that allows to translated from the language of the vectors $\vec{E}, \vec{B}$ to the language of the number of photons. This will be done using the example of a standing EM wave in a cavity.

But before this, let us remember that for traveling waves, given the conditions of Section 8.2, we have

$$\nabla^2\vec{E} = \frac{1}{c^2}\frac{\partial^2\vec{E}}{\partial t^2} \qquad \vec{E}(\vec{r},t) = \vec{E}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t+\delta)} \tag{8.24}$$

$$\nabla^2\vec{B} = \frac{1}{c^2}\frac{\partial^2\vec{B}}{\partial t^2} \qquad \vec{B}(\vec{r},t) = \vec{B}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t+\delta)} \tag{8.25}$$

and $\vec{E} \times \vec{B} \uparrow\uparrow \vec{k}$, as it can be seen in Figure 8.2(left). These are the wave equations for the electric and magnetic field, respectively, in three dimensions, together with their solutions.

Figure 8.2: [Left] For traveling waves, it holds that $\vec{E}\times\vec{B}\uparrow\uparrow\vec{k}$. [Right] We assume that $\vec{E}\times\vec{B}\uparrow\uparrow\vec{k}$, along the axis directions depicted.

.

If the axis directions are the ones shown in Figure 8.2(right), then

$$\nabla^2\vec{E}_x=\frac{1}{c^2}\frac{\partial^2\vec{E}_x}{\partial t^2} \tag{8.26}$$

$$\vec{E}(\vec{r},t)=\vec{E}_{x0}e^{i(k_zz-\omega t+\delta)}=\vec{E}_x(z,t) \tag{8.27}$$

$$\nabla^2\vec{B}_y=\frac{1}{c^2}\frac{\partial^2\vec{B}_y}{\partial t^2} \tag{8.28}$$

$$\vec{B}(\vec{r},t)=\vec{B}_{0y}e^{i(k_zz-\omega t+\delta)}=\vec{B}_y(z,t) \tag{8.29}$$

therefore

$$\frac{\partial^2E_x}{\partial z^2}=\frac{1}{c^2}\frac{\partial^2E_x}{\partial t^2} \tag{8.30}$$

$$\frac{\partial^2B_y}{\partial z^2}=\frac{1}{c^2}\frac{\partial^2B_y}{\partial t^2} \tag{8.31}$$

These are wave equations for the electric and magnetic field, respectively, in one dimension. Let us now see we can draw any conclusions from the Maxwell's equations in vacuum.

$$\vec{\nabla}\cdot\vec{E}=0 \quad (\text{Eq. } 8.2\text{a}) \quad \Rightarrow \frac{\partial E_x}{\partial x}+\cancelto{0}{\frac{\partial E_y}{\partial y}}+\cancelto{0}{\frac{\partial E_z}{\partial z}}=0\Rightarrow\frac{\partial E_x}{\partial x}+0+0=0\Rightarrow$$

$$\frac{\partial E_x}{\partial x}=0,\text{which is expected.} \tag{8.32}$$

$$\vec{\nabla}\cdot\vec{B}=0 \quad (\text{Eq. } 8.2\text{b}) \quad \Rightarrow \cancelto{0}{\frac{\partial B_x}{\partial x}}+\frac{\partial B_y}{\partial y}+\cancelto{0}{\frac{\partial B_z}{\partial z}}=0\Rightarrow 0+\frac{\partial B_y}{\partial y}+0=0\Rightarrow$$

$$\frac{\partial B_y}{\partial y}=0,\text{which is expected.} \tag{8.33}$$

$$\vec{\nabla}\times\vec{E}=-\frac{\partial\vec{B}}{\partial t} \quad (\text{E}\xi.\ 8.2\text{c})\Rightarrow\begin{vmatrix}\hat{i} & \hat{j} & \hat{k}\\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z}\\ E_x & 0 & 0\end{vmatrix}=-\hat{j}\frac{\partial B_y}{\partial t}\Rightarrow\hat{j}\frac{\partial E_x}{\partial z}=-\hat{j}\frac{\partial B_y}{\partial t}\Rightarrow$$

$$\frac{\partial E_x}{\partial z} = -\frac{\partial B_y}{\partial t}. \tag{8.34}$$

$$\vec{\nabla} \times \vec{B} = \epsilon_0 \mu_0 \frac{\partial \vec{E}}{\partial t} \quad (\text{E}\xi.\ 8.2\text{d}) \Rightarrow \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ 0 & B_y & 0 \end{vmatrix} = \frac{1}{c^2}\frac{\partial E_x}{\partial t}\hat{i} \Rightarrow i\left(-\frac{\partial B_y}{\partial z}\right) = i\frac{1}{c^2}\frac{\partial E_x}{\partial t} \Rightarrow$$

$$\frac{\partial B_y}{\partial z} = -\frac{1}{c^2}\frac{\partial E_x}{\partial t}. \tag{8.35}$$

♠ Now let us place ideally conducting **mirrors** at positions $z = 0$ and $z = L$ (Figure 8.3). The incident wave at each mirror will interfere with the reflected one, hence **standing waves** will be created.

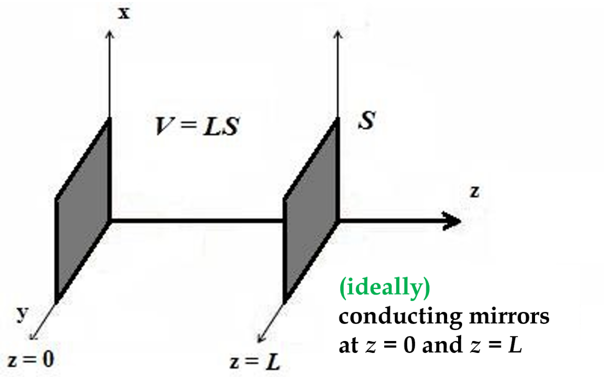


Figure 8.3: We place flat, ideally conducting mirrors at positions $z = 0$ and $z = L$.

Eqs. 8.30 and 8.34, i.e.

$$\frac{\partial^2 E_x}{\partial z^2} = \frac{1}{c^2}\frac{\partial^2 E_x}{\partial t^2} \qquad \frac{\partial E_x}{\partial z} = -\frac{\partial B_y}{\partial t},$$

as well as Eqs. 8.31 and 8.35, i.e.

$$\frac{\partial^2 B_y}{\partial z^2} = \frac{1}{c^2}\frac{\partial^2 B_y}{\partial t^2} \qquad \frac{\partial B_y}{\partial z} = -\frac{1}{c^2}\frac{\partial E_x}{\partial t}$$

continue to hold for the *linear combination* of incident and reflected waves.

We are looking for solutions using separation of variables, assuming that

$$E_x(z,t) = \mathcal{N} Z(z)T(t) \tag{8.36}$$

Let us remember the boundary conditions at the interface between an ideal conductor and vacuum or, in approximation, air (Figure 2.10). The parallel component of $\vec{E}$ becomes zero at this interface. Since $\vec{E}$ has only a x-component (Eq. 8.27) and the flat, perfectly conducting mirrors are placed at $z = 0$ and $z = L$ so that $\vec{E}$ is parallel to them, it follows that

$$E_x(0,t) = 0 = E_x(L,t), \forall\, t. \tag{8.37}$$

From Eqs. 8.30 and 8.36, it follows

$$\mathcal{N} T(t)\frac{d^2 Z}{dz^2} = \mathcal{N}\frac{1}{c^2}Z(z)\frac{d^2 T}{dt^2} \Leftrightarrow$$

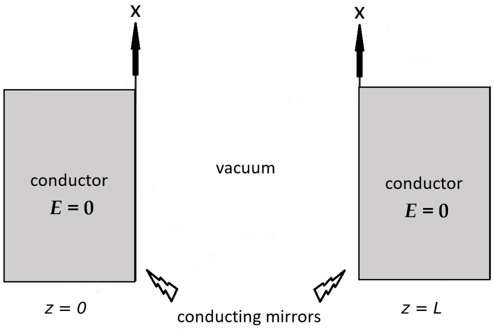


Figure 8.4: Conducting mirrors before $z = 0$ and after $z = L$.

$$\Leftrightarrow \underbrace{\underbrace{\frac{1}{Z(z)}\frac{d^2Z}{dz^2}}_{f(z)} = \underbrace{\frac{1}{T(t)}\frac{1}{c^2}\frac{d^2T}{dt^2}}_{g(t)}}_{\forall z,\, \forall t} \overset{\text{hence}}{=} \text{constant} := -k^2,$$

given that $Z(z) \neq 0$ and $T(t) \neq 0$, while for $Z(z) = 0$ and $T(t) = 0$ the trivial solution holds. Therefore,

$$\boxed{\frac{d^2Z}{dz^2} + k^2 Z(z) = 0} \tag{8.38}$$

and

$$\boxed{\frac{d^2T}{dt^2} + k^2c^2 T(t) = 0}. \tag{8.39}$$

• Let us begin by solving Eq. 8.38, trying solutions of the form $e^{\tilde{\lambda} z}$. Then, we obtain the characteristic polynomial

$$\tilde{\lambda}^2 + k^2 = 0 \Rightarrow \tilde{\lambda}^2 = -k^2 \Rightarrow \tilde{\lambda} = \pm ik, \quad \text{e.g. let us choose} \quad k \in \mathbb{R}_+$$

Thus, the solution will essentially have the form

$$Z(z) = Ae^{ikz} + Be^{-ikz} \tag{8.40}$$

$$Z(0) = 0 \quad \text{boundary condition 1} \tag{8.41}$$

$$Z(L) = 0 \quad \text{boundary condition 2} \tag{8.42}$$

where we have taken into account the boundary conditions of Eq. 8.37. From Eqs. 8.40 and 8.41 it follows that $A + B = 0 \Rightarrow B = -A$, hence Eq. 8.40 becomes

$$Z(z) = Ae^{ikz} - Ae^{-ikz} = 2iA\sin(kz) \tag{8.43}$$

and, applying Eq. 8.42,

$$\sin(kL) = 0 \Rightarrow kL = m\pi, m \in \mathscr{Z}. \tag{8.44}$$

However, given that above we chose $k \in \mathbb{R}_+$, it must hold that $m \in \mathbb{N}$, while, for a non-trivial solution, it must hold that $m \in \mathbb{N}^*$. Thus, $k \in \mathfrak{R}^*_+$. Concisely, k depends on a natural, non-zero index, i.e.

$$\boxed{k_m = \frac{m\pi}{L}, m \in \mathbb{N}^*} \tag{8.45}$$

Hence,

$$Z_m(z) = 2Ai\sin\left(\frac{m\pi z}{L}\right).$$

Additionally, if we demand that Z_m are orthonormal,

$$\int_0^L dzZ_m^*(z)Z_l(z) = \delta_{ml} \Rightarrow \int_0^L dz2iA^2\sin\left(\frac{m\pi z}{L}\right)\sin\left(\frac{l\pi z}{L}\right) = \delta_{ml}.$$

Defining $\psi = \frac{\pi z}{L}$, so that $d\psi = \frac{\pi}{L}dz$, we obtain

$$\int_0^\pi \frac{L}{\pi}d\psi 2iA^2\sin\big(m\psi\big)\sin\big(l\psi\big) = \delta_{ml} \Rightarrow \frac{L}{\pi}4A^2\int_0^\pi d\psi\sin\big(m\psi\big)\sin\big(l\psi\big) = \delta_{ml}.$$

But,

$$\int_0^\pi d\psi\sin\big(m\psi\big)\sin\big(l\psi\big) = \frac{\pi}{2}\delta_{ml}, \tag{8.46}$$

while it also holds that

$$\int_0^\pi d\psi\cos\big(m\psi\big)\cos\big(l\psi\big) = \frac{\pi}{2}\delta_{ml}. \tag{8.47}$$

Hence,

$$\frac{L}{\pi}4A^2\frac{\pi}{2}\delta_{ml} = \delta_{ml} \Rightarrow A^2 = \frac{1}{2L}.$$

Let us choose something convenient, e.g., $A = \frac{1}{\sqrt{2L}}(-i)$. Therefore,

$$\boxed{Z_m(z) = \sqrt{\frac{2}{L}}\sin\left(\frac{m\pi z}{L}\right)} \tag{8.48}$$

- Let us continue by solving Eq. 8.39. We set

$$\omega := kc > 0, \tag{8.49}$$

so that $\omega^2 = k^2c^2$. Using Eq. 8.45

$$\boxed{\omega_m = \frac{m\pi c}{L}, m \in \mathbb{N}^*} \tag{8.50}$$

Trying solutions of the form $e^{\tilde{\lambda}t}$ yields the characteristic polynomial

$$\tilde{\lambda}^2 + \omega_m^2 = 0 \Rightarrow \tilde{\lambda} = \pm i\omega_m, \quad \omega_m \in \mathbb{R}_+^*. \tag{8.51}$$

Thus, the solution will essentially have the form

$$T(t) = \Gamma e^{i\omega_m t} + \Delta e^{-i\omega_m t}, \tag{8.52}$$

and if we impose the initial condition

$$T(0) = 0, \tag{8.53}$$

if follows that $\Gamma + \Delta = 0 \Rightarrow \Delta = -\Gamma$, hence

$$T(t) = \Gamma e^{i\omega_m t} - \Gamma e^{-i\omega_m t} = 2i\Gamma\sin(\omega_m t) \Rightarrow \tag{8.54}$$

$$T_m(t) = 2i\Gamma\sin\left(\frac{m\pi c}{L}t\right). \tag{8.55}$$

Additionally, if we demand that T_m are orthonormal at a time interval from 0 to some value t_κ, i.e.

$$\int_0^{t_\kappa} dtT_m^*(t)T_l(t) = \delta_{ml} \Rightarrow \int_0^{t_\kappa} dt2i\Gamma^2 \sin\left(\frac{m\pi ct}{L}\right)\sin\left(\frac{l\pi ct}{L}\right) = \delta_{ml} \Rightarrow$$

$$\Rightarrow 4\Gamma^2 \int_0^{t_\kappa} dt \sin\left(\frac{m\pi ct}{L}\right)\sin\left(\frac{l\pi ct}{L}\right) = \delta_{ml}.$$

Defining $\chi = \frac{\pi ct}{L}$, so that $d\chi = \frac{\pi c}{L}dt$, we obtain

$$4\Gamma^2\frac{L}{\pi c}\int_0^{\frac{\pi c}{L}\cdot t_\kappa} d\chi \sin(m\chi)\sin(l\chi) = \delta_{ml} \tag{8.56}$$

Hence, having Eq. 8.46 in mind, it is convenient to set $\frac{\pi c}{L}\cdot t_\kappa = \pi \Rightarrow$

$$\boxed{t_\kappa = \frac{L}{c} := \tau} \tag{8.57}$$

Defining the quantity τ this way gives the **time of photon flight through the cavity**, hence this was not an unreasonable choice. Finally, the orthonoramalization is

$$\int_0^{\tau} dtT_m^*(t)T_l(t) = \delta_{ml}. \tag{8.58}$$

We end up obtaining

$$4\Gamma^2\frac{L}{\pi c}\int_0^{\pi} d\chi \sin(m\chi)\sin(l\chi) = \delta_{ml} \Rightarrow |\Gamma|^2 = \frac{c}{2L}.$$

Let us choose something convenient, e.g., $\Gamma = (-i)\sqrt{\frac{c}{2L}}$. Then,

$$\boxed{T_m(t) = \sqrt{\frac{2c}{L}}\sin\left(\frac{m\pi c}{L}t\right)} \tag{8.59}$$

Hence, to sum up, using Eqs. 8.36, 8.48, 8.59, we obtain

$$\boxed{E_x^m(z,t) = \frac{2\sqrt{c}}{L}\mathscr{N}\sin\left(\frac{m\pi z}{L}\right)\sin\left(\frac{m\pi ct}{L}\right)} \tag{8.60}$$

Regarding units, it must hold that $\left[\frac{2\sqrt{c}}{L}\mathscr{N}\right] = \frac{\mathrm{V}}{\mathrm{m}} = \frac{\mathrm{N}}{\mathrm{C}} \Rightarrow$

$$[\mathscr{N}] = \frac{\mathrm{V}}{\sqrt{\mathrm{m/s}}}. \tag{8.61}$$

In order to determine the magnetic field, we will use Eq. 8.35 combined with Eq. 8.60:

$$\frac{\partial B_y^m}{\partial z} = -\frac{1}{c^2}\frac{2\sqrt{c}}{L}\mathscr{N}\sin\left(\frac{m\pi z}{L}\right)\frac{m\pi c}{L}\cos\left(\frac{m\pi ct}{L}\right) \Rightarrow \tag{8.62}$$

$$\int_0^{z'} dz\frac{\partial B_y^m}{\partial z} = -\frac{2m\pi}{\sqrt{c}L^2}\mathscr{N}\cos\left(\frac{m\pi ct}{L}\right)\int_0^{z'} dz \sin\left(\frac{m\pi z}{L}\right) \Rightarrow \tag{8.63}$$

$$B_y^m(z',t) - B_y^m(0,t) = -\frac{2m\pi}{\sqrt{c}L^2}\mathscr{N}\cos\left(\frac{m\pi ct}{L}\right)\frac{L}{m\pi}\left[-\cos\left(\frac{m\pi z}{L}\right)\right]_0^{z'} \Rightarrow \tag{8.64}$$

$$B_y^m(z',t) - B_y^m(0,t) = \frac{2\mathscr{N}}{\sqrt{c}L}\cos\left(\frac{m\pi ct}{L}\right)\left[\cos\left(\frac{m\pi z'}{L}\right) - \cancelto{1}{\cos 0}\right]. \tag{8.65}$$

Therefore, by properly imposing the value of $B_y^m(0,t)$ and performing the change of variables $z' \to z$, it occurs that

$$\boxed{B_y^m(z,t) = \frac{2\mathscr{N}}{\sqrt{c}L}\cos\left(\frac{m\pi z}{L}\right)\cos\left(\frac{m\pi ct}{L}\right)} \tag{8.66}$$

For the energy density, it holds that

$$U = \frac{\epsilon_0}{2}E^2 + \frac{1}{2\mu_0}B^2 = \frac{\epsilon_0}{2}[E^2 + c^2B^2]. \tag{8.67}$$

We note that the units of the energy density are $[U] = \frac{\mathrm{J}}{\mathrm{m}^3}$. For example, $\left[\frac{\epsilon_0}{2}E^2\right] = \frac{\mathrm{F}}{\mathrm{m}}\frac{\mathrm{V}^2}{\mathrm{m}^2} = \frac{\mathrm{CV}^2}{\mathrm{Vm}^3} = \frac{\mathrm{J}}{\mathrm{m}^3}$ and $\left[\frac{B^2}{2\mu_0}\right] = \frac{\mathrm{T}^2\mathrm{A}}{\mathrm{Tm}} = \frac{\mathrm{TA}}{\mathrm{m}} = \frac{\mathrm{N}}{\mathrm{m}^2} = \frac{\mathrm{Nm}}{\mathrm{m}^3} = \frac{\mathrm{J}}{\mathrm{m}^3}$, e.g., given the known relations $B = \mu_0 H$, $F = BIl$ and $c^2 = \frac{1}{\epsilon_0\mu_0}$. Hence, from Eqs. 8.60, 8.66, 8.67, we obtain the energy density of mode m as

$$U_m = \frac{\epsilon_0}{2}\frac{4c\mathscr{N}^2}{L^2}\left[\sin^2\left(\frac{m\pi z}{L}\right)\sin^2\left(\frac{m\pi ct}{L}\right) + \cos^2\left(\frac{m\pi z}{L}\right)\cos^2\left(\frac{m\pi ct}{L}\right)\right]. \tag{8.68}$$

Thus, the energy of mode m, which is obtained by integrating the energy density of mode m over the volume of the cavity $V = LS$, is

$$\mathrm{E}_m = \int_{V=LS} d^3r\, U_m. \tag{8.69}$$

Therefore,

$$\mathrm{E}_m = \frac{2\epsilon_0 c\mathscr{N}^2 S}{L^2}\left[\sin^2\left(\frac{m\pi ct}{L}\right)\int_0^L dz\sin^2\left(\frac{m\pi z}{L}\right) + \cos^2\left(\frac{m\pi ct}{L}\right)\int_0^L dz\cos^2\left(\frac{m\pi z}{L}\right)\right].$$

We set $\psi = \frac{\pi z}{L} \Rightarrow d\psi = \frac{\pi}{L}dz$, so that, given Eqs. 8.46-8.47, the integrals over z become $\frac{L}{\pi}\int_0^\pi d\psi\sin^2(m\psi) = \frac{L}{\pi}\frac{\pi}{2} = \frac{L}{2}$ and $\frac{L}{\pi}\int_0^\pi d\psi\cos^2(m\psi) = \frac{L}{\pi}\frac{\pi}{2} = \frac{L}{2}$. Then, we substitute in the above equation and, finally, having followed this *classical* approach, we obtain

$$\boxed{\mathrm{E}_m = \frac{\epsilon_0 c\mathscr{N}^2 S}{L}\left[\sin^2\left(\frac{m\pi ct}{L}\right) + \cos^2\left(\frac{m\pi ct}{L}\right)\right] = \frac{\epsilon_0 c\mathscr{N}^2 S}{L}} \tag{8.70}$$

Let us now view E_m in a somewhat different manner:

$$\mathrm{E}_m = \frac{\epsilon_0 c\mathscr{N}^2 S}{L^3}\left[L^2\sin^2\left(\frac{m\pi ct}{L}\right) + L^2\cos^2\left(\frac{m\pi ct}{L}\right)\right], \tag{8.71}$$

We will define a "generalized position" and a "generalized momentum". So, we call the quantity

$$\boxed{q_m(t) := L\sin\left(\frac{m\pi ct}{L}\right)} \tag{8.72}$$

"generalized position", and the quantity

$$\boxed{\dot{q}_m(t) := m\pi c\ \cos\left(\frac{m\pi ct}{L}\right)} \tag{8.73}$$

"generalized momentum", so that $[q_m(t)] = \text{m}$ and $[\dot{q}_m(t)] = \text{m/s}$. Then, Eq. 8.71 is written as

$$\mathrm{E}_m = \frac{\epsilon_0 c \mathcal{N}^2 S}{L^3} \left\{ [q_m(t)]^2 + \frac{L^2}{m^2 \pi^2 c^2} [\dot{q}_m(t)]^2 \right\}, \tag{8.74}$$

At this point, we could see an analogy between Eq. 8.74 an the Simple Harmonic Oscillator (SHO), whose energy is

$$\mathrm{E} = \frac{K}{2} x^2 + \frac{M}{2} v^2 = \frac{K}{2} \left[x^2 + \frac{M}{K} v^2 \right]. \tag{8.75}$$

Therefore,

$$\frac{\epsilon_0 c \mathcal{N}^2 S}{L^3} = \frac{K}{2}, \tag{8.76}$$

$$\frac{L^2}{m^2 \pi^2 c^2} = \frac{M}{K}. \tag{8.77}$$

In other words, we obtain a "spring constant"

$$K = \frac{2\epsilon_0 c \mathcal{N}^2 S}{L^3}, \tag{8.78}$$

and a "mass"

$$M_m = \frac{2\epsilon_0 \mathcal{N}^2 S}{c L m^2 \pi^2}. \tag{8.79}$$

We note that the "mass" is dependent on m, which means that it is different for each mode of the EM field. We can easily verify that M_m has units of mass (we will need Eq. 8.61) and that the relationship $K = M_m \omega_m^2$ is satisfied. Hence, classically, there is a typical similarity between our problem and a SHO with angular frequency ω_m (Eq. 8.50) and "mass" M_m (Eq. 8.79). In other words, Eq. 8.71 or 8.74 can be written as

$$\boxed{\mathrm{E}_m = \frac{M_m \omega_m^2}{2} q_m^2 + \frac{M_m}{2} \dot{q}_m^2} \tag{8.80}$$

Therefore, we can deduce that the quantum analogue for a mode m of an EM field, i.e. the Hamiltonian of the EM field for a mode m, is

$$\boxed{\hat{H}_{\mathrm{EM},\, m} = \frac{M_m \omega_m^2}{2} \hat{q}_m^2 + \frac{M_m}{2} \hat{\dot{q}}_m^2}, \tag{8.81}$$

with energy eigenvalues

$$\boxed{E_{m,n_m} = \hbar \omega_m \left(n_m + \frac{1}{2} \right)}, \tag{8.82}$$

where $m \in \mathbb{N}^*$ refers to the mode of the EM field and $n_m \in \mathbb{N}$ refers to the number of photons at mode m. Consequently, the Hamiltonian of all the modes of the EM field will be

$$\boxed{\hat{H}_{\mathrm{EM}} = \sum_m \hat{H}_{\mathrm{EM},\, m}} \tag{8.83}$$

Next, we notice that from Eqs. 8.60 and 8.72 it follows that

$$E_x^m(z,t) = \frac{2\sqrt{c}}{L^2} \mathcal{N} \sin\left(\frac{m\pi z}{L} \right) q_m(t), \tag{8.84}$$

hence, the quantum analogue is

$$\hat{E}_x^m(z,t) = \frac{2\sqrt{c}}{L^2}\mathcal{N}\sin\left(\frac{m\pi z}{L}\right)\hat{q}_m(t). \tag{8.85}$$

Additionally, from Eqs. 8.66 and 8.73 it follows that

$$B_y^m(z,t) = \frac{2\mathcal{N}}{L\sqrt{c}}\frac{1}{m\pi c}\cos\left(\frac{m\pi z}{L}\right)\dot{q}_m(t), \tag{8.86}$$

hence, the quantum analogue is

$$\hat{B}_y^m(z,t) = \frac{2\mathcal{N}}{L\sqrt{c}}\frac{1}{m\pi c}\cos\left(\frac{m\pi z}{L}\right)\hat{\dot{q}}_m(t). \tag{8.87}$$

From Eqs. 8.84, 8.79 and 8.50 it follows that

$$\boxed{E_x^m(z,t) = \left(\frac{2M_m{\omega_m}^2}{\epsilon_0 V}\right)^{1/2}\sin\left(\frac{m\pi z}{L}\right)q_m(t)}, \tag{8.88}$$

hence, the quantum analogue is

$$\boxed{\hat{E}_x^m(z,t) = \left(\frac{2M_m{\omega_m}^2}{\epsilon_0 V}\right)^{1/2}\sin\left(\frac{m\pi z}{L}\right)\hat{q}_m(t)} \tag{8.89}$$

From Eqs. 8.86, 8.79 and 8.50 it follows that

$$\boxed{B_y^m(z,t) = \frac{1}{c}\left(\frac{2M_m}{\epsilon_0 V}\right)^{1/2}\cos\left(\frac{m\pi z}{L}\right)\dot{q}_m(t)}, \tag{8.90}$$

hence, the quantum analogue is

$$\boxed{\hat{B}_y^m(z,t) = \frac{1}{c}\left(\frac{2M_m}{\epsilon_0 V}\right)^{1/2}\cos\left(\frac{m\pi z}{L}\right)\hat{\dot{q}}_m(t)}. \tag{8.91}$$

Finally, from the above equations, it follows, as expected, that $\left[\frac{E_x}{B_y}\right] = [c]$.

8.4 Hamiltonian of the EM field using photon creation and annihilation (or raising and lowering) operators.

Let us now discuss photon creation and annihilation operators. Having reached this point, it is now easy to quantize the Hamiltonian that describes the EM field by introducing the operators

$$\hat{q}_m = q_m \tag{8.92}$$

$$\hat{p}_m = -i\hbar\frac{\partial}{\partial q_m} \tag{8.93}$$

We also introduce the operators:

$$\boxed{\hat{a}_m = \frac{1}{\sqrt{2M_m\hbar\omega_m}}(M_m\omega_m\hat{q}_m + i\hat{p}_m)} \quad \text{“annihilation”} \tag{8.94}$$

$$\boxed{\hat{a}_m^\dagger = \frac{1}{\sqrt{2M_m\hbar\omega_m}}(M_m\omega_m\hat{q}_m - i\hat{p}_m)} \quad \text{“creation”} \tag{8.95}$$

The following property holds:

$$\underbrace{[\hat{q}_m, \hat{p}_m]}_{\text{commutator}} = \hat{q}_m\hat{p}_m - \hat{p}_m\hat{q}_m = i\hbar. \tag{8.96}$$

Hence,

$$\underbrace{[\hat{a}_m, \hat{a}_m^\dagger]}_{\text{commutator}} = \hat{a}_m\hat{a}_m^\dagger - \hat{a}_m^\dagger\hat{a}_m = 1. \tag{8.97}$$

Therefore, the operators $\hat{q}_m$ and $\hat{p}_m$ can now be written as

$$\hat{q}_m = \left(\frac{\hbar}{2M_m\omega_m}\right)^{1/2}(\hat{a}_m^\dagger + \hat{a}_m), \tag{8.98}$$

$$\hat{p}_m = i\left(\frac{M_m\hbar\omega_m}{2}\right)^{1/2}(\hat{a}_m^\dagger - \hat{a}_m). \tag{8.99}$$

Thus, the Hamiltonian of mode m of the EM field is

$$\boxed{\hat{H}_{\mathrm{EM},\,m} = \hbar\omega_m\left(\hat{a}_m^\dagger\hat{a}_m + \frac{1}{2}\right)}. \tag{8.100}$$

Let us denote the state of the m mode of the EM field with n_m photons by $|n_m\rangle$. We call this a “photon number state”. $|n_m\rangle$ form a complete set, i.e. it holds that $\langle n_m|l_m\rangle = \delta_{nl}$.

The operators $\hat{a}_m^\dagger$ and $\hat{a}_m$ have the properties

$$\hat{a}_m^\dagger\,|n_m\rangle = \sqrt{n_m + 1}\,|n_m + 1\rangle\,, \tag{8.101}$$

$$\hat{a}_m\,|n_m\rangle = \sqrt{n_m}\,|n_m - 1\rangle\,, \tag{8.102}$$

$$\hat{a}_m\,|0\rangle = 0. \tag{8.103}$$

From Eqs. 8.101 and 8.102, it follows that

$$\hat{a}_m^\dagger\hat{a}_m\,|n_m\rangle = n_m\,|n_m\rangle\,, \tag{8.104}$$

i.e. the operator $\hat{N}_m = \hat{a}_m^\dagger\hat{a}_m$ counts the photon number of EM mode m, hence we can refer to it as the photon number operator of EM mode m. Furthermore, it occurs inductively that

$$|n_m\rangle = \frac{1}{\sqrt{n_m!}}(\hat{a}_m^\dagger)^{n_m}\,|0\rangle\,. \tag{8.105}$$

Due to Eqs. 8.100 and 8.104, it follows that

$$\hat{H}_{\mathrm{EM},\,m}\,|n_m\rangle = \hbar\omega_m\left(n_m + \frac{1}{2}\right)|n_m\rangle\,, \tag{8.106}$$

i.e. the Hamiltonian $\hat{H}_{\text{EM},\, m}$ yields the energy eigenvalues

$$\boxed{E_{m,n_m} = \hbar\omega_m\left(n_m + \frac{1}{2}\right)}. \tag{8.107}$$

The ground state of the SHO, $|0\rangle$, with eigenenergy $\frac{1}{2}\hbar\omega_m$ corresponds to vacuum, i.e. without any particles, the first excited state of the SHO, $|1\rangle$, with eigenenergy $\frac{3}{2}\hbar\omega_m$ corresponds to one particle, the second excited state of the SHO, $|1\rangle$, with eigenenergy $\frac{5}{2}\hbar\omega_m$ corresponds to two particles, and so forth. In this occasion, these particles are called photons. They are created or destroyed by the creation and annihilation operators, starting from a reference point, which here is vacuum. (see Figure 8.5). They obey to the bosonic commutation relations (see Section 9.3). This representation is also known as second quantization.

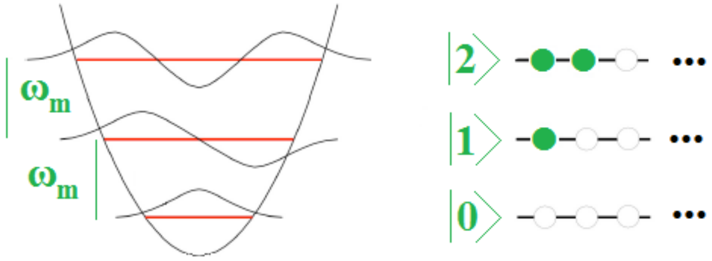


Figure 8.5: Particles (here photons, represented by green dots) are created and destroyed though the action of the creation and annihilation operators, respectively. They obey to the bosonic commutation relations (see Section 9.3). This representation is also known as second quantization. The photon number is equal to the number of nodes in the eigenfunction.

The Hamiltonian of mode m of the EM field is

$$\hat{H}_{\text{EM},\, m} = \hbar\omega_m\left(\hat{a}_m^\dagger\hat{a}_m + \frac{1}{2}\right) = \hbar\omega_m\left(\hat{N}_m + \frac{1}{2}\right). \tag{8.108}$$

Ignoring the term $\frac{\hbar\omega_m}{2}$, it can be written as

$$\hat{H}_{\text{EM},\, m} = \hbar\omega_m\hat{a}_m^\dagger\hat{a}_m = \hbar\omega_m\hat{N}_m. \tag{8.109}$$

We can have any number of photons in the quantum state $\hbar\omega_m$, since photons are bosons. $\hat{a}_m^\dagger$ is a raising operator, since it raises the energy by creating a photon with energy $\hbar\omega_m$; this is why it is also called the creation operator. $\hat{a}_m$ is a lowering operator, since it lowers the energy by destroying a photon with energy $\hbar\omega_m$; this is why it is also called the annihilation operator.

Finally, let us note that from Eqs. 8.89 and 8.98 it follows that

$$\boxed{\hat{E}_x^m(z,t) = \left(\frac{\hbar\omega_m}{\epsilon_0 V}\right)^{1/2} \sin\left(\frac{m\pi z}{L}\right)(\hat{a}_m^\dagger + \hat{a}_m)}, \tag{8.110}$$

while, from Eqs. 8.91 and 8.99 it follows that

$$\boxed{\hat{B}_y^m(z,t) = \frac{i}{c}\left(\frac{\hbar\omega_m}{\epsilon_0 V}\right)^{1/2} \cos\left(\frac{m\pi z}{L}\right)(\hat{a}_m^\dagger - \hat{a}_m)} \tag{8.111}$$

8.5 Hamiltonian of a two-level system using spinors and creation and annihilation (or raising and lowering) operators.

Let us consider the Hamiltonian of a two-level system with spinors and electron creation and annihilation (or raising and lowering) operators. In other words, we will now describe the raising and lowering of an electron between the energy levels of a two-level system, e.g., of an atom, using spinors. A spinor is a column vector with two components. Let us start with some definitions (e.g. [1]):

$$|\rangle = \begin{pmatrix}\circ\\ \circ\end{pmatrix} = \begin{pmatrix}0\\0\end{pmatrix} = |0\rangle, \quad |{\downarrow}\rangle = \begin{pmatrix}\circ\\ \bullet\end{pmatrix} = \begin{pmatrix}0\\1\end{pmatrix} = |1\rangle, \quad |{\uparrow}\rangle = \begin{pmatrix}\bullet\\ \circ\end{pmatrix} = \begin{pmatrix}1\\0\end{pmatrix} = |2\rangle \tag{8.112}$$

The first one represents an empty two-level system, the second one a two-level system with the electron lying at the lower level, with energy E_1, and the third one a two level system lying at the upper level, with energy E_2. Now, let us define the operators

$$\hat{S}_+ = \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}, \quad \hat{S}_- = \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}, \tag{8.113}$$

for which it actually holds that $\hat{S}_+^\dagger = \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}^\dagger = \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix} = \hat{S}_-$. Let us find out what the result of their action is on the spinors we defined right above:

$$\begin{aligned}
\hat{S}_+ |0\rangle &= \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}\begin{pmatrix}0\\0\end{pmatrix} = \begin{pmatrix}0\\0\end{pmatrix} = |0\rangle && \text{no action}\\
\hat{S}_+ |{\downarrow}\rangle &= \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}1\\0\end{pmatrix} = |{\uparrow}\rangle && \text{raises it}\\
\hat{S}_+ |{\uparrow}\rangle &= \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}0\\0\end{pmatrix} = |0\rangle && \text{throws it out}
\end{aligned} \tag{8.114}$$

$$\begin{aligned}
\hat{S}_- |0\rangle &= \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}\begin{pmatrix}0\\0\end{pmatrix} = \begin{pmatrix}0\\0\end{pmatrix} = |0\rangle && \text{no action}\\
\hat{S}_- |{\downarrow}\rangle &= \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}0\\0\end{pmatrix} = |0\rangle && \text{throws it out}\\
\hat{S}_- |{\uparrow}\rangle &= \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}0\\1\end{pmatrix} = |{\downarrow}\rangle && \text{lowers it}
\end{aligned} \tag{8.115}$$

Thus, $\hat{S}_+$ is called the raising operator, while o $\hat{S}_-$ is called the lowering operator of the electron. Let us examine some more properties. It holds that

$$\hat{S}_+\hat{S}_- = \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix} = \begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix}, \tag{8.116}$$

$$\hat{S}_-\hat{S}_+ = \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix} = \begin{pmatrix}0 & 0\\ 0 & 1\end{pmatrix}. \tag{8.117}$$

Thus,

$$\hat{S}_+\hat{S}_- + \hat{S}_-\hat{S}_+ = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} = \hat{\mathbf{I}} \tag{8.118}$$

which is the identity matrix. The above can also be written in the form

$$\{\hat{S}_+, \hat{S}_-\} = \hat{\mathbf{I}}. \tag{8.119}$$

$\{A, B\}$ or $[A, B]_+$ is the Poisson bracket or the anticommutator, defined as

$$\{A, B\} = AB + BA, \tag{8.120}$$

while $[A, B]$ or $[A, B]_-$ is the commutator, defined as

$$[A, B] = AB - BA. \tag{8.121}$$

When $\{A, B\} = 0 \Rightarrow AB + BA = 0 \Rightarrow AB = -BA$, i.e. the quantities A, A anticommute with each other, while when $[A, B] = 0 \Rightarrow AB - BA = 0 \Rightarrow AB = BA$, i.e. the quantities commute with each other; this is where the names come from. As we will see below, the Poisson bracket or anticommutator is used in the anticommutation relationships that hold for electrons, which are fermions, while the commutator is used in the commutation relationships that hold for photons, which are bosons.. Sadly, it is common in Greek textbooks for secondary education that the commutative property is mistitled as "anticommutative" property; it seems we have been lost in translation...

Now, let us remember the Pauli matrices $\hat{\sigma}_x$, $\hat{\sigma}_y$, $\hat{\sigma}_z$ and see how they are related to the raising and lowering operators, $\hat{S}_+$ and $\hat{S}_-$, respectively.

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{8.122}$$

We can show that it holds that

$$[\hat{\sigma}_x, \hat{\sigma}_y] = 2i\hat{\sigma}_z, \tag{8.123}$$

as well as its cyclic permutations. Moreover,

$$\hat{\sigma}_x^2 = \hat{\sigma}_y^2 = \hat{\sigma}_z^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \hat{\mathbf{I}}, \tag{8.124}$$

and

$$\begin{aligned} \{\hat{\sigma}_x, \hat{\sigma}_y\} &= \hat{\sigma}_x\hat{\sigma}_y + \hat{\sigma}_y\hat{\sigma}_x = \hat{0}, \\ \{\hat{\sigma}_y, \hat{\sigma}_z\} &= \hat{\sigma}_y\hat{\sigma}_z + \hat{\sigma}_z\hat{\sigma}_y = \hat{0}, \\ \{\hat{\sigma}_z, \hat{\sigma}_x\} &= \hat{\sigma}_z\hat{\sigma}_x + \hat{\sigma}_x\hat{\sigma}_z = \hat{0}, \end{aligned} \tag{8.125}$$

i.e. the Pauli matrices anticommute with each other. For example,

$$\{\hat{\sigma}_x, \hat{\sigma}_y\} = \hat{\sigma}_x\hat{\sigma}_y + \hat{\sigma}_y\hat{\sigma}_x = \\ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} + \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} = \hat{0}$$

Additionally, we can easily show that

$$\begin{aligned} \hat{S}_+ + \hat{S}_- &= \hat{\sigma}_x, \\ \hat{S}_+ - \hat{S}_- &= i\hat{\sigma}_y, \end{aligned}$$

and, using Eqs. 8.116 and 8.116, that

$$\hat{S}_+\hat{S}_- - \hat{S}_-\hat{S}_+ = [\hat{S}_+, \hat{S}_-] = \hat{\sigma}_z. \tag{8.126}$$

The Hamiltonian of the two-level system, $\hat{H}_{2\mathrm{LS}}$, is

$$E_2\hat{S}_+\hat{S}_- + E_1\hat{S}_-\hat{S}_+ = E_2\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + E_1\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} E_2 & 0 \\ 0 & E_1 \end{pmatrix}, \tag{8.127}$$

since

$$\begin{pmatrix} E_2 & 0 \\ 0 & E_1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} E_2 \\ 0 \end{pmatrix} = E_2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \tag{8.128}$$

$$\begin{pmatrix} E_2 & 0 \\ 0 & E_1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ E_1 \end{pmatrix} = E_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{8.129}$$

Hence, concisely, we have shown that

$$\boxed{\hat{H}_{2\mathrm{LS}} = E_2 \hat{S}_+ \hat{S}_- + E_1 \hat{S}_- \hat{S}_+}. \tag{8.130}$$

Now, if we set $E_1 = 0 \Rightarrow E_2 = \hbar\Omega$ (remember Eq. 5.44 and Eq. 5.14), then

$$\boxed{\hat{H}_{2\mathrm{LS}} = \hbar\Omega \hat{S}_+ \hat{S}_-} \tag{8.131}$$

The operator $\hat{S}_+ \hat{S}_-$ counts the number of electrons in the upper level, since

$$\hat{S}_+ \hat{S}_- |1\rangle = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} = |0\rangle \Rightarrow \hat{S}_+ \hat{S}_- |1\rangle = 0\,|1\rangle, \tag{8.132}$$

$$\hat{S}_+ \hat{S}_- |2\rangle = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |2\rangle \Rightarrow \hat{S}_+ \hat{S}_- |2\rangle = 1\,|2\rangle. \tag{8.133}$$

The operator $\hat{S}_- \hat{S}_+$ counts the number of electrons in the lower level, since

$$\hat{S}_- \hat{S}_+ |1\rangle = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = |1\rangle \Rightarrow \hat{S}_- \hat{S}_+ |1\rangle = 1\,|1\rangle, \tag{8.134}$$

$$\hat{S}_- \hat{S}_+ |2\rangle = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} = |0\rangle \Rightarrow \hat{S}_- \hat{S}_+ |2\rangle = 0\,|2\rangle. \tag{8.135}$$

Concisely, for the operators $\hat{S}_+$ and $\hat{S}_-$ we can show that $(\hat{S}_+)^\dagger = \hat{S}_-$ as well as that

$$\begin{aligned} \{\hat{S}_+, \hat{S}_+^\dagger\} &= \{\hat{S}_+, \hat{S}_-\} = \hat{S}_+ \hat{S}_- + \hat{S}_- \hat{S}_+ = \hat{\mathbf{I}} \\ \{\hat{S}_-, \hat{S}_-^\dagger\} &= \{\hat{S}_-, \hat{S}_+\} = \hat{S}_- \hat{S}_+ + \hat{S}_+ \hat{S}_- = \hat{\mathbf{I}} \\ \{\hat{S}_+, \hat{S}_+\} &= \{\hat{S}_-^\dagger, \hat{S}_-^\dagger\} = \hat{S}_+ \hat{S}_+ + \hat{S}_+ \hat{S}_+ = \hat{\mathbf{0}} \\ \{\hat{S}_-, \hat{S}_-\} &= \{\hat{S}_+^\dagger, \hat{S}_+^\dagger\} = \hat{S}_- \hat{S}_- + \hat{S}_- \hat{S}_- = \hat{\mathbf{0}} \end{aligned} \tag{8.136}$$

where $\hat{\mathbf{I}}$ is the 2×2 identity matrix and $\hat{\mathbf{0}}$ is the 2×2 zero matrix. Eqs. 8.136 show that the operators $\hat{S}_+$ and $\hat{S}_-$ obey to the fermion anticommutation relations which are discussed in Section 9.3. $\hat{S}_+$ is a raising operator, since it raises the energy by creating an electron with $\hbar\Omega$; this is where the name creation operator comes from. $\hat{S}_-$ is a lowering operator, since it lowers the energy by annihilating an electron with energy $\hbar\Omega$; this is where the name annihilation operator comes from. We can only have a single electron with energy $\hbar\Omega$, since electrons are fermions.

Let us also notice that, as the notation in Eq. 8.112 suggests, there are several ways to denote the (fermion) creation and annihilation operators in the literature, such as

$$\begin{aligned} \hat{S}_- &= |{\downarrow}\rangle\langle{\uparrow}| = |1\rangle\langle 2| = \hat{a}_{12} = \hat{c}_2 \\ \hat{S}_+ &= |{\uparrow}\rangle\langle{\downarrow}| = |2\rangle\langle 1| = \hat{a}_{12}^\dagger = \hat{c}_2^\dagger, \end{aligned}$$

which are totally equivalent. Therefore, some equivalent ways to write the Hamiltonian of the two-level system (Eq. 8.131) are

$$\hat{H}_{2\mathrm{LS}} = \hbar\Omega \hat{S}_+ \hat{S}_- = \hbar\Omega\,|{\uparrow}\rangle\langle{\uparrow}| = \hbar\Omega\,|2\rangle\langle 2| = \hbar\Omega \hat{a}_{12}^\dagger \hat{a}_{12} = \hbar\Omega \hat{c}_2^\dagger \hat{c}_2$$

8.6 Hamiltonian of three- and multi-level systems using spinors and creation and annihilation (or raising and lowering) operators.

In accordance with the above, for a three level system with eigenenergies $\mathrm{E}_1 = 0 < \mathrm{E}_2 < \mathrm{E}_3$, we can define the column vectors

$$|0\rangle = \begin{pmatrix}0\\0\\0\end{pmatrix}, \quad |1\rangle = \begin{pmatrix}1\\0\\0\end{pmatrix}, \quad |2\rangle = \begin{pmatrix}0\\1\\0\end{pmatrix}, \quad |3\rangle = \begin{pmatrix}0\\0\\1\end{pmatrix}. \tag{8.137}$$

The first one represents an empty three-level system, and the rest a three-level system with the electron lying at level n, with energy E_n. In order to describe its elementary excitations from the ground state, we can define the creation and annihilation operators

$$\hat{\mathrm{a}}_{12} = |1\rangle\langle 2| = \begin{pmatrix}1\\0\\0\end{pmatrix}\begin{pmatrix}0 & 1 & 0\end{pmatrix} = \begin{pmatrix}0 & 1 & 0\\0 & 0 & 0\\0 & 0 & 0\end{pmatrix} = \hat{\mathrm{a}}_{21}^{\dagger}$$

$$\hat{\mathrm{a}}_{21} = |2\rangle\langle 1| = \begin{pmatrix}0\\1\\0\end{pmatrix}\begin{pmatrix}1 & 0 & 0\end{pmatrix} = \begin{pmatrix}0 & 0 & 0\\1 & 0 & 0\\0 & 0 & 0\end{pmatrix} = \hat{\mathrm{a}}_{12}^{\dagger}$$

$$\hat{\mathrm{a}}_{13} = |1\rangle\langle 3| = \begin{pmatrix}1\\0\\0\end{pmatrix}\begin{pmatrix}0 & 0 & 1\end{pmatrix} = \begin{pmatrix}0 & 0 & 1\\0 & 0 & 0\\0 & 0 & 0\end{pmatrix} = \hat{\mathrm{a}}_{31}^{\dagger}$$

$$\hat{\mathrm{a}}_{31} = |3\rangle\langle 1| = \begin{pmatrix}0\\0\\1\end{pmatrix}\begin{pmatrix}1 & 0 & 0\end{pmatrix} = \begin{pmatrix}0 & 0 & 0\\0 & 0 & 0\\1 & 0 & 0\end{pmatrix} = \hat{\mathrm{a}}_{13}^{\dagger},$$

whose action is

$$\begin{aligned}
\hat{\mathrm{a}}_{12}|1\rangle &= \hat{\mathrm{a}}_{21}^{\dagger}|1\rangle = |1\rangle\langle 2|1\rangle = |0\rangle\\
\hat{\mathrm{a}}_{21}|1\rangle &= \hat{\mathrm{a}}_{12}^{\dagger}|1\rangle = |2\rangle\langle 1|1\rangle = |2\rangle\\
\hat{\mathrm{a}}_{13}|1\rangle &= \hat{\mathrm{a}}_{31}^{\dagger}|1\rangle = |1\rangle\langle 3|1\rangle = |0\rangle\\
\hat{\mathrm{a}}_{31}|1\rangle &= \hat{\mathrm{a}}_{13}^{\dagger}|1\rangle = |3\rangle\langle 1|1\rangle = |3\rangle
\end{aligned}$$

$$\begin{aligned}
\hat{\mathrm{a}}_{12}|2\rangle &= \hat{\mathrm{a}}_{21}^{\dagger}|2\rangle = |1\rangle\langle 2|2\rangle = |1\rangle\\
\hat{\mathrm{a}}_{21}|2\rangle &= \hat{\mathrm{a}}_{12}^{\dagger}|2\rangle = |2\rangle\langle 1|2\rangle = |0\rangle\\
\hat{\mathrm{a}}_{13}|2\rangle &= \hat{\mathrm{a}}_{31}^{\dagger}|2\rangle = |1\rangle\langle 3|2\rangle = |0\rangle\\
\hat{\mathrm{a}}_{31}|2\rangle &= \hat{\mathrm{a}}_{13}^{\dagger}|2\rangle = |3\rangle\langle 1|2\rangle = |0\rangle
\end{aligned}$$

$$\begin{aligned}
\hat{\mathrm{a}}_{12}|3\rangle &= \hat{\mathrm{a}}_{21}^{\dagger}|3\rangle = |1\rangle\langle 2|3\rangle = |0\rangle\\
\hat{\mathrm{a}}_{21}|3\rangle &= \hat{\mathrm{a}}_{12}^{\dagger}|3\rangle = |2\rangle\langle 1|3\rangle = |0\rangle\\
\hat{\mathrm{a}}_{13}|3\rangle &= \hat{\mathrm{a}}_{31}^{\dagger}|3\rangle = |1\rangle\langle 3|3\rangle = |1\rangle\\
\hat{\mathrm{a}}_{31}|3\rangle &= \hat{\mathrm{a}}_{13}^{\dagger}|3\rangle = |3\rangle\langle 1|3\rangle = |0\rangle.
\end{aligned}$$

Using these operators, the Hamiltonian describing the elementary excitations of a three-level system from its ground state $|1\rangle$ (with $E_1 = 0$) can be written in the equivalent forms:

$$\hat{H}_{\mathrm{3LS}} = E_2\hat{\mathrm{a}}_{12}^{\dagger}\hat{\mathrm{a}}_{12} + E_3\hat{\mathrm{a}}_{13}^{\dagger}\hat{\mathrm{a}}_{13} = E_2|2\rangle\langle 2| + E_3|3\rangle\langle 3| = E_2\hat{c}_2^{\dagger}\hat{c}_2 + E_3\hat{c}_3^{\dagger}\hat{c}_3. \tag{8.138}$$

In a completely analogous manner, for a multi-level system with N levels and eigenenergies $E_1 = 0 < E_2 < \ldots E_N$, we can define $N + 1$ column vectors, 1 for the vacuum state and N describing the state $|n\rangle$ of an electron lying at level n, with energy E_n. Using these operators, the Hamiltonian describing the elementary excitations of a multi-level system from its ground state $|1\rangle$ (with $E_1 = 0$) can be written in the equivalent forms:

$$\hat{H}_{\mathrm{MLS}} = \sum_{n=2}^{N} E_n \hat{a}_{1n}^{\dagger} \hat{a}_{1n} = \sum_{n=2}^{N} E_n |n\rangle \langle n| = \sum_{n=2}^{N} E_n \hat{c}_n^{\dagger} \hat{c}_n. \tag{8.139}$$

8.7 Interaction Hamiltonian between two-level system and EM field.

Let $q > 0$ be $-q < 0$ be two opposite electric charges, placed at points P and M, respectively. If $\vec{d} = \overrightarrow{\mathrm{MP}}$ is the position vector of the positive charge with respect to the negative one, then the **electric dipole moment** is defined as

$$\vec{\mathscr{P}} = q\vec{d}. \tag{8.140}$$

For example, in the hydrogen atom, if N represents the nucleus and E the electron and, as usually, we define $\vec{r} = \overrightarrow{\mathrm{PE}}$, then $\vec{\mathscr{P}} = q\vec{d} = e(-\vec{r}) \Rightarrow$

$$\vec{\mathscr{P}} = -e\vec{r}. \tag{8.141}$$

This is depicted in the upper panel of Figure 8.6.

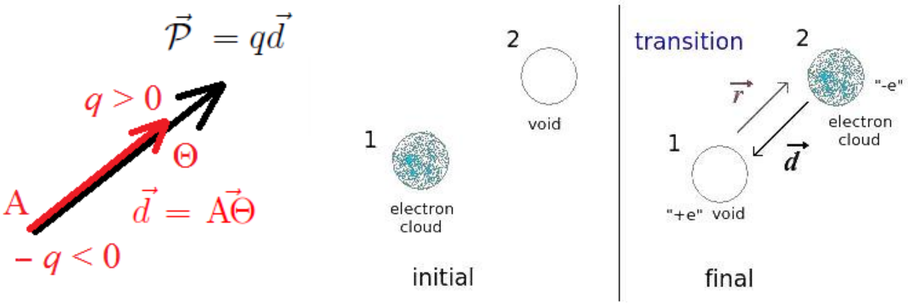


Figure 8.6: Left. Electric dipole moment. Right. Transition (electric) dipole moment.

The **potential energy**, $U_{\mathscr{E}}$, **of an electric dipole subject to an electric field** $\vec{\mathscr{E}}$ is

$$U_{\mathscr{E}} = -\vec{\mathscr{P}} \cdot \vec{\mathscr{E}}. \tag{8.142}$$

In accordance with the above, we can analogously define a dipole moment when a part of the electron cloud is transitioned from an initial to a final area. This is how the transition (electric) dipole moment[1] is defined. This is depicted in the lower panel of Figure 8.6. If the charge of the transitioning charge is $-e$, then, again, $\vec{p} = q\vec{d} = e(-\vec{r}) \Rightarrow \vec{p} = -e\vec{r}$. In other words, this means that, for region 2, the difference between the final and the initial state is equivalent to the transition of charge $-e$, while, for region 1, the difference between the final and the initial state is equivalent to the transition of charge $+e$.

The **transition (electric) dipole moment operator** is alternatively denoted by $\hat{\vec{d}}$ or $\hat{\vec{p}}$. Written on the basis of the energy eigenstates of the unperturbed atom (or system), it is defined as

$$\hat{\vec{d}} = \hat{\vec{p}} := \sum_{i=1}^{N} \sum_{j=1}^{N} \vec{d}_{ij} |\Phi_i\rangle \langle\Phi_j|, \tag{8.143}$$

---

[1] The word “electric” has been put in parenthesis because it is commonly implied.

again, with the alternative notations

$$\vec{d}_{ij} = \vec{p}_{ij} := -e \langle \Phi_i | \hat{\vec{r}} | \Phi_j \rangle \tag{8.144}$$

for the matrix element of the transition (electric) dipole moment between states $|\Phi_i\rangle$ and $|\Phi_j\rangle$. We recall that the position operator $\hat{\vec{r}}$ is such that

$$\hat{\vec{r}}\,|\vec{r}\rangle = \vec{r}\,|\vec{r}\rangle\,. \tag{8.145}$$

We also recall that

$$\begin{aligned}
\langle \Phi_i | \hat{\vec{r}} | \Phi_j \rangle &= \sum_{|\vec{r}'\rangle, |\vec{r}''\rangle} \langle \Phi_i | \vec{r}' \rangle \, \langle \vec{r}' | \hat{\vec{r}} | \vec{r}'' \rangle \, \langle \vec{r}'' | \Phi_j \rangle = \sum_{|\vec{r}'\rangle} \langle \Phi_i | \vec{r}' \rangle \; \vec{r}' \; \langle \vec{r}' | \Phi_j \rangle \\
&= \sum_{|\vec{r}\rangle} \langle \Phi_i | \vec{r} \rangle \; \vec{r} \; \langle \vec{r} | \Phi_j \rangle = \int dV \Phi_i(\vec{r})^* \vec{r}\, \Phi_j(\vec{r}),
\end{aligned}$$

since

$$\langle \vec{r}' | \hat{\vec{r}} | \vec{r}'' \rangle = \vec{r}'' \, \langle \vec{r}' | \vec{r}'' \rangle = \vec{r}'' \delta_{\vec{r}', \vec{r}''}\,. \tag{8.146}$$

Therefore,

$$\vec{d}_{11} = -e \langle \Phi_1 | \hat{\vec{r}} | \Phi_1 \rangle = -e \int dV \, \underbrace{\Phi_1(\vec{r})^* \vec{r}\, \Phi_1(\vec{r})}_{\text{odd}} = 0, \quad \star \tag{8.147}$$

$$\vec{d}_{12} = -e \langle \Phi_1 | \hat{\vec{r}} | \Phi_2 \rangle = -e \int dV \Phi_1(\vec{r})^* \vec{r}\, \Phi_2(\vec{r}) \neq 0, \tag{8.148}$$

$$\vec{d}_{21} = -e \langle \Phi_1 | \hat{\vec{r}} | \Phi_1 \rangle = -e \int dV \Phi_2(\vec{r})^* \vec{r}\, \Phi_1(\vec{r}) \neq 0, \tag{8.149}$$

$$\vec{d}_{22} = -e \langle \Phi_2 | \hat{\vec{r}} | \Phi_2 \rangle = -e \int dV \, \underbrace{\Phi_2(\vec{r})^* \vec{r}\, \Phi_2(\vec{r})}_{\text{odd}} = 0. \quad \star \tag{8.150}$$

In other words, while the diagonal elements become zero, $\vec{d}_{12}$ and $\vec{d}_{21}$ are not zero ("by identity"). Let us now find out what $\hat{\vec{p}}$ does at a two-level system.

$$\begin{aligned}
\hat{\vec{p}} &= \vec{d}_{11} \, |\Phi_1\rangle \, \langle \Phi_1| + \vec{d}_{12} \, |\Phi_1\rangle \, \langle \Phi_2| + \vec{d}_{21} \, |\Phi_2\rangle \, \langle \Phi_1| + \vec{d}_{22} \, |\Phi_2\rangle \, \langle \Phi_2| \\
&= \vec{d}_{11} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \end{pmatrix} + \vec{d}_{12} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \end{pmatrix} + \vec{d}_{21} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \end{pmatrix} + \vec{d}_{22} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \end{pmatrix} \\
&= \underbrace{\cancelto{0}{\vec{d}_{11}}}_{\text{diagonal element}} \star \; \underbrace{\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}}_{\text{part of diagonal matrix}} + \underbrace{\vec{d}_{12}}_{\text{off-diagonal element}} \underbrace{\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}}_{\text{part of antidiagonal matrix}} \\
&\quad + \underbrace{\vec{d}_{21}}_{\text{off-diagonal element}} \underbrace{\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}}_{\text{part of antidiagonal matrix}} + \underbrace{\cancelto{0}{\vec{d}_{22}}}_{\text{diagonal element}} \star \; \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}}_{\text{part of diagonal matrix}}
\end{aligned}$$

From Eqs. (8.148)-(8.149) we conclude that $\vec{d}_{12} = \vec{d}_{21}$, given that $\Phi_i(\vec{r})$ are real, thus

$$\hat{\vec{p}} = \vec{d}_{12} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{8.151}$$

Question: And what does the operator $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ do?

Answer:

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

In other words, it transitions from one energy level to the other, as it should!

At this point, we can define the **potential energy operator**. We assume that the EM field - 2LS interaction has the form of an electric dipole mechanism. We ignore other interactions, such as electric quadrupole or magnetic dipole. Since $U_{\mathscr{E}} = -\vec{\mathscr{P}} \cdot \vec{\mathscr{E}}$, it is implied that

$$U_{\mathscr{E}}^{m} = -\vec{\mathscr{P}} \cdot \vec{\mathscr{E}}^{m}, \tag{8.152}$$

where the index m denotes the m mode of the EM field. The respective operator can be defined ass

$$\hat{U}_{\mathscr{E}}^{m} = -\hat{\vec{p}} \cdot \hat{\vec{\mathscr{E}}}^{m}. \tag{8.153}$$

Therefore,

$$\hat{U}_{\mathscr{E}}^{m} = -\sum_{i=1}^{N}\sum_{j=1}^{N} \vec{d}_{ij} \left|\Phi_i\right\rangle \left\langle\Phi_j\right| \cdot \hat{E}_x^m(z,t)\hat{i}.$$

$\hat{i}$ is the unit vector of the x-axis, since we have assumed this direction for the electric field (see Figure 8.2). Alternatively, due to Eq. 8.151,

$$\hat{U}_{\mathscr{E}}^{m} = -\vec{d}_{12} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \cdot \hat{E}_x^m(z,t)\hat{i}. \tag{8.154}$$

But

$$\vec{d}_{12} \cdot \hat{i} = -e \int dV \Phi_1(\vec{r})^*(\vec{r} \cdot \hat{i})\Phi_2(\vec{r}) = -ex_{12} = \mathscr{P}_{x_{12}} := \mathscr{P}. \tag{8.155}$$

Thus,

$$\hat{U}_{\mathscr{E}}^{m} = ex_{12} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \hat{E}_x^m(z,t). \tag{8.156}$$

We recall Eqs. 8.110 and 8.111

$$\hat{E}_x^m(z,t) = \left(\frac{\hbar\omega_m}{\varepsilon_0 V}\right)^{\frac{1}{2}} \sin\left(\frac{m\pi z}{L}\right)(\hat{a}_m^\dagger + \hat{a}_m)$$

$$\hat{B}_y^m(z,t) = \left(\frac{\hbar\omega_m}{\varepsilon_0 V}\right)^{\frac{1}{2}} \frac{1}{c} \cos\left(\frac{m\pi z}{L}\right) i(\hat{a}_m^\dagger - \hat{a}_m).$$

out of which, however, only the first one is needed in the context of our assumptions. Moreover, we recall that

$$\hat{S}_+ + \hat{S}_- = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

Thus, finally,

$$\hat{U}_{\mathscr{E}}^{m} = ex_{12} \left(\frac{\hbar\omega_m}{\varepsilon_0 V}\right)^{\frac{1}{2}} \sin\left(\frac{m\pi z}{L}\right)(\hat{S}_+ + \hat{S}_-)(\hat{a}_m^\dagger + \hat{a}_m). \tag{8.157}$$

We can alternatively write

$$\boxed{\hbar g^m = e x_{12}\left(\frac{\hbar\omega_m}{\varepsilon_0 V}\right)^{\frac{1}{2}}\sin\left(\frac{m\pi z}{L}\right)} \tag{8.158}$$

$$\boxed{\hat{U}^m_{\mathscr{E}} = \hbar g^m(\hat{S}_+ + \hat{S}_-)(\hat{a}^\dagger_m + \hat{a}_m)} \tag{8.159}$$

So, this is the **interaction Hamiltonian** between the 2LS and the mode m of the EM field. In the context of atomic physics, this is also denoted as $\hat{H}^m_{\mathrm{AF}}$, where AF stands for Atom-Field.

From Eq. 8.158 it follows that

$$\hbar|g^m| = |\mathscr{P}|\left|\left(\frac{\hbar\omega_m}{\varepsilon_0 V}\right)^{\frac{1}{2}}\sin\left(\frac{m\pi z}{L}\right)\right|. \tag{8.160}$$

We can also define, for reasons that will be explained below, the Rabi frequency as

$$\Omega^m_R := 2\sqrt{n}g^m. \tag{8.161}$$

Thus,

$$\Omega^m_R = \frac{|\mathscr{P}|}{\hbar}\left|\left(\frac{4\hbar\omega_m n}{\varepsilon_0 V}\right)^{\frac{1}{2}}\sin\left(\frac{m\pi z}{L}\right)\right| := \frac{|\mathscr{P}|E^m_0}{\hbar}, \tag{8.162}$$

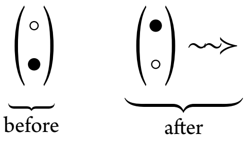
where, however, the "amplitude" E^m_0 is spatially configured, i.e. it depends on the position z of the atom inside the cavity. In other words, $E^m_0 = E^m_0(z)$. If the EM mode m we refer to is implied, we can use the simpler notation $|g|$ or Ω_R. Additionally, to avoid vector norms we can choose the phase of the wavefunctions to be such that g is real and positive [2]. Concisely,

$$\boxed{\Omega_R = \frac{g}{2\sqrt{n}} := \frac{|\mathscr{P}|E^m_0}{\hbar}} \tag{8.163}$$

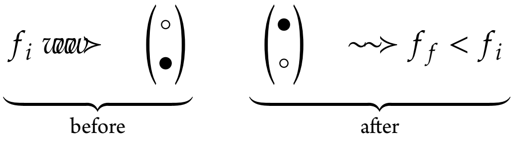
Let us examine the EM field-2LS interaction Hamiltonian (Eq. 8.159) a bit more. For *a single, unique* mode m, this Hamiltonian is analyzed into four terms

$$\begin{aligned}\hat{U}^m_{\mathscr{E}} &= \hbar g^m(\hat{S}_+ + \hat{S}_-)(\hat{a}^\dagger_m + \hat{a}_m) = \\ &= \hbar g^m\{\underbrace{\hat{S}_+\hat{a}^\dagger_m}_{\text{1st}} + \underbrace{\hat{S}_+\hat{a}_m}_{\text{2nd}} + \underbrace{\hat{S}_-\hat{a}^\dagger_m}_{\text{3rd}} + \underbrace{\hat{S}_-\hat{a}_m}_{\text{4th}}\}.\end{aligned}$$

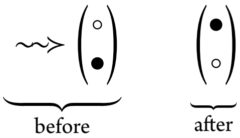
- <u>1st TERM</u>. The electron is raised an a photon is created/emitted. Therefore, the energy difference is $\Delta E > 0$. Hence, this term does not conserve the energy by itself and seems unreasonable. Schematically:

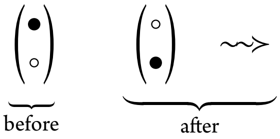
  However, it is possible that such terms are kept if multiple modes (m) hence multiple frequencies (Eq. 8.50), are supported, i.e. if the EM field - 2LS Hamiltonian is a sum of terms, as in Eq. 8.159. In such a case, it is possible that the 2LS absorbs a high frequency photon and is raised, and, at the same time, a lower frequency photon is created/emitted. Schematically:

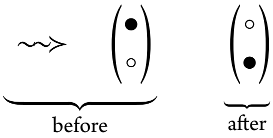
- 2nd TERM. The electron is raised and a photon is destroyed/absorbed. This term conserves the energy even for a single mode (m). Schematically:



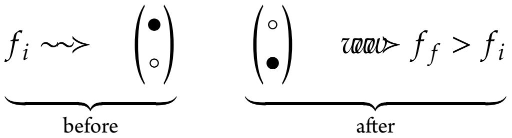
- 3rd TERM. The electron is lowered and a photon is created/emitted. This term conserves the energy even for a single mode (m), as well. Schematically:



- 4th TERM. The electron is lowered and a photon is destroyed/absorbed. Therefore, the energy difference is $\Delta E < 0$. Hence, this term does not conserve the energy by itself, just like the 1st TERM. Schematically:



However, it is possible that such terms are kept if multiple modes (m) hence multiple frequencies (Eq. 8.50), are supported, i.e. if the EM field - 2LS Hamiltonian is a sum of terms, as in Eq. 8.159. In such a case, it is possible that the 2LS absorbs a low frequency photon and is lowered, and, at the same time, a higher frequency photon is created/emitted. Schematically:



If we ignore the 1st and the 4th term, which to not themselves conserve the energy, then

$$\hat{U}^m_{\mathscr{E}} = \hbar g^m \left(\hat{S}_+ \hat{a}_m + \hat{S}_- \hat{a}^\dagger_m\right). \tag{8.164}$$

This approximation is somehow analogous to the RWA, which was discussed in Chapter 5. There, we kept only the slower term of the Rabi equations, in which the EM field and the two-level system are approximately at resonance, i.e., $\Omega \simeq \omega$. In other words, we kept the slow terms containing $e^{\pm i(\Omega-\omega)t}$ and ignored the fast terms containing $e^{\pm i(\Omega+\omega)t}$.

8.8 Synopsis of Hamiltonians.

Let us summarize what we have done so far.

In Section 8.4, we arrived at Eq. 8.100, which describes an EM mode m, i.e.

$$\boxed{\hat{H}_{\text{EM},\,m} = \hbar\omega_m \left(\hat{a}^\dagger_m \hat{a}_m + \frac{1}{2}\right)}.$$

Ignoring the term $\frac{\hbar\omega_m}{2}$, the above equation becomes Eq. 8.109

$$\boxed{\hat{H}_{\text{EM}, m} = \hbar\omega_m \hat{a}_m^\dagger \hat{a}_m = \hbar\omega_m \hat{N}_m}.$$

8.4, we arrived at Eq. 8.100, which describes an EM mode m, i.e. In Section 8.5, we arrived at Eq. 8.130, which describes a 2LS, i.e.

$$\boxed{\hat{H}_{2\text{LS}} = E_2 \hat{S}_+ \hat{S}_- + E_1 \hat{S}_- \hat{S}_+}.$$

Setting $E_1 = 0 \Rightarrow E_2 = \hbar\Omega$ (remember Eq. 5.44 and Eq. 5.14), the above equation becomes Eq. 8.131

$$\boxed{\hat{H}_{2\text{LS}} = \hbar\Omega \hat{S}_+ \hat{S}_-}.$$

The picture is competed in Section 8.7, where the interaction between a mode m of the EM field and the 2LS is described, i.e.,

$$\boxed{\hat{U}_{\mathscr{E}}^m = \hbar g^m (\hat{S}_+ + \hat{S}_-)(\hat{a}_m^\dagger + \hat{a}_m)}.$$

Therefore, the Hamiltonian that describes an EM mode m, a 2LS, and the interaction between them (which is often called the Rabi Hamiltonian) can be written as

$$\boxed{\hat{H}_R^m = \hbar\omega_m \hat{a}_m^\dagger \hat{a}_m + \hbar\Omega \hat{S}_+ \hat{S}_- + \hbar g^m (\hat{S}_+ + \hat{S}_-)(\hat{a}_m^\dagger + \hat{a}_m)}, \tag{8.165}$$

while the states (of the electron and the EM mode m, without the interaction between them) is

$$|\uparrow, n_m\rangle, \tag{8.166}$$

$$|\downarrow, n_m\rangle. \tag{8.167}$$

Concisely, while for the total Hamiltonian for an EM mode m we obtain the Rabi Hamiltonian

$$\hat{H}_R^m = \hbar\omega_m \hat{a}_m^\dagger \hat{a}_m + \hbar\Omega \hat{S}_+ \hat{S}_- + \hbar g^m (\hat{S}_+ \hat{a}_m^\dagger + \hat{S}_+ \hat{a}_m + \hat{S}_- \hat{a}_m^\dagger + \hat{S}_- \hat{a}_m), \tag{8.168}$$

according to the discussion of Section 8.7, we can ignore, in first approximation, the so-called counter-rotating terms

$$\boxed{\hat{H}_{\text{counter-rotating}} = \hbar g^m (\hat{S}_+ \hat{a}_m^\dagger + \hat{S}_- \hat{a}_m)}, \tag{8.169}$$

so that we arrive at the so-called Jaynes-Cummings Hamiltonian [3]

$$\boxed{\hat{H}_{JC}^m = \hbar\omega_m \hat{a}_m^\dagger \hat{a}_m + \hbar\Omega \hat{S}_+ \hat{S}_- + \hbar g^m (\hat{S}_+ \hat{a}_m + \hat{S}_- \hat{a}_m^\dagger)}. \tag{8.170}$$

We note that in paper [3] the authors take the average energy between the two levels as a reference point. In such a case, i.e. if we set $E_1 = -\frac{\hbar\Omega}{2}$ and $E_2 = \frac{\hbar\Omega}{2}$, the second term, initially given by Eq. 8.130,

$$\hat{H}_{2\text{LS}} = E_2 \hat{S}_+ \hat{S}_- + E_1 \hat{S}_- \hat{S}_+,$$

would become (see Eq. 8.126)

$$\hat{H}_{2\text{LS}} = \frac{\hbar\Omega}{2} \hat{\sigma}_z. \tag{8.171}$$

However, we will continue to use E_1 as a reference point, so that our second term is

$$\hat{H}_{2\text{LS}} = \hbar\Omega \hat{S}_+ \hat{S}_-.$$

In exercise 1 of this chapter we neglect for simplicity the index m. (A) We find what terms $\hat{a}^\dagger\hat{a}$, $\hat{a}\hat{a}^\dagger$, $\hat{S}_+\hat{S}_-$, $\hat{S}_-\hat{S}_+$, $\hat{S}_+\hat{a}^\dagger$, $\hat{S}_+\hat{a}$, $\hat{S}_-\hat{a}^\dagger$, $\hat{S}_-\hat{a}$, do on states $|\downarrow, n\rangle$ and $|\uparrow, n\rangle$. (B) We calculate $\langle\hat{a}^\dagger\hat{a}\rangle$, $\langle\hat{a}\hat{a}^\dagger\rangle$, $\langle\hat{S}_+\hat{S}_-\rangle$, $\langle\hat{S}_-\hat{S}_+\rangle$, $\langle\hat{S}_+\hat{a}^\dagger\rangle$, $\langle\hat{S}_+\hat{a}\rangle$, $\langle\hat{S}_-\hat{a}^\dagger\rangle$, $\langle\hat{S}_-\hat{a}\rangle$, for states $|\downarrow, n\rangle$ and $|\uparrow, n\rangle$.

8.9 Mean (expected) values of quantities related to the Jaynes-Cummings Hamiltonian.

Let us not calculate the average (i.e. the expected) values of the operators involved in the Jaynes-Cummings Hamiltonian

$$\hat{H}^m_{JC} = \hbar\omega_m \hat{a}^\dagger_m \hat{a}_m + \hbar\Omega \hat{S}_+\hat{S}_- + \hbar g^m(\hat{S}_+\hat{a}_m + \hat{S}_-\hat{a}^\dagger_m),$$

i.e. $\langle \hat{a}^\dagger_m \hat{a}_m\rangle$, $\langle \hat{S}_+\hat{S}_-\rangle$, $\langle \hat{S}_+\hat{a}_m\rangle$, $\langle \hat{S}_-\hat{a}^\dagger_m\rangle$ for the states:

- (A) $|\Psi_A(t)\rangle = c_1(t)\,|{\downarrow}, n\rangle + c_2(t)\,|{\uparrow}, n-1\rangle$
- (E) $|\Psi_E(t)\rangle = c_1(t)\,|{\downarrow}, n+1\rangle + c_2(t)\,|{\uparrow}, n\rangle$

Case (A)

$$\begin{aligned}
\langle \hat{a}^\dagger_m \hat{a}_m\rangle_{(A)} &= \langle \psi_A(t)|\hat{a}^\dagger_m|\psi_A(t)\rangle = \Big\{c_1^*\,\langle{\downarrow}, n| + c_2^*\,\langle{\uparrow}, n-1|\,\Big\}\hat{a}^\dagger_m\hat{a}_m\Big\{c_1\,|{\downarrow}, n\rangle + c_2\,|{\uparrow}, n-1\rangle\,\Big\} \\
&= |c_1|^2\,\langle{\downarrow}, n|\hat{a}^\dagger_m\hat{a}_m|{\downarrow}, n\rangle + c_1^*c_2\,\langle{\downarrow}, n|\hat{a}^\dagger_m\hat{a}_m|{\uparrow}, n-1\rangle \\
&\quad + c_2^*c_1\,\langle{\uparrow}, n-1|\hat{a}^\dagger_m\hat{a}_m|{\downarrow}, n\rangle + |c_2|^2\,\langle{\uparrow}, n-1|\hat{a}^\dagger_m\hat{a}_m|{\uparrow}, n-1\rangle \\
&= |c_1|^2\sqrt{n}\sqrt{n}\,\langle{\downarrow}, n|{\downarrow}, n\rangle + c_1^*c_2\sqrt{n-1}\sqrt{n-1}\,\langle{\downarrow}, n|{\uparrow}, n-1\rangle \\
&\quad + c_2^*c_1\sqrt{n}\sqrt{n}\,\langle{\uparrow}, n-1|{\downarrow}, n\rangle + |c_2|^2\sqrt{n-1}\sqrt{n-1}\,\langle{\uparrow}, n-1|{\uparrow}, n-1\rangle \\
&= n|c_1|^2\cdot 1 + c_1^*c_2(n-1)\cdot 0 + c_2^*c_1 n\cdot 0 + (n-1)|c_2|^2\cdot 1 \\
&= n|c_1|^2 + n|c_2|^2 - |c_2|^2 = n\Big(|c_1|^2 + |c_2|^2\Big) - |c_2|^2 = n - |c_2|^2 \Rightarrow
\end{aligned}$$

$$\boxed{\langle \hat{a}^\dagger_m \hat{a}_m\rangle_{(A)} = n - |c_2(t)|^2} \tag{8.172}$$

$$\begin{aligned}
\langle \hat{S}_+\hat{S}_-\rangle_{(A)} &= \langle \psi_A(t)|\hat{S}_+\hat{S}_-|\psi_A(t)\rangle = \Big\{c_1^*\,\langle{\downarrow}, n| + c_2^*\,\langle{\uparrow}, n-1|\,\Big\}\hat{S}_+\hat{S}_-\Big\{c_1\,|{\downarrow}, n\rangle + c_2\,|{\uparrow}, n-1\rangle\,\Big\} \\
&= |c_1|^2\,\langle{\downarrow}, n|\hat{S}_+\hat{S}_-|{\downarrow}, n\rangle + c_1^*c_2\,\langle{\downarrow}, n|\hat{S}_+\hat{S}_-|{\uparrow}, n-1\rangle \\
&\quad + c_2^*c_1\,\langle{\uparrow}, n-1|\hat{S}_+\hat{S}_-|{\downarrow}, n\rangle + |c_2|^2\,\langle{\uparrow}, n-1|\hat{S}_+\hat{S}_-|{\uparrow}, n-1\rangle \\
&= |c_1|^2\cdot 0 + c_1^*c_2\,\cancelto{0}{\langle{\downarrow}, n|{\uparrow}, n-1\rangle} + c_2^*c_1\cdot 0 + |c_2|^2\,\langle{\uparrow}, n-1|{\uparrow}, n-1\rangle \Rightarrow
\end{aligned}$$

$$\boxed{\langle \hat{S}_+\hat{S}_-\rangle_{(A)} = |c_2(t)|^2} \tag{8.173}$$

Hence,

$$\boxed{\langle \hat{a}^\dagger_m \hat{a}_m\rangle_{(A)} + \langle \hat{S}_+\hat{S}_-\rangle_{(A)} = n} \tag{8.174}$$

$$\begin{aligned}
\langle \hat{S}_+\hat{a}_m\rangle_{(A)} &= \langle \psi_A(t)|\hat{S}_+\hat{a}_m|\psi_A(t)\rangle = \Big\{c_1^*\,\langle{\downarrow}, n| + c_2^*\,\langle{\uparrow}, n-1|\,\Big\}\hat{S}_+\hat{a}_m\Big\{c_1\,|{\downarrow}, n\rangle + c_2\,|{\uparrow}, n-1\rangle\,\Big\} \\
&= |c_1|^2\,\langle{\downarrow}, n|\hat{S}_+\hat{a}_m|{\downarrow}, n\rangle + c_1^*c_2\,\langle{\downarrow}, n|\hat{S}_+\hat{a}_m|{\uparrow}, n-1\rangle \\
&\quad + c_2^*c_1\,\langle{\uparrow}, n-1|\hat{S}_+\hat{a}_m|{\downarrow}, n\rangle + |c_2|^2\,\langle{\uparrow}, n-1|\hat{S}_+\hat{a}_m|{\uparrow}, n-1\rangle \\
&= |c_1|^2\sqrt{n}\,\cancelto{0}{\langle{\downarrow}, n|{\uparrow}, n-1\rangle} + c_1^*c_2\sqrt{n-1}\,\cancelto{0}{\langle{\downarrow}, n|\hat{S}_+|{\uparrow}, n-2\rangle} \\
&\quad + c_2^*c_1\sqrt{n}\,\langle{\uparrow}, n-1|{\uparrow}, n-1\rangle + |c_2|^2\sqrt{n-1}\,\cancelto{0}{\langle{\uparrow}, n-1|\hat{S}_+|{\uparrow}, n-2\rangle} \Rightarrow
\end{aligned}$$

$$\boxed{\langle \hat{S}_+\hat{a}_m\rangle_{(A)} = c_2^*(t)c_1(t)\sqrt{n}} \tag{8.175}$$

$$\begin{aligned}\langle \hat{S}_{-}\hat{a}_m^{\dagger}\rangle_{(A)} &= \langle \psi_A(t)|\hat{S}_{-}\hat{a}_m^{\dagger}|\psi_A(t)\rangle = \Big\{c_1^*\,\langle \downarrow,n| + c_2^*\,\langle \uparrow,n-1|\Big\}\hat{S}_{-}\hat{a}_m^{\dagger}\Big\{c_1\,|\downarrow,n\rangle + c_2\,|\uparrow,n-1\rangle\Big\}\\ &= |c_1|^2\,\langle \downarrow,n|\hat{S}_{-}\hat{a}_m^{\dagger}|\downarrow,n\rangle + c_1^*c_2\,\langle \downarrow,n|\hat{S}_{-}\hat{a}_m^{\dagger}|\uparrow,n-1\rangle\\ &\quad + c_2^*c_1\,\langle \uparrow,n-1|\hat{S}_{-}\hat{a}_m^{\dagger}|\downarrow,n\rangle + |c_2|^2\,\langle \uparrow,n-1|\hat{S}_{-}\hat{a}_m^{\dagger}|\uparrow,n-1\rangle\\ &= |c_1|^2\sqrt{n+1}\,\cancelto{0}{\langle \downarrow,n|\hat{S}_{-}|\downarrow,n+1\rangle} + c_1^*c_2\sqrt{n}\,\langle \downarrow,n|\downarrow,n\rangle\\ &\quad + c_2^*c_1\,\cancelto{0}{\langle \uparrow,n-1|\hat{S}_{-}|\downarrow,n+1\rangle}\sqrt{n+1} + |c_2|^2\,\cancelto{0}{\langle \uparrow,n-1|\downarrow,n\rangle}\sqrt{n} \Rightarrow\end{aligned}$$

$$\boxed{\langle \hat{S}_{-}\hat{a}_m^{\dagger}\rangle_{(A)} = c_1^*(t)c_2(t)\sqrt{n}} \tag{8.176}$$

Case (E)

$$\begin{aligned}\langle \hat{a}_m^{\dagger}\hat{a}_m\rangle_{(E)} &= \langle \psi_E(t)|\hat{a}_m^{\dagger}\hat{a}_m|\psi_E(t)\rangle = \Big\{c_1^*\,\langle \downarrow,n+1| + c_2^*\,\langle \uparrow,n|\Big\}\hat{a}_m^{\dagger}\hat{a}_m\Big\{c_1\,|\downarrow,n+1\rangle + c_2\,|\uparrow,n\rangle\Big\}\\ &= |c_1|^2\,\langle \downarrow,n+1|\hat{a}_m^{\dagger}\hat{a}_m|\downarrow,n+1\rangle + c_1^*c_2\,\langle \downarrow,n+1|\hat{a}_m^{\dagger}\hat{a}_m|\uparrow,n\rangle\\ &\quad + c_2^*c_1\,\langle \uparrow,n|\hat{a}_m^{\dagger}\hat{a}_m|\downarrow,n+1\rangle + |c_2|^2\,\langle \uparrow,n|\hat{a}_m^{\dagger}\hat{a}_m|\uparrow,n\rangle\\ &= |c_1|^2\sqrt{n+1}\sqrt{n+1}\,\langle \downarrow,n+1|\downarrow,n+1\rangle + c_1^*c_2 n\,\cancelto{0}{\langle \downarrow,n+1|\uparrow,n\rangle}\\ &\quad + c_2^*c_1(n+1)\,\cancelto{0}{\langle \uparrow,n|\downarrow,n+1\rangle} + |c_2|^2 n\,\langle \uparrow,n|\uparrow,n\rangle\\ &= |c_1|^2(n+1) + n|c_2|^2 = n\Big(|c_1|^2 + |c_2|^2\Big) + |c_1|^2 \Rightarrow\end{aligned}$$

$$\boxed{\langle \hat{a}_m^{\dagger}\hat{a}_m\rangle_{(E)} = n + |c_1(t)|^2} \tag{8.177}$$

$$\begin{aligned}\langle \hat{S}_{+}\hat{S}_{-}\rangle_{(E)} &= \langle \psi_E(t)|\hat{S}_{+}\hat{S}_{-}|\psi_E(t)\rangle = \Big\{c_1^*\,\langle \downarrow,n+1| + c_2^*\,\langle \uparrow,n|\Big\}\hat{S}_{+}\hat{S}_{-}\Big\{c_1\,|\downarrow,n+1\rangle + c_2\,|\uparrow,n\rangle\Big\}\\ &= |c_1|^2\cdot 0 + c_1^*c_2\,\cancelto{0}{\langle \downarrow,n+1|\uparrow,n\rangle} + c_2^*c_1\cdot 0 + |c_2|^2\,\langle \uparrow,n|\uparrow,n\rangle \Rightarrow\end{aligned}$$

$$\boxed{\langle \hat{S}_{+}\hat{S}_{-}\rangle_{(E)} = |c_2(t)|^2} \tag{8.178}$$

Hence,

$$\boxed{\langle \hat{a}_m^{\dagger}\hat{a}_m\rangle_{(E)} + \langle \hat{S}_{+}\hat{S}_{-}\rangle_{(E)} = n+1} \tag{8.179}$$

$$\begin{aligned}\langle \hat{S}_{+}\hat{a}_m\rangle_{(E)} &= \langle \psi_E(t)|\hat{S}_{+}\hat{a}_m|\psi_E(t)\rangle = \Big\{c_1^*\,\langle \downarrow,n+1| + c_2^*\,\langle \uparrow,n|\Big\}\hat{S}_{+}\hat{a}_m\Big\{c_1\,|\downarrow,n+1\rangle + c_2\,|\uparrow,n\rangle\Big\}\\ &= |c_1|^2\,\langle \downarrow,n+1|\hat{S}_{+}\hat{a}_m|\downarrow,n+1\rangle + c_1^*c_2\,\langle \downarrow,n+1|\hat{S}_{+}\hat{a}_m|\uparrow,n\rangle\\ &\quad + c_2^*c_1\,\langle \uparrow,n|\hat{S}_{+}\hat{a}_m|\downarrow,n+1\rangle + |c_2|^2\,\langle \uparrow,n|\hat{S}_{+}\hat{a}_m|\uparrow,n\rangle\\ &= |c_1|^2\sqrt{n+1}\,\cancelto{0}{\langle \downarrow,n+1|\uparrow,n\rangle} + c_1^*c_2\cdot 0 + c_2^*c_1\sqrt{n+1}\,\langle \uparrow,n|\uparrow,n\rangle + |c_2|^2\cdot 0 \Rightarrow\end{aligned}$$

$$\boxed{\langle \hat{S}_{+}\hat{a}_m\rangle_{(E)} = c_2^*(t)c_1(t)\sqrt{n+1}} \tag{8.180}$$

$$\begin{aligned}
\langle\hat{S}_-\hat{a}_m^\dagger\rangle_{(E)} &= \langle\psi_E(t)|\hat{S}_-\hat{a}_m^\dagger|\psi_E(t)\rangle = \Big\{c_1^*\langle\downarrow,n+1| + c_2^*\langle\uparrow,n|\Big\}\hat{S}_-\hat{a}_m^\dagger\Big\{c_1|\downarrow,n+1\rangle + c_2|\uparrow,n\rangle\Big\}\\
&= |c_1|^2\langle\downarrow,n+1|\hat{S}_-\hat{a}_m^\dagger|\downarrow,n+1\rangle + c_1^*c_2\langle\downarrow,n+1|\hat{S}_-\hat{a}_m^\dagger|\uparrow,n\rangle\\
&\quad + c_2^*c_1\langle\uparrow,n|\hat{S}_-\hat{a}_m^\dagger|\downarrow,n+1\rangle + |c_2|^2\langle\uparrow,n|\hat{S}_-\hat{a}_m^\dagger|\uparrow,n\rangle\\
&= |c_1|^2\sqrt{n+2}\,\cancelto{0}{\langle\downarrow,n+1|\uparrow,n+2\rangle} + c_1^*c_2\sqrt{n+1}\,\langle\downarrow,n+1|\downarrow,n+1\rangle\\
&\quad + c_2^*c_1\cdot 0 + |c_2|^2\,\cancelto{0}{\langle\uparrow,n|\downarrow,n+1\rangle}\sqrt{n+1} \Rightarrow
\end{aligned}$$

$$\boxed{\langle\hat{S}_-\hat{a}_m^\dagger\rangle_{(E)} = c_1^*(t)c_2(t)\sqrt{n+1}} \tag{8.181}$$

The relationships we have shown above will be useful in what follows, in Sections 8.10-8.11.

8.10 Photon absorption.

Let us focus on the problem of photon absorption, which is described by the equations

$$|\Psi_A(t)\rangle = c_1(t)\,|\downarrow,n_m\rangle + c_2(t)\,|\uparrow,n_m-1\rangle\,, \tag{8.182}$$

$$i\hbar\frac{\partial}{\partial t}\,|\Psi_A(t)\rangle = \hat{H}\,|\Psi_A(t)\rangle\,, \tag{8.183}$$

$$\hat{H} = \hat{H}_{\rm JC}^m = \hbar\omega_m\hat{a}_m^\dagger\hat{a}_m + \hbar\Omega\hat{S}_+\hat{S}_- + \hbar g^m(\hat{S}_+\hat{a}_m + \hat{S}_-\hat{a}_m^\dagger), \tag{8.184}$$

and the initial conditions

$$c_1(0) = 1, \qquad c_2(0) = 0. \tag{8.185}$$

The left-hand side of the time-dependent Schrödinger equation 8.183 becomes

$$i\hbar\frac{\partial}{\partial t}\,|\Psi_A(t)\rangle = i\hbar\dot{c}_1\,|\downarrow,n_m\rangle + i\hbar\dot{c}_2\,|\uparrow,n_m-1\rangle\,, \tag{8.186}$$

while the right-hand side becomes

$$\begin{aligned}
\hat{H}\,|\Psi_A(t)\rangle &= (\hbar\omega_m\hat{a}_m^\dagger\hat{a}_m + \hbar\Omega\hat{S}_+\hat{S}_- + \hbar g^m\hat{S}_+\hat{a}_m + \hbar g^m\hat{S}_-\hat{a}_m^\dagger)(c_1\,|\downarrow,n_m\rangle + c_2\,|\uparrow,n_m-1\rangle)\\
&= c_1\hbar\omega_m n_m\,|\downarrow,n_m\rangle + c_1\hbar\Omega\,|0,n_m\rangle + c_1\hbar g^m\,|\uparrow,n_m-1\rangle\,\sqrt{n_m} + c_1\hbar g^m\sqrt{n_m+1}\,|0,n_m+1\rangle\\
&\quad + c_2\hbar\omega_m(n_m-1)\,|\uparrow,n_m-1\rangle + c_2\hbar\Omega\,|\uparrow,n_m-1\rangle +\\
&\quad c_2\hbar g^m\sqrt{n_m-1}\,|0,n_m-2\rangle + \hbar g^m\,|\downarrow,n_m\rangle\,\sqrt{n_m}c_2\\
&= c_1\hbar\omega_m n_m\,|\downarrow,n_m\rangle + c_1\hbar g^m\,|\uparrow,n_m-1\rangle\,\sqrt{n_m}\\
&\quad + c_2\hbar\omega_m(n_m-1)\,|\uparrow,n_m-1\rangle + c_2\hbar\Omega\,|\uparrow,n_m-1\rangle + \hbar g^m\,|\downarrow,n_m\rangle\,\sqrt{n_m}c_2
\end{aligned}$$

Acting with $\langle\downarrow,n|$ on both sides,

$$\left.\begin{aligned}
&\text{the left-hand side becomes} && i\hbar\dot{c}_1\\
&\text{the right-hand side becomes} && \hbar\omega_m n_m c_1 + \hbar g^m\sqrt{n_m}c_2
\end{aligned}\right\}\Rightarrow$$

$$i\dot{c}_1 = n_m\omega_m c_1 + g^m\sqrt{n_m}c_2. \tag{8.187}$$

Accordingly, acting with $\langle\uparrow, n-1|$ on both sides,

$$\left.\begin{array}{ll}\text{the left-hand side becomes} & i\hbar\dot{c}_2 \\ \text{the right-hand side becomes} & \hbar g^m\sqrt{n_m}c_1 + \hbar\omega_m(n_m-1)c_2 + \hbar\Omega c_2\end{array}\right\} \Rightarrow$$

$$i\dot{c}_2 = g^m\sqrt{n_m}c_1 + [\Omega + (n_m-1)\omega_m]c_2 \tag{8.188}$$

Thus, we obtain the System of Differential equations

$$\boxed{i\begin{pmatrix}\dot{c}_1\\ \dot{c}_2\end{pmatrix} = \begin{pmatrix} n_m\omega_m & g^m\sqrt{n_m} \\ g^m\sqrt{n_m} & \Omega + (n_m-1)\omega_m\end{pmatrix}\begin{pmatrix}c_1\\ c_2\end{pmatrix}} \tag{8.189}$$

Now, we define the **generalized Rabi frequency**

$$\boxed{\Omega_{n_m} := \left[\left(\frac{\omega_m - \Omega}{2}\right)^2 + g_m^2 n_m\right]^{1/2}}. \tag{8.190}$$

or, omitting, for simplicity, the index m denoting the EM mode,

$$\boxed{\Omega_n := \left[\left(\frac{\omega - \Omega}{2}\right)^2 + g^2 n\right]^{1/2}}. \tag{8.191}$$

The above System of Differential Equations (8.189) can be solved, e.g., with the eigenvalue method (see Appendix B.7), i.e. the same way we saw in Chapter 5. Performing the calculations for the problem of photon absorption [i.e. for initial conditions $c_1(0) = 1, c_2(0) = 0$] yields

$$\boxed{|c_2(t)|^2 = \frac{ng^2}{\Omega_n^2}\sin^2(\Omega_n t)} \tag{8.192}$$

and

$$\boxed{|c_1(t)|^2 = 1 - |c_2(t)|^2 = 1 - \frac{ng^2}{\Omega_n^2}\sin^2(\Omega_n t)}. \tag{8.193}$$

Hence, from Equation 8.172 it follows that

$$\boxed{\langle\hat{a}_m^\dagger\hat{a}_m\rangle_{(A)} = n - \frac{ng^2\sin^2(\Omega_n t)}{\Omega_n^2}}, \tag{8.194}$$

i.e. the average (expected) value of the photon number in the cavity as a function of time will perform oscillations. The index (A) denotes absorption. Moreover, from Eq 8.173 it follows that

$$\boxed{\langle\hat{S}_+\hat{S}_-\rangle_{(A)} = \frac{ng^2}{\Omega_n^2}\sin^2(\Omega_n t)}, \tag{8.195}$$

i.e. the average (expected) value of the number of electrons at the upper level E_2 as a function of time will perform oscillations. Those oscillations are commonly called the **Rabi oscillations**. Two examples of Rabi oscillations during photon absorption can be seen in Figure 8.7.

Since $\sin^2(\Omega_n t) = \frac{1}{2} - \frac{1}{2}\cos(2\Omega_n t)$, the period of these oscillations is

$$\boxed{T = \frac{2\pi}{2\Omega_n} = \frac{\pi}{\Omega_n} = \frac{\pi}{\left[\left(\frac{\omega-\Omega}{2}\right)^2 + g^2 n\right]^{1/2}}} \tag{8.196}$$

Hence, when $\omega = \Omega$, i.e. at resonance, the period reaches its maximum at

$$T = \frac{\pi}{g\sqrt{n}}. \tag{8.197}$$

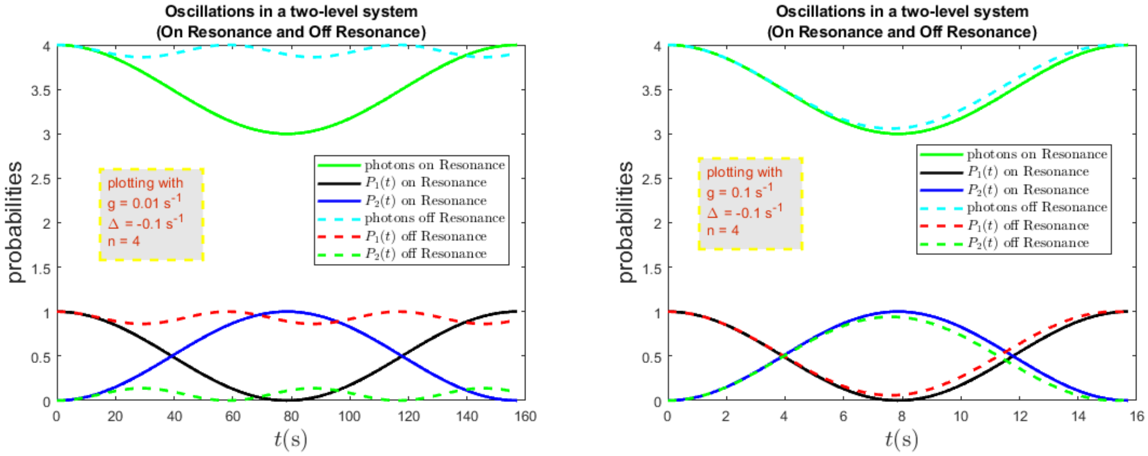


Figure 8.7: Two examples of Rabi oscillations during photon absorption, i.e., the initial condition is 4 photons in the cavity and 1 electron at the lower level. We use some arbitrary values of the parameters to make an indicative figure. On the right, the two levels are tangled more strongly (the parameter g is larger). We present the temporal evolution of the expected value of the number of photons in the cavity, $\langle \hat{a}_m^{\dagger}\hat{a}_m \rangle = n - \frac{ng^2}{\Omega_n^2}\sin^2(\Omega_n t)$, both on resonance ($\Delta = 0$) and out of resonance ($\Delta \neq 0$), as well as of the expected value of the number of electrons at the upper level, $P_2(t) = \langle \hat{S}_+\hat{S}_- \rangle = \frac{ng^2}{\Omega_n^2}\sin^2(\Omega_n t)$ and at the lower level, $P_1(t)$.

The maximum transfer percentage between the two levels, $\mathscr{A}$, is, as evident from Eqs. 8.195 and 8.190,

$$\boxed{\mathscr{A} = \frac{g^2 n}{\Omega_n^2} = \frac{g^2 n}{\left(\frac{\omega-\Omega}{2}\right)^2 + g^2 n}} \tag{8.198}$$

Therefore,

- for $\Omega = \omega$ (resonance) $\Rightarrow \mathscr{A} = 1$, while
- for $\Omega \neq \omega$ (out of resonance) $\Rightarrow \mathscr{A} < 1$.

To conclude, the number of photons in the cavity, n, the quantity g (Eq. 8.158) and the detuning, defined in Eq. 5.49 as $\Delta := \omega - \Omega$, determine the maximum transfer percentage and the period of oscillations.

8.11 Photon emission.

Let us focus on the problem of photon emission, which is described by the equations

$$|\Psi_E(t)\rangle = c_1(t)\,|\downarrow, n_m+1\rangle + c_2\,|\uparrow, n_m\rangle \tag{8.199}$$

$$i\hbar\frac{\partial}{\partial t}|\Psi_E(t)\rangle = \hat{H}\,|\Psi_E(t)\rangle \tag{8.200}$$

$$\hat{H} = \hat{H}^m_{\text{JC}} = \hbar\omega_m\hat{a}^\dagger_m\hat{a}_m + \hbar\Omega\hat{S}_+\hat{S}_- + \hbar g^m(\hat{S}_+\hat{a}_m + \hat{S}_-\hat{a}^\dagger_m), \tag{8.201}$$

and the initial conditions

$$c_1(0) = 0, \qquad c_2(0) = 1. \tag{8.202}$$

The left-hand side of the time-dependent Schrödinger equation 8.200 becomes

$$i\hbar\frac{\partial}{\partial t}|\Psi_E(t)\rangle = i\hbar\dot{c}_1\,|\downarrow, n_m+1\rangle + i\hbar\dot{c}_2\,|\uparrow, n_m\rangle \tag{8.203}$$

while the right-hand side becomes

$$\begin{aligned}
\hat{H}\,|\Psi_E(t)\rangle &= (\hbar\omega_m\hat{a}^\dagger_m\hat{a}_m + \hbar\Omega\hat{S}_+\hat{S}_- + \hbar g^m\hat{S}_+\hat{a}_m + \hbar g^m\hat{S}_-\hat{a}^\dagger_m)\,(c_1\,|\downarrow, n_m+1\rangle + c_2\,|\uparrow, n_m\rangle)\\
&= \hbar\omega_m c_1(n_m+1)\,|\downarrow, n_m+1\rangle + \hbar\Omega c_1\cdot 0 + \hbar g^m c_1\,|\uparrow, n_m\rangle\sqrt{n_m+1} + \hbar g^m c_1\cdot 0\\
&\quad + \hbar\omega_m c_2 n_m\,|\uparrow, n_m\rangle + \hbar\Omega c_2\,|\uparrow, n_m\rangle + \hbar g^m c_2\cdot 0 + \hbar g^m c_2\,|\downarrow, n_m+1\rangle\sqrt{n_m+1}\\
&= \hbar\omega_m c_1(n_m+1)\,|\downarrow, n_m+1\rangle + \hbar g^m c_1\sqrt{n_m+1}\,|\uparrow, n_m\rangle\\
&\quad + \hbar\omega_m c_2 n_m\,|\uparrow, n_m\rangle + \hbar\Omega c_2\,|\uparrow, n_m\rangle + \hbar g^m c_2\sqrt{n_m+1}\,|\downarrow, n_m+1\rangle
\end{aligned} \tag{8.204}$$

Acting with $\langle\downarrow, n+1|$ on both sides,

$$\left.\begin{aligned}&\text{the left-hand side becomes} && i\hbar\dot{c}_1\\ &\text{the right-hand side becomes} && \hbar\omega_m c_1(n_m+1) + \hbar g^m c_2\sqrt{n_m+1}\end{aligned}\right\}\Rightarrow$$

$$i\dot{c}_1 = \omega_m(n_m+1)c_1 + g^m\sqrt{n_m+1}c_2 \tag{8.205}$$

Accordingly, acting with $\langle\uparrow, n|$ on both sides,

$$\left.\begin{aligned}&\text{the left-hand side becomes} && i\hbar\dot{c}_2\\ &\text{the right-hand side becomes} && \hbar g^m c_1\sqrt{n_m+1} + \hbar\omega_m c_2 n_m + \hbar\Omega c_2\end{aligned}\right\}\Rightarrow$$

$$i\dot{c}_2 = g^m\sqrt{n_m+1}c_1 + (n_m\omega_m + \Omega)c_2 \tag{8.206}$$

Thus, we obtain the System of Differential equations

$$i\begin{pmatrix}\dot{c}_1\\ \dot{c}_2\end{pmatrix} = \begin{pmatrix}(n_m+1)\omega_m & g^m\sqrt{n_m+1}\\ g^m\sqrt{n_m+1} & \Omega + n_m\omega_m\end{pmatrix}\begin{pmatrix}c_1\\ c_2\end{pmatrix} \tag{8.207}$$

Now, we define the **generalized Rabi frequency**

$$\boxed{\Omega_{n_m+1} := \left[\left(\frac{\omega_m - \Omega}{2}\right)^2 + g_m^2(n_m+1)\right]^{1/2}}. \tag{8.208}$$

or, omitting, for simplicity, the index m denoting the EM mode,

$$\boxed{\Omega_{n+1} := \left[\left(\frac{\omega - \Omega}{2}\right)^2 + g^2(n+1)\right]^{1/2}}. \tag{8.209}$$

The above System of Differential Equations (8.207) can be solved, e.g., with the eigenvalue method (see Appendix B.7), i.e. the same way we saw in Chapter 5. Performing the calculations for the problem of photon emission [i.e. for initial conditions $c_1(0) = 0, c_2(0) = 1$] yields

$$\boxed{|c_1(t)|^2 = \frac{(n+1)g^2}{\Omega_{n+1}^2}\sin^2(\Omega_{n+1}t)} \tag{8.210}$$

and

$$\boxed{|c_2(t)|^2 = 1 - |c_1(t)|^2 = 1 - \frac{(n+1)g^2}{\Omega_{n+1}^2}\sin^2(\Omega_{n+1}t)}. \tag{8.211}$$

Hence, from Equation 8.177 it follows that

$$\boxed{\langle \hat{a}_m^\dagger \hat{a}_m \rangle_{(E)} = n + \frac{g^2(n+1)}{\Omega_{n+1}^2}\sin^2(\Omega_{n+1}t)} \tag{8.212}$$

i.e. the average (expected) value of the photon number in the cavity as a function of time will perform oscillations. The index (E) denotes emission. Moreover, from Eq 8.178 it follows that

$$\boxed{\langle \hat{S}_+ \hat{S}_- \rangle_{(E)} = 1 - \frac{g^2(n+1)}{\Omega_{n+1}^2}\sin^2(\Omega_{n+1}t)} \tag{8.213}$$

i.e. the average (expected) value of the number of electrons at the upper level E_2 as a function of time will perform oscillations. Two examples of Rabi oscillations during photon absorption can be seen in Figure 8.8.

Since $\sin^2(\Omega_{n+1}t) = \frac{1}{2} - \frac{1}{2}\cos(2\Omega_{n+1}t)$, the period of these oscillations is

$$\boxed{T = \frac{2\pi}{2\Omega_{n+1}} = \frac{\pi}{\Omega_{n+1}} = \frac{\pi}{\left[\left(\frac{\omega-\Omega}{2}\right)^2 + g^2(n+1)\right]^{1/2}}} \tag{8.214}$$

Hence, when $\omega = \Omega$, i.e. at resonance, the period reaches its maximum at

$$T = \frac{\pi}{g\sqrt{n+1}}. \tag{8.215}$$

The maximum transfer percentage between the two levels, $\mathscr{A}$, is, as evident from Eqs. 8.213 and 8.208,

$$\mathscr{A} = \frac{g^2(n+1)}{\Omega_{n+1}^2} = \frac{g^2(n+1)}{\left(\frac{\omega-\Omega}{2}\right)^2 + g^2(n+1)} \tag{8.216}$$

Therefore,

- for $\Omega = \omega$ (resonance) $\Rightarrow \mathscr{A} = 1$
- for $\Omega \neq \omega$ (out of resonance) $\Rightarrow \mathscr{A} < 1$

To conclude, just like in the case of photon absorption, the number of photons in the cavity, n, the quantity g (Eq. 8.158) and the detuning, defined in Eq. 5.49 as $\Delta := \omega - \Omega$, determine the maximum transfer percentage and the period of oscillations.

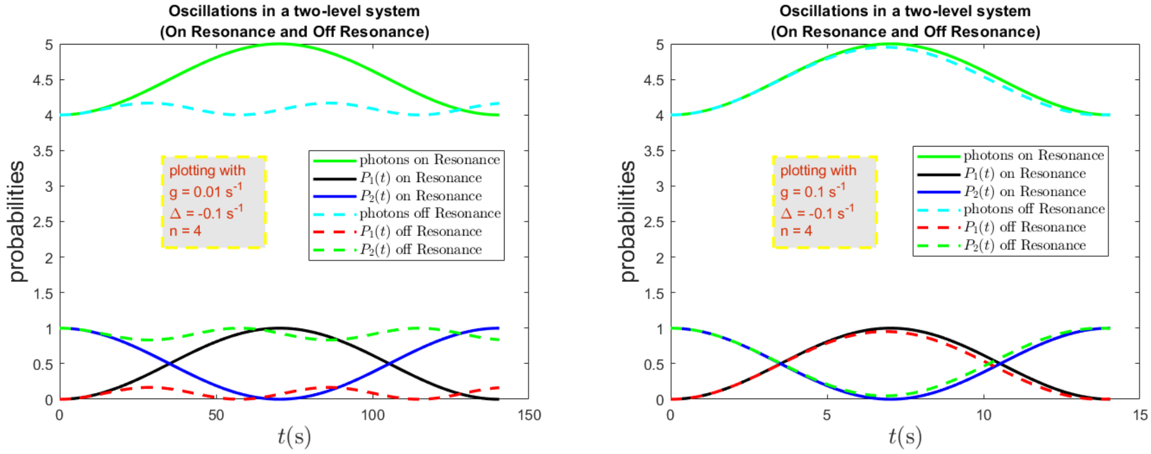


Figure 8.8: Two examples of Rabi oscillations during photon emission, i.e., the initial condition is 4 photons in the cavity and 1 electron at the upper level. We use some arbitrary values of the parameters to make an indicative figure. On the right, the two levels are tangled more strongly (the parameter g is larger). We present the temporal evolution of the expected value of the number of photons in the cavity, $\langle \hat{a}_m^\dagger \hat{a}_m \rangle_{(E)} = n + \frac{g^2(n+1)}{\Omega_{n+1}^2} \sin^2(\Omega_{n+1} t)$, both on resonance ($\Delta = 0$) and out of resonance ($\Delta \neq 0$), as well as of the expected value of the number of electrons at the lower level, $P_1(t) = \langle \hat{S}_+ \hat{S}_- \rangle = \frac{g^2(n+1)}{\Omega_{n+1}^2} \sin^2(\Omega_{n+1} t)$, and at the upper level, $P_2(t)$.

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CHAPTER 9

QUANTUM MECHANICAL APPROACH II

In this Chapter:
We continue with the quantum mechanical treatment. We discuss the analogy between the quantities, which describe Rabi oscillations in the semiclassical and in the full quantum mechanical approach. We describe the solution of the relevant differential equations with the general eigenvalue method for one and for many photons in the cavity. We continue by analyzing the boson (as photons are) commutation relations and the fermion (as electrons are) anticommutation relations and we clarify what commutation and anticommutation is. Also, we discuss somehow the ladder operators and the second quantization. Finally, we describe encyclopaedically the fifth state of matter, i.e., the Bose-Einstein condensate.
Prerequisite knowledge: Basic knowledge of Quantum Physics.

9.1 Photon absorption: analogy between the semiclassical and the quantum mechanical approach for quantities describing Rabi oscillations.

Let us recall the case of photon absorption within the *quantum mechanical* approach. We found that the expected value of both the number of electrons at each level and the number of photons inside the cavity perform Rabi oscillations with period (Eq. 8.196)

$$T = \frac{2\pi}{\sqrt{4g^2 n + (\omega - \Omega)^2}},$$

while, the maximum transfer percentage between the levels is (Eq. 8.198)

$$\mathscr{A} = \frac{g^2 n}{\Omega_n^2} = \frac{g^2 n}{\left(\frac{\omega-\Omega}{2}\right)^2 + g^2 n}.$$

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Kallipos, Open Academic Editions. https://dx.doi.org/10.57713/kallipos-186

Additionally, if we recall that in Eq. 8.163 we defined the Rabi frequency as

$$\Omega_R = \frac{g}{2\sqrt{n}},$$

we can easily realize that

$$\boxed{T = \frac{2\pi}{\sqrt{4g^2 n + (\omega - \Omega)^2}} = \frac{2\pi}{\sqrt{\Omega_R^2 + \Delta^2}}, \qquad \mathscr{A} = \frac{4g^2 n}{4g^2 n + \Delta^2} = \frac{\Omega_R^2}{\Omega_R^2 + \Delta^2}}. \tag{9.1}$$

These are the Equations 5.78 and 5.80, at which we arrived within the *semiclassical* approximation. Hence, there is a **complete analogy** between the semiclassical and quantum approximations.

9.2 Photon absorption: solution of the relevant differential equations with the eigenvalue method for one or many photons inside the cavity.

In Chapter 8 we presented the solutions of the problems of photon absorption and emission without performing the calculation. Here, we present some indicative calculations for photon absorption, considering two cases: the presence of a single photon inside the cavity and the presence of n photons inside the cavity.

As we have already seen, the problem is reduced to finding the eigenvalues and eigenvectors of the matrix (see Eq. 8.189)

$$A = \begin{pmatrix} n\omega & g\sqrt{n} \\ g\sqrt{n} & \Omega + (n-1)\omega \end{pmatrix}, \tag{9.2}$$

where we have omitted, for simplicity, the index m denoting the EM mode.

9.2.1 One photon inside the cavity.

In the case of a single photon inside the cavity, the form of the matrix is simplified, i.e.

$$A = \begin{pmatrix} \omega & g \\ g & \Omega \end{pmatrix}. \tag{9.3}$$

Its eigenvalues are found by the roots of the determinant

$$\det(A - \lambda \mathrm{I}),$$

where I is the unit 2×2 matrix. Thus,

$$(\omega - \lambda)(\Omega - \lambda) - g^2 = 0 \Rightarrow \lambda^2 - (\omega + \Omega)\lambda + \omega\Omega - g^2 = 0.$$

Therefore, the eigenvalues are

$$\boxed{\lambda_{2,1} = \frac{\omega + \Omega}{2} \pm \sqrt{\left(\frac{\omega - \Omega}{2}\right)^2 + g^2} := H_1 \pm \Omega_1}. \tag{9.4}$$

Let us now find the eigenvectors corresponding to these eigenvalues.

- For the eigenvalue $\lambda_1 = H_1 - \Omega_1$, we have

$$A\vec{v}_1 = \lambda_1 \vec{v}_1 \Rightarrow \begin{pmatrix} \omega & g \\ g & \Omega \end{pmatrix} \begin{pmatrix} v_{11} \\ v_{21} \end{pmatrix} = (H_1 - \Omega_1) \begin{pmatrix} v_{11} \\ v_{21} \end{pmatrix} \Rightarrow \left. \begin{aligned} g v_{21} &= (H_1 - \Omega_1 - \omega) v_{11} \\ g v_{11} &= (H_1 - \Omega_1 - \Omega) v_{21} \end{aligned} \right\}.$$

Substituting the second equation to the first one, it follows that

$$v_{21} = \frac{(H_1 - \Omega_1 - \omega)(H_1 - \Omega_1 - \Omega)}{g^2} v_{21}.$$

To obtain a non-trivial solution, the fraction that appears in the above equation must be equal to unity. Replacing the definitions of H_1 and Ω_1, we can easily find out that this is indeed the case. Hence, the choice of v_{21} is arbitrary (apart from zero) Let us choose $v_{21} = 1$. Then,

$$g v_{11} = (H_1 - \Omega_1 - \Omega) \Rightarrow v_{11} = \frac{\omega - \Omega - 2\Omega_1}{2g}$$

Hence, finally,

$$\vec{v}_1 = \begin{pmatrix} \frac{\omega-\Omega-2\Omega_1}{2g} \\ 1 \end{pmatrix}. \tag{9.5}$$

- For the eigenvalue $\lambda_2 = H_1 + \Omega_1$, using completely similar considerations, it follows that

$$\vec{v}_2 = \begin{pmatrix} \frac{\omega-\Omega+2\Omega_1}{2g} \\ 1 \end{pmatrix}. \tag{9.6}$$

We recall that the general solution has the form

$$\vec{x}(t) := \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \sigma_1 \vec{v}_1 e^{-i\lambda_1 t} + \sigma_2 \vec{v}_2 e^{-i\lambda_2 t},$$

where the coefficients σ_1, σ_2 are determined by the initial conditions. For photon absorption, these are $c_1(0) = 1, c_2(0) = 0$. Hence,

$$\left.\begin{aligned} 1 &= \sigma_1 \frac{\omega-\Omega-2\Omega_1}{2g} + \sigma_2 \frac{\omega-\Omega+2\Omega_1}{2g} \\ 0 &= \sigma_1 + \sigma_2 \Rightarrow \sigma_2 = -\sigma_1 \end{aligned}\right\} \Rightarrow 2g = \sigma_1(\omega - \Omega - 2\Omega_1) - \sigma_1(\omega - \Omega + 2\Omega_1) \Rightarrow$$

$$\sigma_1 = -\frac{g}{2\Omega_1} = -\sigma_2. \tag{9.7}$$

Therefore,

$$\begin{aligned} c_2(t) &= -\frac{g}{2\Omega_1} e^{-i(H_1-\Omega_1)t} + \frac{g}{2\Omega_1} e^{-i(H_1+\Omega_1)t} \\ &= -\frac{g}{2\Omega_1} e^{-iH_1 t} \left(e^{i\Omega_1 t} - e^{-i\Omega_1 t} \right) = -\frac{g}{\Omega_1} e^{-iH_1 t} i \sin(\Omega_1 t) \\ \Rightarrow c_2(t) &= e^{-i\frac{\omega+\Omega}{2}t} \left[-i\frac{g}{\Omega_1} \sin(\Omega_1 t) \right]. \end{aligned}$$

Thus, it follows that

$$\boxed{|c_2(t)|^2 = \frac{g^2}{\Omega_1^2} \sin^2(\Omega_1 t)} \tag{9.8}$$

and

$$\boxed{|c_1(t)|^2 = 1 - |c_2(t)|^2 = 1 - \frac{g^2}{\Omega_1^2} \cos^2(\Omega_1 t)}. \tag{9.9}$$

The above relationships are Eqs. 8.192 and 8.193, studied in Chapter 8 for the problem of photon absorption, in the case $n = 1$.

9.2.2 Mamy photons inside the cavity.

In the case of multiple (n) photons inside the cavity, we need to find the eigenvalues and eigenvectors of the matrix

$$A = \begin{pmatrix} n\omega & g\sqrt{n} \\ g\sqrt{n} & \Omega + (n-1)\omega \end{pmatrix}.$$

Its eigenvalues are found by the roots of the determinant

$$\det(A - \lambda \mathrm{I}),$$

where I is the unit 2 × 2 matrix. Thus,

$$\begin{aligned} (n\omega - \lambda)[\Omega + (n-1)\omega - \lambda] - ng^2 &= 0 \\ \Rightarrow \lambda^2 - [\Omega + (2n-1)\omega]\lambda + n\omega[\Omega + (n-1)\omega] - ng^2 &= 0. \end{aligned}$$

Therefore, the eigenvalues are

$$\boxed{\lambda_{2,1} = \frac{\Omega + (2n-1)\omega}{2} \pm \sqrt{\left(\frac{\omega - \Omega}{2}\right)^2 + ng^2} := H_n \pm \Omega_n}. \tag{9.10}$$

Let us now find the eigenvectors corresponding to these eigenvalues.

- For the eigenvalue $\lambda_1 = H_n - \Omega_n$, we have

$$\begin{aligned} A\vec{v}_1 = \lambda_1 \vec{v}_1 \Rightarrow \begin{pmatrix} n\omega & g\sqrt{n} \\ g\sqrt{n} & \Omega + (n-1)\omega \end{pmatrix} \begin{pmatrix} v_{11} \\ v_{21} \end{pmatrix} &= (H_n - \Omega_n) \begin{pmatrix} v_{11} \\ v_{21} \end{pmatrix} \\ \Rightarrow \left. \begin{aligned} g\sqrt{n} v_{21} &= (H_n - \Omega_n - n\omega) v_{11} \\ g\sqrt{n} v_{11} &= \{H_n - \Omega_n - [\Omega + (n-1)\omega]\} v_{21} \end{aligned} \right\}. \end{aligned}$$

  Substituting the second equation to the first one, it follows that

$$v_{21} = \frac{(H_n - \Omega_n - n\omega)\{H_n - \Omega_n - [\Omega + (n-1)\omega]\}}{ng^2} v_{21}.$$

  To obtain a non-trivial solution, the fraction that appears in the above equation must be equal to unity. Replacing the definitions of H_n and Ω_n, we can easily find out that this is indeed the case. Hence, the choice of v_{21} is arbitrary (apart from zero) Let us choose $v_{21} = 1$. Then,

$$g\sqrt{n} v_{11} = (H_n - \Omega_n - [\Omega + (n-1)\omega] \Rightarrow v_{11} = \frac{\omega - \Omega - 2\Omega_n}{2g\sqrt{n}}$$

  Hence, finally,

$$\vec{v}_1 = \begin{pmatrix} \frac{\omega - \Omega - 2\Omega_n}{2g\sqrt{n}} \\ 1 \end{pmatrix}. \tag{9.11}$$

- For the eigenvalue $\lambda_2 = H_n + \Omega_n$, using completely similar considerations, it follows that

$$\vec{v}_2 = \begin{pmatrix} \frac{\omega - \Omega + 2\Omega_n}{2g\sqrt{n}} \\ 1 \end{pmatrix}. \tag{9.12}$$

We recall that the general solution has the form

$$\vec{x}(t) := \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \sigma_1 \vec{v}_1 e^{-i\lambda_1 t} + \sigma_2 \vec{v}_2 e^{-i\lambda_2 t},$$

where the coefficients σ_1, σ_2 are determined by the initial conditions. For photon absorption, these are $c_1(0) = 1, c_2(0) = 0$. Hence,

$$\left.\begin{aligned} 1 &= \sigma_1 \frac{\omega-\Omega-2\Omega_n}{2\sqrt{ng}} + \sigma_2 \frac{\omega-\Omega+2\Omega_n}{2\sqrt{ng}} \\ 0 &= \sigma_1 + \sigma_2 \Rightarrow \sigma_2 = -\sigma_1 \end{aligned}\right\} \Rightarrow \sigma_1 \frac{-4\Omega_n}{2\sqrt{ng}} = 1 \Rightarrow \sigma_1 = -\frac{g\sqrt{n}}{2\Omega_n} = -\sigma_2.$$

Therefore,

$$\begin{aligned} c_2(t) &= -\frac{g\sqrt{n}}{2\Omega_n} e^{-i(H_n-\Omega_n)t} + \frac{g\sqrt{n}}{2\Omega_n} e^{-i(H_n+\Omega_n)t} \\ &= -\frac{g\sqrt{n}}{2\Omega_n} e^{-iH_n t}\left(e^{i\Omega_n t} - e^{-i\Omega_n t}\right) = -\frac{g\sqrt{n}}{\Omega_n} e^{-iH_n t} i \sin(\Omega_n t) \\ \Rightarrow c_2(t) &= e^{-i\frac{\Omega+(2n-1)\omega}{2}t}\left[-i\frac{g\sqrt{n}}{\Omega_n}\sin(\Omega_n t)\right]. \end{aligned}$$

Thus, it follows that

$$\boxed{|c_2(t)|^2 = \frac{ng^2}{\Omega_n^2}\sin^2(\Omega_1 t)} \tag{9.13}$$

and

$$\boxed{|c_1(t)|^2 = 1 - |c_2(t)|^2 = 1 - \frac{ng^2}{\Omega_n^2}\cos^2(\Omega_n t)}. \tag{9.14}$$

The above relationships are Eqs. 8.192 and 8.193, studied in Chapter 8 for the problem of photon absorption.

9.3 Commutation relations for bosons and anticommutation relations for fermions.

Let us call $\hat{a}_m$ the **boson** annihilation operator and $\hat{a}_m^\dagger$ the **boson** creation operator at the state or mode m. For bosons, the following commutation relations hold:

$$\begin{aligned} [\hat{a}_m, \hat{a}_\ell^\dagger] &= \delta_{ml} \\ [\hat{a}_m, \hat{a}_\ell] &= 0 \\ [\hat{a}_m^\dagger, \hat{a}_\ell^\dagger] &= 0 \end{aligned} \tag{9.15}$$

$[A, B]$ or $[A, B]_-$ is the commutator, defined as

$$[A, B] = AB - BA, \tag{9.16}$$

hence, when $[A, B] = 0 \Rightarrow AB - BA = 0 \Rightarrow AB = BA$, i.e., the quantities A and B commute, which shows the name origin.

Let us call $\hat{\mathrm{a}}_i$ the **fermion** annihilation operator and $\hat{\mathrm{a}}_i^\dagger$ the **fermion** creation operator at state i. Then, for fermions, the following anticommutation relations hold:

$$\begin{aligned} \{\hat{\mathrm{a}}_i, \hat{\mathrm{a}}_j^\dagger\} &= \delta_{ij} \\ \{\hat{\mathrm{a}}_i, \hat{\mathrm{a}}_j\} &= 0 \\ \{\hat{\mathrm{a}}_i^\dagger, \hat{\mathrm{a}}_j^\dagger\} &= 0 \end{aligned} \tag{9.17}$$

$\{A, B\}$ or $[A, B]_+$ is the Poisson bracket or anticommutator, defined as

$$\{A, B\} = AB + BA, \tag{9.18}$$

hence, when $\{A, B\} = 0 \Rightarrow AB + BA = 0 \Rightarrow AB = -BA$, i.e., the quantities A and B anticommute, which shows the name origin. If we apply the relation $\{\hat{a}_i^\dagger, \hat{a}_j^\dagger\} = 0$ for the same state, e.g. putting $i = j = r$, we obtain $\{\hat{a}_r^\dagger, \hat{a}_r^\dagger\} = 0 \Rightarrow \hat{a}_r^\dagger \hat{a}_r^\dagger = 0$, which means that we cannot put two fermions at the same state, which is the Pauli exclusion principle.

9.4 Ladder operators.

In linear algebra as well as in its applications in quantum mechanics, we define the raising operator, which increases the eigenvalue of another operator, and the lowering operator, which decreases the eigenvalue of another operator. These are collectively called ladder operators. In quantum mechanics, the raising operator is frequently called creation operator, and the lowering operator is frequently called annihilation operator. Well-known applications of ladder operators are in the simple harmonic oscillator and in angular momentum. In quite a few areas of physics and chemistry, the use of these operators instead of wavefunctions is known as second quantization.

9.5 Bose-Einstein condensate.

The **Bose - Einstein condensate** (BEC) is a state of a boson gas cooled to temperatures close to absolute zero (0 K or −273.15 °C). Under such conditions, many bosons occupy the same quantum state. Then, quantum phenomena are reflected at the macroscopic scale. This state of matter was predicted by **Satyendra Nath Bose** [1] and **Albert Einstein** [2, 3]. Bose, not being able to publish his paper regarding the statistics of light quanta (which are now called photons), sent the work to Einstein, who understood its value and helped him publish it by submitting it on behalf of Bose [1]. Let us note that the photon has spin $s = \hbar$. In the following years, Einstein worked on the subject as well [2, 3], and extended Bose's ideas to other, more complex particles with mass, whose spin s is a natural multiple $(0, 1, 2, \dots)$ of $\hbar$.

The result of the efforts by Bose and Einstein is the concept of the **Bose gas**, which is governed by the so-called Bose-Einstein statistics that describe the distribution of identical particles whose spin is a natural multiple $(0, 1, 2, \dots)$ of $\hbar$. Today, these particles are called **bosons**. Bosons do not obey to any exclusion principles such as the Pauli's exclusion principle that holds for fermions. Hence, two or more bosons can occupy the same quantum state or, stated otherwise, any number of bosons can be described by the same wavefunction; this is called **boson condensation**. Cooling bosons at very low temperatures causes them to drop into the lowest available quantum state, i.e., they are "condensed", which leads to a new state of matter. Thus, in the case of bosons, **coherent waves** with macroscopic amplitudes can be constructed. Such waves can be described classically. For example, photons are bosons and the respective classical field is our familiar electromagnetic field which satisfies the Maxwell equations. This is how any number of photons can occupy the same quantum state, as it happens inside lasers.

The carriers of interactions, the **Higgs boson**, the -more complex- **mesons**, and even **larger particles** whose total angular momentum is a natural multiple of $\hbar$, all fall into the category of **bosons**. This is the case even for **whole atoms**.

For example, ${}^4_2$He has a nucleus consisting of two protons and two neutrons. Both protons and neutrons are baryons are composite fermions, with spin $\frac{\hbar}{2}$. However, they are configured in a way such that the total nuclear angular momentum is $\mathrm{I} = 0$. Hence, the ${}^4_2$He nucleus is a boson. Moreover, ${}^4_2$He has also two electrons, which are fermions with spin $\frac{\hbar}{2}$. However, these two electrons are placed in the 1s subshell (which corresponds to angular momentum $L = 0$) with opposite spins, so that the total electron angular momentum is $J = 0$. Therefore, since $I = 0$ and $J = 0$, it follows that the atomic spin of $^{4}_{2}$He is $F = I + J = 0$. In other words, the neutral $^{4}_{2}$He atom is a boson. Hence, many $^{4}_{2}$He atoms can occupy the same quantum state at very low temperatures (BEC).

Thus, some atoms like $^{4}_{2}$He have a total atomic angular momentum that is a natural multiple of $\hbar$, i.e. are bosons and follow the Bose-Einstein statistics, hence they can occupy the same quantum state (condensate) and create coherent waves with macroscopic amplitudes! Moreover, in analogy with the laser, in which multiple photons can occupy the same state, an "atom laser" can be constructed [4]. The first one was developed at MIT by W. Ketterle's group in 1996. We might also add all the "atomic spins" to obtain a "molecular spin" or even add all the "molecular spins" and so on.

Maybe the most impressive demonstration of BEC is the condensation of alkali atomic gases (e.g. rubidium [5] and sodium [6]) whose spin is a natural multiple of $\hbar$. Previously, demonstrations of BEC appeared in more complex systems, in low temperatures. On the contrary, when BEC was discovered in cooled alkali vapors in 1995 (Figure 9.1), the experimental evidence was very strong. Additionally, the interference between two atomic Na Bose-Einstein condensates, with distance $40\ \mu\mathrm{m}$ was observed for the first time [7]; in specific, interference fringes with period $15\ \mu\mathrm{m}$ occurs, which showed that Na atoms behave just like photons in lasers, i.e. they are coherent. Images of interference patterns for beams of atoms in BEC state can be found at the webpages of Atomic Quantum Gases @ MIT[1]. The first pulsed atom laser was constructed in 1997, while, in 2010, BEC of photons in a cavity was demonstrated [8].

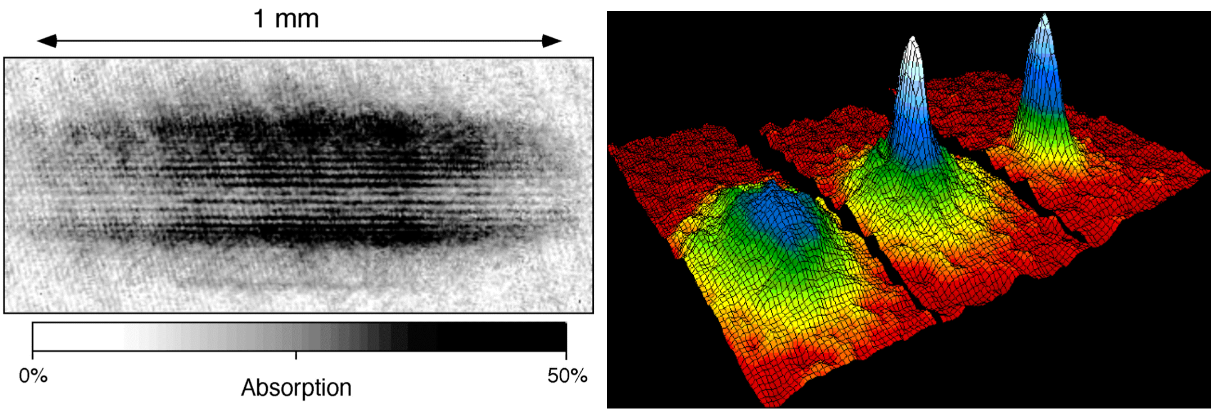

Figure 9.1: (Left). Interference pattern of beams of atoms in BEC state. More images like this can be found at the webpages of Atomic Quantum Gases @ MIT. This image (`https://www.rle.mit.edu/cua_pub/ketterle_group/Projects_1997/Interference/Straight_Int.jpg`) belongs to the MIT group and is a courtesy of Professor Wolfgang Ketterle. (Right). Colored representation of the velocity distribution of a $^{87}_{37}$Rb atomic vapor BEC as the temperature decreases. From left to right: just before BEC has occurred, just after BEC has occurred and an almost pure BEC [5]. Image from [9].

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CHAPTER 10

DENSITY MATRIX AND OPERATOR

In this Chapter:
We are introduced to the discussion about the density matrix and the density operator. We discriminate between pure states and mixed states. We focus on the density matrix and the density operator of a two-level system. We continue by analyzing the temporal evolution of the density matrix with the von Neumann equation. Finally, we discuss the form of the temporal evolution of the density matrix in the presence of decay mechanisms
Prerequisite knowledge: Basic knowledge of Quantum Physics.

10.1 Pure state and mixed state.

Maybe in all quantum mechanics studied by the reader so far, the examined cases involved a wavefunction, say $\Psi(\vec{r}, t)$, that describes the system under study. Then, $|\Psi(\vec{r}, t)|^2$ is the probability that the coordinates lie close to the position $\vec{r}$ at time t. This wavefunction can be obtained, at least in principle, by the Schrödinger equation. Since the wavefunction is known, we can calculate the expected value of any given operator $\hat{A}$, as $\langle \hat{A} \rangle = \langle \Psi | \hat{A} | \Psi \rangle$. This is commonly done by finding a complete basis, say $\{\Phi_k(\vec{r})\}$, where k is some collective quantum number able to describe the system. We usually study finite systems, hence k can be considered as discrete, and we can use sums $\sum_k$; however, in other cases k could be continuous, hence we would use integrals $\int dk$. If our basis is complete, then the wavefunction can be written as a linear combination of the form

$$\Psi(\vec{r}, t) = \sum_k c_k(t) \Phi_k(\vec{r}). \tag{10.1}$$

Therefore, the problem is reduced to obtaining the coefficients $c_k(t)$. When they have been obtained, the expected value of the operator $\hat{A}$ is (for calculations, see Appendix B.6)

$$\langle \hat{A} \rangle = \langle \Psi(t) | \, \hat{A} \, | \Psi(t) \rangle = \sum_{k,k'} c_k(t) c^*_{k'}(t) A_{k'k} \Rightarrow \tag{10.2}$$

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$$\boxed{\langle \hat{A} \rangle = \sum_{k,k'} \rho_{kk'}(t) A_{k'k}}, \tag{10.3}$$

where $A_{kk'}$ is the matrix element of the operator $\hat{A}$ between states $|\Phi_k\rangle$ and $|\Phi'_k\rangle$, and we have defined

$$\boxed{\rho_{kk'}(t) = c_k(t) c^*_{k'}(t)}. \tag{10.4}$$

Hence, in principle, everything can be calculated. Such a scenario, in which the system is described by one wavefunction is called a **pure state** [1].

However, it is not always possible to describe a system by a single wavefunction. In many cases the system of interest is coupled to a reservoir (R) with which it exchanges heat, particles, etc. If the total (T) system, i.e. the system of interest plus the reservoir, is isolated, then we can define a wavefunction for the total system, say $\Psi_{\mathrm{T}}(\vec{r}, \vec{r}_{\mathrm{R}}, t)$. In the absence of interactions, this wavefunction could be separated into a product $\Psi(\vec{r}, t)\Psi_{\mathrm{R}}(\vec{r}_{\mathrm{R}}, t)$, which shows that what the system of interest is doing is independent to what the reservoir is doing, since the two do not interact with each other. Then, we can isolate $\Psi(\vec{r}, t)$ as the wavefunction of the system of interest. On the other hand, if the system of interest interacts with the reservoir, then we cannot separate its wavefunction from the one of the reservoir. However, we might not want to work with $\Psi_{\mathrm{T}}(\vec{r}, \vec{r}_{\mathrm{R}}, t)$, since it contains all the information about what the reservoir is doing; this may not interest us or we may not need it or it may be extremely complex. This raises the following question: How can we address such cases, in which there is no well-defined wavefunction for the system of interest? Such a scenario, in which there is no well-defined wavefunction for the system of interest is called a **mixed state** [1].

However, even in such scenarios, there is a route to follow. We will assume that the system of interest it at the state described by the wavefunction $\Psi_i(\vec{r}, t)$ with probability w_i. In other words, instead of saying that the system of interest is certainly in a specific state, described by a specific wavefunction, we allow it to lie in different states, described by different wavefunctions, with different probabilities. Of course, the total probability must be equal to unity, i.e.

$$\sum_i w_i = 1. \tag{10.5}$$

In this mixed state, the expected value of an operator $\hat{A}$ is

$$\langle \hat{A} \rangle = \sum_i w_i \langle \hat{A} \rangle_i , \tag{10.6}$$

since the system has a probability w_i to be in state $\Psi_i(\vec{r}, t)$, in which the expected value of the operator $\hat{A}$ is

$$\langle \hat{A} \rangle_i = \langle \Psi_i(t) | \hat{A} | \Psi_i(t) \rangle = \int d^3 r \Psi^*_i(\vec{r}, t) \hat{A} \Psi_i(\vec{r}, t). \tag{10.7}$$

More detailed calculations can be found in Appendix B.6. However, each of the possible wavefunctions $\Psi_i(\vec{r}, t)$ can be expanded using a complete basis $\{\Phi_k(\vec{r})\}$ as

$$\Psi_i(\vec{r}, t) = \sum_k c^i_k(t) \Phi_k(\vec{r}), \tag{10.8}$$

with

$$\sum_k |c^i_k(t)|^2 = 1. \tag{10.9}$$

Hence, if we know the coefficients $c_k^i(t)$ and probabilities w_i, we can write

$$\begin{aligned}\langle\hat{A}\rangle &= \sum_i w_i \int d^3r \sum_{k'} c_{k'}^{i*}(t)\Phi_{k'}^*(\vec{r})\hat{A}\sum_k c_k^i(t)\Phi_k(\vec{r}) \\ &= \sum_i w_i \sum_{k,k'} c_{k'}^{i*}(t)c_k^i(t)\int d^3r\Phi_{k'}^*(\vec{r})\hat{A}\Phi_k(\vec{r}) \\ &= \sum_i w_i \sum_{k,k'} c_{k'}^{i*}(t)c_k^i(t)A_{k'k} = \sum_{k,k'}\left[\sum_i w_i c_k^i(t)c_{k'}^{i*}(t)\right]A_{k'k} \Rightarrow\end{aligned}$$

$$\boxed{\langle\hat{A}\rangle = \sum_{k,k'}\rho_{kk'}(t)A_{k'k}}, \tag{10.10}$$

where we have defined

$$\boxed{\rho_{kk'}(t) = \sum_i w_i c_k^i(t)c_{k'}^{i*}(t)}. \tag{10.11}$$

We observe that Eq. 10.4, which holds for a pure state, is a partial case of Eq. 10.11, which holds for a mixed state. In other words, when we are at a pure state, then there is only one possible i with $w_i = 1$, so that Eq. 10.11 becomes identical to Eq. 10.4. With this in mind, the expression of Eqs. 10.3, 10.10, which give the expected value of $\hat{A}$, become identical, as well. The matrix ρ, whose elements are given by Eqs. 10.4, 10.11 is called the **density matrix**. So, we can see that both pure and mixed states can be described with the help of the density matrix.

10.2 Density matrix and density operator.

The **density matrix** ρ, which is a representation of the **density operator** $\hat{\rho}$, constitutes a more general description of a quantum system than the description we commonly use with the help of the wavefunctions $\Psi(\vec{r}, t)$ or the state vectors $|\Psi(t)\rangle$. The terms density matrix and density operators are often used interchangeably, in a loose sense. The density matrix and density operator, as a formalism, were introduced independently by John von Neumann [2] and Lev Landau [3] in 1927. Both the matrix and the operator are Hermitian and have a unit trace [4].

While a wavefunction or a state vector is enough to describe a quantum system in a pure quantum state, the density matrix can also describe a quantum system in a mixed quantum state. For example, it is also useful in cases of decoherence due to the interactions between the system of interest and a reservoir with which it exchanges energy or particles.

Eqs. 10.3, 10.10 show that, to calculate expected values of operators, we only need the quantities $\rho_{kk'}(t)$ of Eqs. 10.4, 10.11 instead of all possible Ψ_i and w_i. Since expected values is, in final analysis, all we are looking for, all the useful information about the system of interest is encoded in the elements of the density matrix, $\rho_{kk'}(t)$. Therefore, the density operator $\hat{\rho}$ can be defined in a way such that

$$\boxed{\langle\Phi_k(\vec{r})|\hat{\rho}(t)|\Phi_{k'}(\vec{r})\rangle = \rho_{kk'}(t)}. \tag{10.12}$$

Using this definition, Eqs. 10.3, 10.10 are written as

$$\boxed{\langle\hat{A}\rangle = \sum_{k,k'}\rho_{kk'}(t)A_{k'k} = \mathrm{Tr}(\rho(t)\cdot A)}. \tag{10.13}$$

We denote by Tr the sum of the diagonal elements of a square matrix. This is called the trace of a matrix. Eq. 10.13 holds because $\sum_{k'} \rho_{kk'}(t)A_{k'k}$ is the diagonal, kk, element of the matrix that occurs by multiplying the matrices $\rho(t)$ and A. Thus, if we add up these diagonal elements, i.e. if we take the sum over k, we obtain the trace of $\rho(t) \cdot A$, which is denoted by $\mathrm{Tr}(\rho(t) \cdot A)$. The trace of a matrix is equal to the sum of its eigenvalues and remains unchanged if we choose another basis. Let us see some properties of the density operator.

1. We can give an alternative definition of the density matrix for a pure state, i.e. Eq. 10.4 can also be written as

$$\boxed{\hat{\rho} = |\Psi\rangle\langle\Psi|}, \tag{10.14}$$

since, the representation

$$|\Psi\rangle = \begin{bmatrix} c_1(t) \\ c_2(t) \\ \vdots \end{bmatrix},$$

which implies

$$\langle\Psi| = \begin{bmatrix} c_1^*(t) & c_2^*(t) & \cdots \end{bmatrix},$$

yields

$$|\Psi\rangle\langle\Psi| = \begin{bmatrix} c_1(t) \\ c_2(t) \\ \vdots \end{bmatrix} \begin{bmatrix} c_1^*(t) & c_2^*(t) \cdots & \end{bmatrix} = \begin{bmatrix} c_1(t)c_1^*(t) & c_1(t)c_2^*(t) & \cdots \\ c_2(t)c_1^*(t) & c_2(t)c_2^*(t) & \cdots \\ \vdots & \vdots & \end{bmatrix} = \rho \tag{10.15}$$

2. The probability to find the system at the state ℓ of the basis $\{\Phi_k(r)\}$ is $\rho_{\ell\ell}(t)$. This follows by the definition of Eq. 10.11 for $k = k' = \ell$. That is,

$$\rho_{\ell\ell}(t) = \sum_i w_i c_\ell^i(t) c_\ell^{i*}(t) = \sum_i w_i |c_\ell^i(t)|^2. \tag{10.16}$$

Each term in this some is the probability to find the system at state i *times* the probability, being in i, to find it at the state ℓ of the basis $\{\Phi_k(r)\}$. Therefore, the sum is the total probability to find the system at the state ℓ of the basis $\{\Phi_k(r)\}$.

3. The trace of the density matrix is equal to unity, i.e.

$$\mathrm{Tr}(\rho(t)) = 1. \tag{10.17}$$

This follows from Eq. 10.16 by summing over ℓ, i.e.

$$\sum_\ell \rho_{\ell\ell}(t) = \sum_\ell \sum_i w_i |c_\ell^i(t)|^2 = \sum_i w_i \sum_\ell |c_\ell^i(t)|^2 = \sum_i w_i = 1, \tag{10.18}$$

since $\sum_\ell |c_\ell^i(t)|^2 = 1$ (Eq. 10.9) and $\sum_i w_i = 1$ (Eq. 10.5). Alternatively, we can consider Eq. 10.13 for $\hat{A} = \hat{1}$, where $\hat{1}$ is the unit operator, hence

$$\langle\hat{1}\rangle = \mathrm{Tr}(\rho(t) \cdot 1) = \mathrm{Tr}(\rho(t)) \tag{10.19}$$

and observe that the expected value of the unit operator is 1. This property essentially replaces the normalization condition for the wavefunction of a system at a pure state.

4. The density operator is Hermitian, $\hat{\rho} = \hat{\rho}^\dagger$, i.e. for the elements of the density matrix it holds that $\rho_{kk'} = \rho_{k'k}^*$. This can occur directly, by obtaining the complex conjugate of Eqs.. 10.4, 10.11.

5. The density operator $\hat{\rho}$ is positive semidefinite, i.e. the eigenvalues of ϱ are ≥ 0. This can be obtained as follows: Since the operator $\hat{\rho}$ is Hermitian, there is a complete basis $\{\Phi_n(\vec{r})\}$ such that the matrix ρ is diagonal. Since the operator $\hat{\rho}$ is Hermitian, its eigenvalues must be real. From property 2., we know that these eigenvalues, which are the diagonal elements of ρ using the basis, represent probabilities, hence they are not only real, but also positive or zero. Since the matrix ρ is diagonal in this basis, $\rho_{n,n'} = \delta_{n,n'}\varrho_n$, ϱ_n is the respective eigenvalue, which, using property 2., is also the probability to find the system at state n.

6. $\mathrm{Tr}(\rho^2) \leq 1$. This can be shown as follows: Since the trace does not depend on the basis we use, let us calculate it in the basis that makes ρ diagonal, i.e. in $\{\Phi_n(\vec{r})\}$. Therefore, $\mathrm{Tr}(\rho^2) = \sum_n \varrho_n^2$. However, ϱ_n are probabilities, hence $0 \leq \varrho_n \leq 1$. Thus, $\sum_n \varrho_n^2 \leq (\sum_n \varrho_n)^2 = \mathrm{Tr}^2(\rho) = 1^2 = 1$.

7. If the system is at a pure state, then $\mathrm{Tr}(\rho^2) = 1$. This is due to property 1. That is, for a pure state Eq. 10.14,

   $$\hat{\rho} = |\Psi\rangle\langle\Psi|,$$

   holds, thus,

   $$\hat{\rho}^2 = |\Psi\rangle\,\langle\Psi|\Psi\rangle\langle\Psi| = |\Psi\rangle\langle\Psi| = \hat{\rho}.$$

   Hence, $\mathrm{Tr}(\rho^2) = \mathrm{Tr}(\rho) = 1$, due to property 3. Therefore, the value of $\mathrm{Tr}(\rho^2)$ tells us whether the system is at a pure state $(\mathrm{Tr}(\rho^2) = 1)$ or a mixed state $(\mathrm{Tr}(\rho^2) < 1)$.

Finally, we need something analogous to the Schrödinger equation. When we are at a pure state, the Schrödinger equation allows us to find the wavefunction at any given time, since we know it at the initial time. We would like to have a similar equation which yields $\hat{\rho}(t)$, given that we know $\hat{\rho}(0)$. This equation exists, is called the Liouville-von Neumann equation, and has the form

$$i\hbar\frac{\partial\hat{\rho}(t)}{\partial t} = [\hat{H}, \hat{\rho}(t)]\,, \tag{10.20}$$

where [,] denotes the commutator and $\hat{H}$ is the Hamiltonian of the system. See Eqs. 10.31 or 10.39 below. We have to notice that this equation can be used only as long as the Hamiltonian of the system exists (i.e. the system is isolated). If the system interacts with a reservoir, then we have to include the result of the interaction within the evolution of the density operator. See, for example Eq. 10.53.

10.3 Density matrix and density operator for a two-level system at a pure state.

Following the notation we used in previous chapters, the state of a two-level system can be described by the equation

$$|\Psi(t)\rangle = c_1(t)\,|{\downarrow}\rangle + c_2(t)\,|{\uparrow}\rangle = c_1(t)\,|\Phi_1\rangle + c_2(t)\,|\Phi_2\rangle\,. \tag{10.21}$$

Multiplying by $\langle\vec{r}|$,

$$\langle\vec{r}|\Psi(t)\rangle = c_1(t)\,\langle\vec{r}|{\downarrow}\rangle + c_2(t)\,\langle\vec{r}|{\uparrow}\rangle = c_1(t)\,\langle\vec{r}|\Phi_1\rangle + c_2(t)\,\langle\vec{r}|\Phi_2\rangle\,,$$

we obtain the spatial representation

$$\Psi(\vec{r}, t) = c_1(t)\Phi_1(\vec{r}) + c_2(t)\Phi_2(\vec{r}). \tag{10.22}$$

Thus, the probability to find the electron at the ground or the excited level is expressed by

$$\boxed{|c_1(t)|^2 = c_1(t)\,c_1(t)^* \quad \text{and} \quad |c_2(t)|^2 = c_2(t)\,c_2(t)^*} \tag{10.23}$$

Let us calculate the average value of the dipole moment at state 10.22. Since $\hat{\vec{p}} = -e\hat{\vec{r}} = -e\vec{r}$, we have

$$\begin{aligned}\langle\hat{\vec{p}}\rangle &= \int dV \ \left(c_1^*(t)\Phi_1^*(\vec{r}) + c_2^*(t)\Phi_2^*(\vec{r})\right) \ (-e\vec{r}) \ \left(c_1(t)\Phi_1(\vec{r}) + c_2(t)\Phi_2(\vec{r})\right) \\ &= |c_1(t)|^2 \int dV\Phi_1^*(\vec{r})(-e\vec{r})\Phi_1(\vec{r}) + c_1^*(t)c_2(t) \int dV\Phi_1^*(\vec{r})(-e\vec{r})\Phi_2(\vec{r}) \\ &\quad + c_2^*(t)c_1(t) \int dV\Phi_2^*(\vec{r})(-e\vec{r})\Phi_1(\vec{r}) + |c_2(t)|^2 \int dV\Phi_2^*(\vec{r})(-e\vec{r})\Phi_2(\vec{r}).\end{aligned}$$

Therefore,

$$\langle\hat{\vec{p}}\rangle = c_1^*(t)c_2(t)\vec{p}_{12} + c_2^*(t)c_1(t)\vec{p}_{21}, \tag{10.24}$$

since

$$\int dV\Phi_1^*(\vec{r})(-e\vec{r})\Phi_1(\vec{r}) = 0 \quad \text{and} \quad \int dV\Phi_2^*(\vec{r})(-e\vec{r})\Phi_2(\vec{r}) = 0,$$

while

$$\begin{aligned}\vec{p}_{12} &= \int dV\Phi_1^*(\vec{r})(-e\vec{r})\Phi_2(\vec{r}) \\ \vec{p}_{21} &= \int dV\Phi_2^*(\vec{r})(-e\vec{r})\Phi_1(\vec{r}).\end{aligned}$$

And, since

$$\vec{p}_{21} = \vec{p}_{12}^{\,*},$$

the average value of the dipole moment, $\langle\hat{\vec{p}}\rangle$, is a real number, as a sum of two complex conjugate numbers.

Eq. 10.24 contains the quantities

$$\boxed{c_1(t)^*c_2(t) \quad \text{and} \quad c_2(t)^*c_1(t)}. \tag{10.25}$$

Eq. 10.23 contains the "diagonal elements" and Eq. 10.25 contains the "off-diagonal elements" of the 2×2 (in this case) density matrix, which has the form

$$\boxed{\rho = \begin{bmatrix} c_1c_1^* & c_1c_2^* \\ c_2c_1^* & c_2c_2^* \end{bmatrix} = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix},} \tag{10.26}$$

where we have omitted time-dependence, which is implied. In other words the density matrix element is

$$\boxed{\rho_{nm} := c_nc_m^*}. \tag{10.27}$$

And, since we can use the representation

$$|\Psi\rangle = \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \tag{10.28}$$

and

$$\langle\Psi| = \begin{bmatrix} c_1^* & c_2^* \end{bmatrix}, \tag{10.29}$$

it follows that

$$|\Psi\rangle\langle\Psi| = \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}\begin{bmatrix} c_1^* & c_2^* \end{bmatrix} = \begin{bmatrix} c_1c_1^* & c_1c_2^* \\ c_2c_1^* & c_2c_2^* \end{bmatrix} = \rho. \tag{10.30}$$

10.4 Time evolution of the density matrix: the von Neumann equation.

The von Neumann or Liouville-von Neumann equation describes the time-evolution of the density matrix. It has the form

$$i\hbar\frac{\partial\hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}]\,, \tag{10.31}$$

where [,] denotes the commutator.

Let us now prove Eq. 10.31. From Eq. 10.27 it follows that the rate of change for a density matrix element is

$$\dot{\rho}_{nm} = \dot{c}_n c_m^* + c_n \dot{c}_m^*. \tag{10.32}$$

Of course * and $\dot{}$ can be performed in any order, since e.g., if $z = \alpha + i\beta, z \in \mathbb{C}, \alpha, \beta \in \mathbb{R}$, then $z^* = \alpha - i\beta$, $\dot{z} = \dot{\alpha} + i\dot{\beta}$, and $(\dot{z^*}) = \dot{\alpha} - i\dot{\beta} = (\dot{z})^*$. From the Schrödinger equation

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

and Eq. 10.22, it follows that

$$i\hbar\dot{c}_n = \sum_k c_k H_{nk}. \tag{10.33}$$

We used the definition of the matrix element of an operator (Eq. 5.29) and the orthonormality of $\Phi_k(\vec{r})$, i.e. $\int dV \Phi_n(\vec{r})^* \Phi_k(\vec{r}) = \delta_{nk}$. Thus,

$$-i\hbar\dot{c}_n^* = \sum_k c_k^* H_{nk}^*. \tag{10.34}$$

But $H_{nk}^* = H_{kn}$, since the Hamiltonian is a Hermitian operator. Combining the above, the time evolution of the density matrix element occurs as

$$\boxed{i\hbar\dot{\rho}_{nm} = \sum_k (H_{nk}\rho_{km} - \rho_{nk}H_{km})}\,. \tag{10.35}$$

In a somewhat different formulation, if we consider the temporal evolution of the general definition (Eq. 10.14), it follows that

$$\dot{\hat{\rho}} = |\dot{\Psi}\rangle\langle\Psi| + |\Psi\rangle\langle\dot{\Psi}|, \tag{10.36}$$

while, from the Schrödinger equation

$$i\hbar|\dot{\Psi}\rangle = \hat{H}\,|\Psi\rangle \tag{10.37}$$

it follows that

$$-i\hbar\langle\dot{\Psi}| = \langle\Psi|\,\hat{H}^\dagger. \tag{10.38}$$

But $\hat{H}^\dagger = \hat{H}$, since the Hamiltonian is a Hermitian operator. Combining the above, the time evolution of the density matrix occurs as

$$i\hbar\dot{\hat{\rho}} = \hat{H}\,|\Psi\rangle\langle\Psi| - |\Psi\rangle\langle\Psi|\,\hat{H} = \hat{H}\hat{\rho} - \hat{\rho}\hat{H},$$

or, more concisely,

$$\boxed{i\hbar\dot{\hat{\rho}} = [\hat{H}, \hat{\rho}]}\,, \tag{10.39}$$

which is Eq. 10.31.

We notice that, according to the definition of the matrix element of an operator (Eq. 5.29),

$$H_{nk} = \int dV \Phi_n(\vec{r})^* \hat{H} \Phi_k(\vec{r}). \tag{10.40}$$

Consider the Hamiltonian of a perturbed two-level sytem, as in Eq. 5.18,

$$\hat{H} = \hat{H}_0 + U_{\mathscr{E}}(\vec{r}, t),$$

where $U_{\mathscr{E}}(\vec{r}, t)$ is the potential energy of the perturbation and $\hat{H}_0$ is the Hamiltonian of the unperturbed two-level system. Then, Eqs. 10.40 and. 5.18 yield

$$\begin{aligned} H_{nk} &= \int dV \Phi_n(\vec{r})^* \hat{H}_0 \Phi_k(\vec{r}) + \int dV \Phi_n(\vec{r})^* U_{\mathscr{E}}(\vec{r}, t) \Phi_k(\vec{r}) \Rightarrow \\ H_{nk} &= E_k \delta_{nk} + U_{\mathscr{E}nk}(t). \end{aligned} \tag{10.41}$$

Combining Eqs. 10.33 and 10.41, we obtain

$$i\hbar \dot{c}_n = c_n E_n + \sum_k c_k U_{\mathscr{E}nk}(t) \tag{10.42}$$

In a two-level system within the dipole approximation, which leads to the diagonal elements $U_{\mathscr{E}kk}(t)$ becoming zero (Section 5.3, Eq. 5.43), it follows that

$$i\hbar \dot{c}_1 = E_1 c_1 + U_{\mathscr{E}12}(t) c_2, \tag{10.43}$$

$$i\hbar \dot{c}_2 = E_2 c_2 + U_{\mathscr{E}21}(t) c_1. \tag{10.44}$$

For real $\Phi_k(\vec{r})$, $U_{\mathscr{E}21}(t) = U_{\mathscr{E}12}(t)$.

10.5 Time evolution of the density matrix in the presence of decay mechanisms.

Eqs. 10.43 and 10.44 that we just obtained in Section 10.4 can be modified so that the decay of the energy levels 1 and 2 can be included. This decay can be due to spontaneous emission or other mechanisms, e.g., collisions of the atoms of the gas mixture inside a gas laser. As we will see in Chapter 11, a fast decay of the lower level (1) contributes to the achievement of population inversion. Moreover, we will see (Eq. 11.42) that, for a laser to operate, the lifetime of the upper level (2) must be larger than the lifetime of the lower level (1), i.e. $t_2 > t_1$. The decay of energy levels 1 and 2 can be achieved by including the term

$$-\frac{i\hbar}{2}\hat{\Gamma}, \tag{10.45}$$

to the Hamiltonian of the perturbed two-level system, i.e. to Eq. 5.18. The operator $\hat{\Gamma}$ has the property $\hat{\Gamma}\Phi_k(\vec{r}) = \gamma_k \Phi_k(\vec{r})$, $\gamma_k \in \mathbb{R}$. In other words,

$$\Gamma_{nk} = \gamma_k \delta_{nk} \tag{10.46}$$

or, in matrix form,

$$\hat{\Gamma} = \begin{bmatrix} \gamma_1 & 0 \\ 0 & \gamma_2 \end{bmatrix}. \tag{10.47}$$

Thus, the Hamiltonian becomes

$$\hat{H} = \hat{H}_0 - \frac{i\hbar}{2}\hat{\Gamma} + U_{\mathscr{E}}(\vec{r}, t). \tag{10.48}$$

In this case, Eq. 10.41 is modified to

$$H_{nk} = E_k \delta_{nk} + U_{\mathscr{E}nk}(t) - \frac{i\hbar}{2}\gamma_k \delta_{nk}. \tag{10.49}$$

Therefore, using Eqs. 10.33 and 10.49, we obtain

$$i\hbar\dot{c}_n = c_n E_n + \sum_k c_k U_{\mathscr{E}nk}(t) - \frac{i\hbar}{2} c_n \gamma_n \tag{10.50}$$

Hence, if we take the decay mechanisms into account in a two-level system, Eqs. 10.43 and 10.44 are replaced by

$$i\hbar\dot{c}_1 = E_1 c_1 + U_{\mathscr{E}12}(t) c_2 - \frac{i\hbar}{2}\gamma_1 c_1, \tag{10.51}$$

$$i\hbar\dot{c}_2 = E_2 c_2 + U_{\mathscr{E}21}(t) c_1 - \frac{i\hbar}{2}\gamma_2 c_2. \tag{10.52}$$

Using Eqs. 10.51 and 10.52, and assuming that $U_{\mathscr{E}21}(t) = U_{\mathscr{E}12}(t)$, it can be shown that the time evolution of the density matrix with decay mechanisms is given by the equation

$$\boxed{i\hbar\dot{\hat{\rho}} = [\hat{H}, \hat{\rho}] - \frac{i\hbar}{2}\{\hat{\Gamma}, \hat{\rho}\}}. \tag{10.53}$$

We recall that [,] denotes the commutator and { , } the anticommutator.

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CHAPTER 11

LASER

In this Chapter:
Initially, we analyze the basic parts of a LASER. As an example, we examine the He-Ne LASER. We derive the rate equations for the populations of the levels, participating in the emission of coherent EM radiation, and for the EM radiation density inside the cavity. We evaluate the number of longitudinal modes of the cavity inside the line width of emission of coherent EM radiation. We find the populations of the levels and the density of EM radiation in the steady state. We explain what critical pumping and population inversion are. We continue by explaining how we solve numerically the rate equations in the general case, i.e., at every instance. Here we include a simulation laboratory: practice at solving rate equations numerically. Then, we discuss the generation of standing EM waves inside a cavity. We discriminate between longitudinal and transverse EM modes. Afterwards, we discuss the shape of transverse modes within a rectangular parallelepiped and within a cylindrical cavity. Also, we list LASER types and indicative applications, and we say a few words about p-n junction LASER or alternatively diode LASER and for quantum dots LASER. Finally, we refer to transverse mode isolation techniques.
Prerequisite knowledge: Basic knowledge of Electromagnetism and Quantum Physics.

The LASER (Light Amplification by Stimulated Emission of Radiation) is based on ideas by Einstein, published in 1916-1917 [1, 2]. Decades later (1950-1960), and after international efforts by many prominent or non-prominent researchers, the first MASERs and LASERs were developed. In 1964, Charles Townes, Nikolay Basov, and Aleksandr Prokhorov shared the Nobel Prize in Physics "for fundamental work in the field of quantum electronics, which has led to the construction of oscillators and amplifiers based on the maser–laser principle". The first LASERS were even characterized as a solution looking for a problem; however, today, LASERS are used in medicine, communications, everyday life, military, industry, cosmetics, etc. A LASER is a device that converts other forms of energy into coherent EM radiation. The incident energy can be EM energy, solar energy, chemical energy, etc, while the outgoing energy is coherent EM radiation. Apart from the acronym LASER, today we have derivative terms, such as "to lase", "lasing", etc. In what follows, we will use the terms LASER and laser interchangeably.

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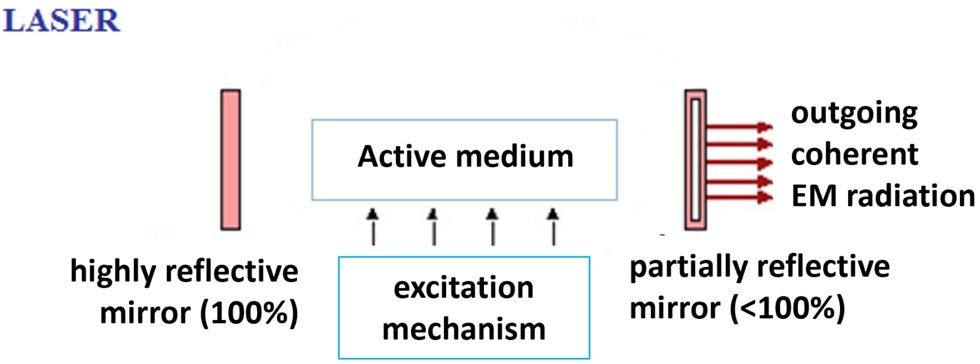

Figure 11.1: A LASER device.

A LASER device is depicted in Figure 11.1. The **active medium** is a collection of building blocks (atoms, molecules, ...). The **cavity** is the space in which the active medium is confined, e.g., a glass tube. There are standing waves along the direction of the mirrors, i.e. parallel to the "optical axis", e.g., the z-axis. The distance between the mirrors, L, determines the allowed **modes** of EM radiation, i.e. it determines ω_m. These are the so-called **longitudinal modes**. The **transverse modes**, which are created by the width of the cavity, determine the energy distribution along the cross-section, i.e., normal to the "optical axis", i.e., the xy-plane.

11.1 He-Ne LASER.

The excitation - pumping mechanism in a He-Ne LASER is presented in Figure 11.2. The active medium is a mixture of gas phase Neon (Ne) and Helium (He) in approximately 1:10 ratio. The Neon atoms play a central role, while the Helium atoms help with the excitation of Neon atoms, as it will be explained below. The excitation mechanism contains the following steps: Initially, an electric discharge creates accelerating electrons which excite the He and Ne atoms. Next, the He atoms excite the Ne atoms. In this LASER type, the most important processes take place between four (4) energy levels, as shown in Figure 11.2. Two meta-stable energy levels, E_5 and E_3, act as upper LASER levels, while the less stable levels E_4 and E_2 act as lower LASER levels. A meta-stable energy level is a "semi-stable" energy level, in the sense that it has a non-negligible, yet finite, lifetime. Thus, the main allowed transitions are: the main visible transition between levels E_5 and E_2, which is the classic characteristic red of the He-Ne LASER in 632.8 nm, the infrared transition between levels E_3 and E_2 in 1.152 μm = 1152 nm, and the infrared transition between levels E_5 and E_4 in 3.391 μm = 3391 nm. The energy levels have a fine structure, i.e., they are in fact complex. Therefore, the resulting energy transitions are not delta functions; instead they have some distribution around a central wavelength. Although the most important, "trademark" transition of the He-Ne LASER corresponds to a wavelength $\lambda_1 = 632.8$ nm (red, slightly to orange), there are more transitions, such as $\lambda_2 = 1152$ nm and $\lambda_2' = 1523$ nm (infrared), $\lambda_3 = 3391$ nm (infrared), $\lambda_4 = 543.5$ nm (green), $\lambda_5 = 594.1$ nm (yellow), $\lambda_6 = 604.6$ nm and $\lambda_6' = 611.9$ nm (orange)). Which of the above prevails depends on the construction of the LASER device, e.g., on the distance between the two mirrors. We can enhance a particular color by using a special coating on the mirrors that mainly reflects the desired photons. For example, if we want to enhance the red light, we use a coating that reflects only the red light. By doing so, the red light is reflected inside the cavity and its photons are multiplied via stimulated emission between levelsE_5 and E_2, while the photons with other wavelengths are forced to always pass through the active medium. Other wavelengths can be enhanced in a similar way. Thus, there are today orange, yellow, and green He-Ne LASERS, which take advantage of transitions that are not depicted in Figure 11.2. However, the red light 632.8 nm is the most efficient one in a He-Ne. Finally, let us note that in some LASER devices there is the possibility of tuning, i.e., we can choose the desired wavelength or even emit two or more wavelengths simultaneously.

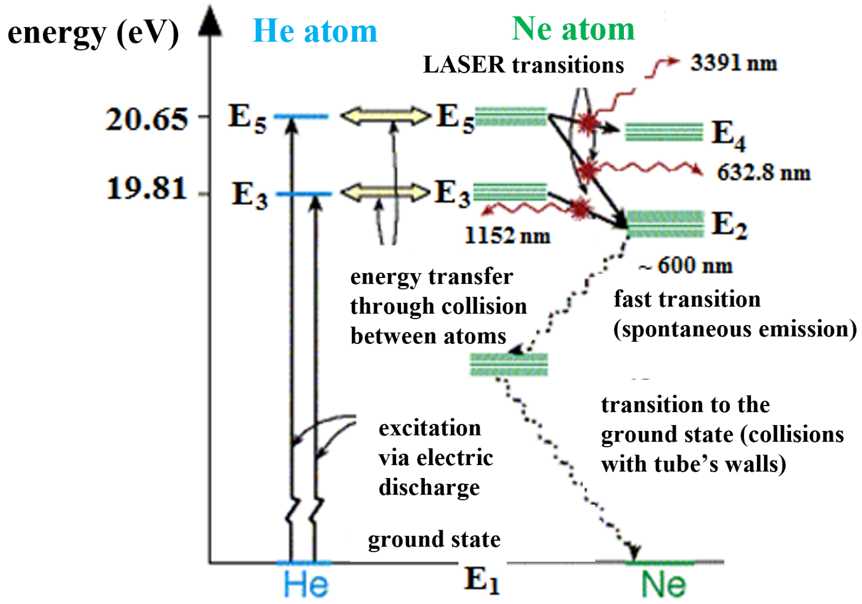

Figure 11.2: Energy diagram of the He-Ne LASER. Only the main levels and transitions are presented.

Although the transitions on which emission of coherent EM radiation depends have to do with Ne atoms, the He has is used in the He-Ne LASER to increase efficiency. This is due to the following two reasons: First, a direct excitation of Ne atoms thought the electric discharge is inefficient, while the excitation of He atoms is efficient. Second, one of the excited levels of the He atom (the one denoted as E_5) has almost the same energy as one of the excited levels of the Ne atom (the one denoted as E_5, too). This is also the case for the excited levels denoted as E_3. The excitation of the Ne atoms occurs in three stages:
1. A high voltage accelerates electrons from the cathode to the anode.
2. These electrons collide with He atoms and transfer to them their kinetic energy, so that the He atoms are excited and transfer energy to higher levels.
3. The excited He atoms collide with Ne atoms and transfer to them the excitation energy.
Thus, the He atoms do not participate in lasing, but increase the efficiency of Ne atoms excitation to the upper levels that participate in lasing. This results in a large increase in efficiency.

In most He-Ne LASER applications, the transitions between levels E_5 and E_2, which yield red light with wavelength $\lambda = 632.8$ nm, are used. This is the strongest line in the visible region. A problem in the creation of these photons is that the energy level E_5 can also emit to the infrared region with $\lambda = 3391$ nm, which corresponds to the transition between E_5 and E_4. This leads to a decrease in the population of the energy level E_5, without emitting visible radiation.

The amplification of coherent EM radiation occurs by stimulated emission. In a common He-Ne LASER, the amplification of the active medium is about 2%. In other words, in a single passage through the active medium, from the one mirror to the other, the amount of radiation increases from 1 to 1.02. Losses are owing to collisions of excited He atoms with the walls of the tube containing the gas, absorption by other molecules, etc. Thus, it must be below 2%. For a LASER to be operational, the lifetime of the lower energy levels that participate in lasing must, as we explain below, be very small, so that population inversion can be achieved. In the Ne has, which is the active medium, the transition from the lower energy level that participates in lasing is not very fast, but it is accelerated thought collisions with the walls of the tube. Since the number of collisions with the tube's walls increases as the tube becomes smaller, amplification of LASER radiation is inversely proportional to the radius of the tube. Thus, the radius of the tube must be as small as possible. The output power of He-Ne LASER commonly varies between 0.1-100 mW. One of the two mirrors is totally reflective, while the other is about 99% reflective. Since the latter mirror lets only 1% of the radiation through, the power inside the cavity is 100 times larger than the emitted power. In He-Ne LASERS, the length of the cavity is of the order of some tens of cm and the thickness of the cavity is of the order of some mm.

11.2 Rate equations for the populations of the levels participating in emission of coherent EM radiation and for the radiation density.

We will derive the rate equations, i.e., the equations that describe the time-evolution of the population of two levels that participate to emission of coherent EM radiation and the equation that describes the time-evolution of EM radiation density inside the cavity. In Figure 11.3, we present a system with four levels, in which electrons are pumped from the ground level (g) to the upper LASER level (2). Thus, here "two-level system" means that there are two levels, (1) and (2), between which coherent EM radiation is emitted, but there are also auxiliary levels such as (h) and (g). The help energy level (h) is needed so that electrons do not stay in (1), i.e., so that population inversion between (1) and (2) can be achieved. Thus, we assume that the spontaneous transition (1) → (h) is relatively faster than the spontaneous transition (2) → (1). Additionally, the transition (1) → (h) is either non-radiative, i.e., the energy is lowered without phonon emission, e.g., through phonons, or, even if it is radiative, the emitted phonons are not supported by the cavity's mirrors. A transition from one level to another is called **non-radiative** if it occurs without absorbing or emitting photons, e.g., by phonons, while it is called **radiative** if it occurs by absorbing or emitting photons.

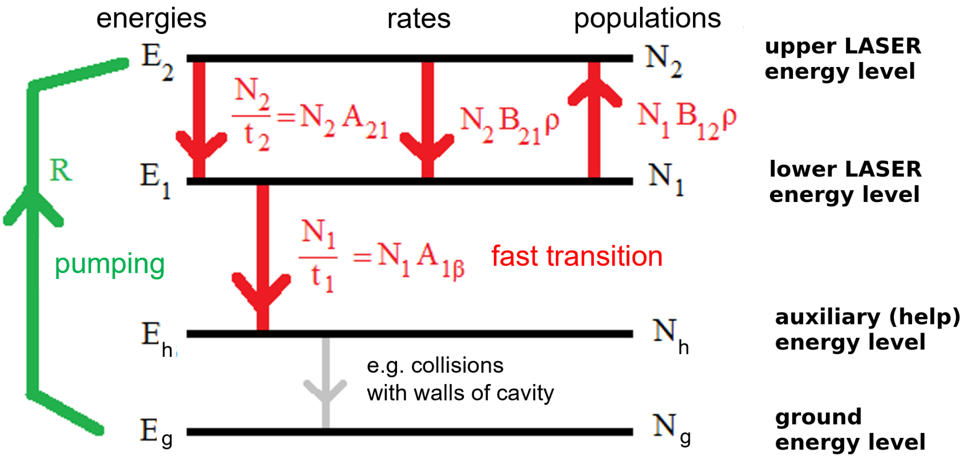

Figure 11.3: Representation of a system with two LASER levels and two auxiliary levels, in which electrons are pumped from the ground level to the upper LASER level.

We start by defining **pumping**, $R_2 \equiv R$, as the rate at which we raise electrons from the ground level (g) to the upper LASER level (2). That is, pumping is the number of electrons that we raise divided by the corresponding time. Thus, its units are $[R] = 1/\text{s}$. Below, we will define several rates that have the same units, $[1/\text{s}]$.

- For an atom, the probability for spontaneous emission from level (1) to the help level (h), in time dt, is

$$dW^{\text{sp. em.}}_{1\to h} = A_{1h} dt. \tag{11.1}$$

We define the “lifetime” of level (1), t_1, through the relationship

$$1 = A_{1h}t_1 \Rightarrow \boxed{t_1 = \frac{1}{A_{1h}}}, \tag{11.2}$$

that is, t_1 is the time needed for $dW_{1\to h}^{\text{sp. em.}}$ to become equal to 1. Therefore, we can write

$$dW_{1\to h}^{\text{sp. em.}} = \frac{dt}{t_1}. \tag{11.3}$$

The number of atoms that transition from level (1) to level (h) in time dt, via spontaneous emission, is

$$dN_{1\to h}^{\text{sp. em.}} = N_1 A_{1h} dt = \frac{N_1}{t_1} dt. \tag{11.4}$$

Therefore, the transition rate from level (1) to level (h) via spontaneous emission is

$$\frac{dN_{1\to h}^{\text{sp. em.}}}{dt} = N_1 A_{1h} = \frac{N_1}{t_1}. \tag{11.5}$$

- For an atom, the probability for spontaneous emission from level (2) to the level (1), in time dt, is

$$dW_{2\to 1}^{\text{sp. em.}} = A_{21} dt. \tag{11.6}$$

We define the “lifetime” of level (2), t_2, through the relationship

$$1 = A_{21}t_2 \Rightarrow \boxed{t_2 = \frac{1}{A_{21}}}, \tag{11.7}$$

that is, t_1 is the time needed for $dW_{2\to 1}^{\text{sp. em.}}$ to become equal to 1. Therefore, we can write

$$dW_{2\to 1}^{\text{sp. em.}} = \frac{dt}{t_2}. \tag{11.8}$$

The number of atoms that transition from level (2) to level (1) in time dt, via spontaneous emission, is

$$dN_{2\to 1}^{\text{sp. em.}} = N_2 A_{21} dt = \frac{N_2}{t_2} dt. \tag{11.9}$$

Therefore, the transition rate from level (2) to level (1) via spontaneous emission is

$$\frac{dN_{2\to 1}^{\text{sp. em.}}}{dt} = N_2 A_{21} = \frac{N_2}{t_2}. \tag{11.10}$$

- For an atom, the probability for stimulated emission from level (2) to the level (1), in time dt, is

$$dW_{2\to 1}^{\text{st. em.}} = B_{21}\rho(\nu) dt. \tag{11.11}$$

The number of atoms that transition from level (2) to level (1) in time dt, via stimulated emission, is

$$dN_{2\to 1}^{\text{st. em.}} = N_2 B_{21}\rho(\nu) dt. \tag{11.12}$$

Therefore, the transition rate from level (2) to level (1) via stimulated emission is

$$\frac{dN_{2\to 1}^{\text{st. em.}}}{dt} = N_2 B_{21}\rho(\nu). \tag{11.13}$$

- For an atom, the probability for stimulated absorption from level (1) to the level (2), in time dt, is

$$dW_{1\to 2}^{\text{st. ab.}} = B_{12}\rho(\nu)dt. \tag{11.14}$$

The number of atoms that transition from level (1) to level (2) in time dt, via stimulated absorption, is

$$dN_{1\to 2}^{\text{st. ab.}} = N_1 B_{12}\rho(\nu)dt. \tag{11.15}$$

Therefore, the transition rate from level (1) to level (2) via stimulated absorption is

$$\frac{dN_{1\to 2}^{\text{st. ab.}}}{dt} = N_1 B_{12}\rho(\nu). \tag{11.16}$$

- If we were in thermodynamic equilibrium, i.e., there were no losses and no pumping, we would write, as we already know,

$$\begin{gathered} dN_{1\to 2} = dN_{2\to 1} \Leftrightarrow \\ N_1 dW_{1\to 2}^{\text{st. ab.}} = N_2[dW_{2\to 1}^{\text{sp. em.}} + dW_{2\to 1}^{\text{st. em.}}] \Leftrightarrow \\ N_1 B_{12}\rho(\nu, T)dt = N_2[A_{21}dt + B_{21}\rho(\nu, T)dt] \end{gathered}$$

and then, by denoting $A_{21} = A$, $B_{21} = B_{12} = B$ and comparing with the Planck's law, we would arrive at the relationship $\frac{A}{B} = \frac{8\pi h\nu^3}{c^3}$. This has been done in Section 3.2, e.g. see Eqs. 3.7 and 3.10.

- However, now we have both losses, expressed by t_0, and pumping R. Additionally, ρ does not correspond to a black body with a specific temperature at thermodynamic equilibrium, so we do not have $\rho(\nu, T)$ but rather $\rho(\nu)$. Thus, we expect to see

$$\begin{gathered} N_1 = N_1(R, t_0) \\ N_2 = N_2(R, t_0) \\ \rho = \rho(R, t_0) \end{gathered}$$

Let us construct the differential equations for the rates, setting $A_{21} = A$, $B_{21} = B_{12} = B$. We consider the positive and negative contributions to the populations of levels (1) and (2) as well as the energy density of EM radiation in an infinitesimal frequency interval.

For the rate of change in the population of level (1), we have

$$\frac{dN_1}{dt} = -\frac{N_1}{t_1} - N_1 B_{12}\rho + N_2 B_{21}\rho + \frac{N_2}{t_2}. \tag{11.17}$$

In the left hand-side of the above equation, the first term corresponds to losses towards level (h), the second one to losses towards level (2), while the third and fourth ones correspond to gains from level (2). Therefore, simplifying the notation ($A_{21} = A$, $B_{21} = B_{12} = B$),

$$\boxed{\frac{dN_1}{dt} = -\frac{N_1}{t_1} + B\rho(N_2 - N_1) + AN_2} \tag{11.18}$$

For the rate of change in the population of level (2), we have

$$\frac{dN_2}{dt} = R + N_1 B_{12}\rho - N_2 B_{21}\rho - \frac{N_2}{t_2}. \tag{11.19}$$

In the left hand-side of the above equation, the first term corresponds to gains from pumping, the second one to gains from level (1), while the third and fourth ones correspond to losses towards level (1). Therefore, simplifying the notation ($A_{21} = A, B_{21} = B_{12} = B$),

$$\boxed{\frac{dN_2}{dt} = R + B\rho(N_1 - N_2) - AN_2} \tag{11.20}$$

For the rate of change in the energy density of EM radiation in an infinitesimal frequency interval, we have

$$\frac{d\rho}{dt} = -\frac{\rho}{t_0} + \left[-N_1B_{12}\rho + N_2B_{21}\rho + A'_{21}N_2\right]\frac{h\nu}{V}F(\nu). \tag{11.21}$$

In the left hand-side of the above equation, the first term describes losses towards the mirrors in a phenomenological manner, the second one corresponds to losses due to stimulated absorption, the third one to gains due to stimulated emission, and and the fourth one to gains due to spontaneous emission. We have to pay attention to the fact that spontaneous emission occurs towards any direction, hence we do not take advantage of the whole term $A_{21}N_2$ to increase EM radiation in the cavity. We only take advantage of those photons that are emitted towards a direction approximately parallel to the axis defined by the mirrors. Therefore, since only a small portion of the total solid angle is of interest, the coefficient A'_{21} occurs, which is much smaller than A_{21}, e.g., $A'_{21} = 10^{-9}A_{21}$. Again, simplifying the notation ($A_{21} = A$, $B_{21} = B_{12} = B$),

$$\boxed{\frac{d\rho}{dt} = -\frac{\rho}{t_0} + \left[B\rho(N_2 - N_1) + A'N_2\right]\frac{h\nu}{V}F(\nu)} \tag{11.22}$$

Eqs. 11.18 and 11.20 are sometimes referred to as "matter equations", while Eq. 11.22 as "field equation".

Let us comment a bit on the units. For the Einstein coefficients, $[A] = 1/\text{s}$ and $[B] = \frac{\text{m}^3}{\text{Js}^2}$, while for the energy density of EM radiation in an infinitesimal frequency interval, $[\rho] = \frac{\text{J}}{\text{m}^3\text{Hz}} = \frac{\text{Js}}{\text{m}^3}$. Thus, $\left[\frac{d\rho}{dt}\right] = \frac{\text{J}}{\text{m}^3}$. As seen in Eq. 11.22, we express the **radiation losses to the mirrors** with a phenomenological term $-\frac{\rho}{t_0}$. That is, we introduce a quantity t_0 with units of time. Thus, losses are expressed in units $[-\frac{\rho}{t_0}] = \frac{\text{J}}{\text{m}^3}$. The parameter t_0 characterizes the time needed to empty the cavity of ρ due to losses to the mirrors, in the absence of an active material. The smaller the reflectance of the mirrors, i.e., the larger the losses, the less the time t_0. N_1 and N_2 are populations with units $[N_1] = [N_2] = 1$. Based on the above,$[N_1B_{12}\rho] = [N_2B_{21}\rho] = [A_{21}N_2] = [A'_{21}N_2] = 1/\text{s}$. $F(\nu)$ is the shape of the transmission line, which, as we have already mentioned, is not a delta function; rather, it has some width. This is schematically depicted in Figure 11.4. $F(\nu)$ is called **spectral line shape function** and has units $[F(\nu)] = 1/\text{Hz}$. FWHM means Full Width at Half Maximum. The shape of this line can be approximated in some cases by a Gaussian or a Lorentzian, but this subject exceeds the scope of this book. V is the volume of the cavity, with units $[V] = \text{m}^3$. Thus, $\left[\frac{h\nu}{V}F(\nu)\right] = \frac{\text{J}}{\text{m}^3\text{Hz}}$. Therefore, the right-hand side of Eq. 11.22 has units $\frac{\text{J}}{\text{m}^3}$.

Eqs. 11.18, 11.20, 11.22 can alternatively be written as

$$\boxed{\frac{dn_1}{dt} = -\frac{n_1}{t_1} + B\rho(n_2 - n_1) + An_2} \tag{11.23}$$

$$\boxed{\frac{dn_2}{dt} = r + B\rho(n_1 - n_2) - An_2} \tag{11.24}$$

$$\boxed{\frac{d\rho}{dt} = -\frac{\rho}{t_0} + \left[B\rho(n_2 - n_1) + A'n_2\right]h\nu F(\nu)} \tag{11.25}$$

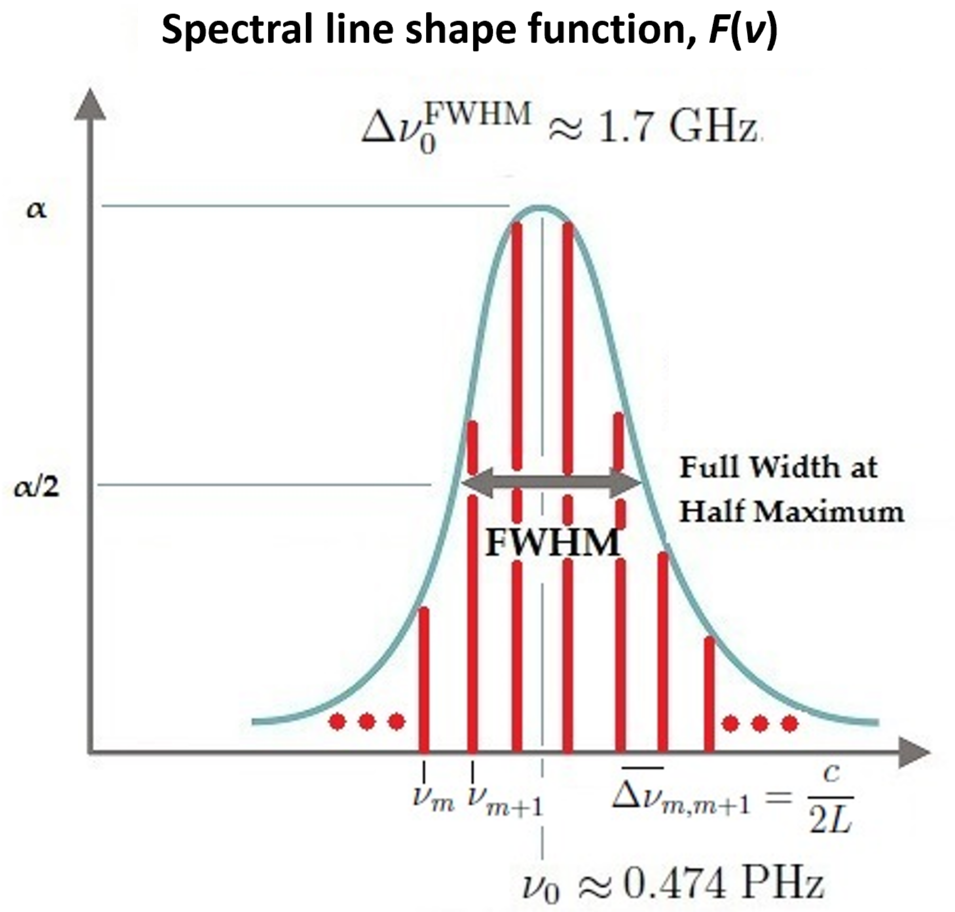

Figure 11.4: The spectral line shape function, $F(\nu)$, expresses the shape of an emission line. FWHM stands for Full Width at Half Maximum. The central frequency, ν_0, its FWHM, $\Delta\nu_0^{\text{FWHM}}$, two consecutive frequencies of longitudinal modes, ν_m, ν_{m+1}, and the distance between them $\Delta\nu_{m,m+1} = \frac{c}{2L}$, are noted. As an example, typical values for the red line of a He-Ne LASER are presented. In this specific example, the FWHM contains 4 longitudinal modes.

where we have set

$$n_i = \frac{N_i}{V}, \tag{11.26}$$

and

$$r = \frac{R}{V}. \tag{11.27}$$

11.3 Number of longitudinal modes within emission line width.

In Chapter 8 (Eq. 8.50) we saw that inside the cavity only EM modes m such that the circular frequency is

$$\omega_m = \frac{m\pi c}{L}, m \in \mathcal{N}^*$$

are supported. L is the distance between the mirrors along the z-axis. Therefore, the frequency is

$$\nu_m = \frac{mc}{2L}, m \in \mathcal{N}^*. \tag{11.28}$$

These EM modes were derived by imposing boundary conditions along the z-axis connecting the two mirrors. Since this dimension of the cavity on the z-axis has usually much larger size than the other two ones on the xy-plane, these modes are called **longitudinal modes**.

The red line has a central wavelength

$$\lambda_0 \approx 632.8 \text{ nm},$$

hence, the corresponding central frequency is $\nu_0 = \frac{c}{\lambda_0} \approx 0.474 \times 10^{15}\text{Hz} \Rightarrow$

$$\nu_0 = 0.474 \text{ PHz}.$$

The FWHM of the red line is $\Delta\nu_0^{\text{FWHM}} \approx 1.7$ GHz. Thus,

$$\frac{\Delta\nu_0^{\text{FWHM}}}{\nu_0} \approx 3.6 \times 10^{-6},$$

i.e., the red line is fairly thin; see Figure 11.4. Let us try to answer the following **question**: Are there modes m supported by the cavity in the frequency region of ν_0 with width $\Delta\nu_0^{\text{FWHM}}$? From Eq. 11.28, we conclude that the frequency distance between longitudinal EM modes is

$$\Delta\nu_{m,m+1} = \frac{c}{2L}. \tag{11.29}$$

Let as assume that the length of the cavity is $L = 0.4$ m. Then, $\Delta\nu_{m,m+1} = 375$ MHz. Within the FWHM of the spectral line there will be

$$\left[\frac{\Delta\nu_0^{\text{FWHM}}}{\Delta\nu_{m,m+1}}\right] \text{ EM modes.} \tag{11.30}$$

Here, [...] denotes the integer part. In this specific example, $\left[\frac{\Delta\nu_0^{\text{FWHM}}}{\Delta\nu_{m,m+1}}\right] = \left[\frac{1.7 \text{ GHz}}{375 \text{ MHz}}\right] = \left[4.5\overline{33}\right] = 4$. Therefore, we see that there are several longitudinal modes inside the linewidth (there are also transverse modes, see Section 11.7). The width of each longitudinal (and transverse, as well, , see Section 11.7) EM mode is of the order of $\Delta\nu_m^{\text{FWHM}} \approx 1$ με 10 MHz and is related to the loss rate of the cavity through the mirrors, t_0 [3].

11.4 Finding level populations and EM radiation density in the steady state. Critical pumping. Population inversion.

In the steady state, we have

$$\frac{dN_1}{dt} = \frac{dN_2}{dt} = 0 = \frac{d\rho}{dt}. \tag{11.31}$$

Thus, Eqs. 11.18 and 11.20 become

$$\boxed{-\frac{N_1}{t_1} + B\rho(N_2 - N_1) + AN_2 = 0} \tag{11.32}$$

$$\boxed{R + B\rho(N_1 - N_2) - AN_2 = 0} \tag{11.33}$$

while, if we ignore A' as much smaller than A, then Eq. 11.22 becomes

$$-\frac{\rho}{t_0} + B\rho(N_2 - N_1) + \frac{h\nu}{V}F(\nu) = 0 \Leftrightarrow \tag{11.34}$$

$$\boxed{B\rho(N_2 - N_1) = \frac{\rho}{t_0 \frac{h\nu}{V} F(\nu)}} \tag{11.35}$$

Adding Eqs. 11.32 and 11.33 by parts, we obtain $R = \frac{N_1}{t_1} \Leftrightarrow$

$$\boxed{N_1 = t_1 R} \tag{11.36}$$

Adding Eqs. 11.33 and 11.35by parts, we obtain

$$R - AN_2 = \frac{\rho}{t_0 \frac{h\nu}{V} F(\nu)} \Leftrightarrow \tag{11.37}$$

$$\boxed{N_2 = \frac{R}{A} - \frac{\rho}{A t_0 \frac{h\nu}{V} F(\nu)}} \tag{11.38}$$

There are two cases for ρ, either (C1) $\rho > 0$ or (C2) $\rho = 0$.

Let the case be (C1), i.e., $\rho > 0$. Then, Eq. 11.37 yields $R > AN_2$. Given Eq. 11.36 and the definition (Eq. 11.7) of the lifetime of level (2) $A = A_{21} = \frac{1}{t_2}$, we obtain $\frac{N_1}{t_1} > \frac{N_2}{t_2} \Leftrightarrow$

$$\boxed{\frac{t_2}{N_2} > \frac{t_1}{N_1}} \tag{11.39}$$

Now, from Eqs. 11.35, 11.36, 11.38, since $\rho \neq 0$, it follows that

$$B\left(\frac{R}{A} - \frac{\rho}{A t_0 \frac{h\nu}{V} F(\nu)}\right) - B t_1 R = \frac{1}{t_0 \frac{h\nu}{V} F(\nu)} \Leftrightarrow \tag{11.40}$$

$$\rho = R t_0 \frac{h\nu}{V} F(\nu) \frac{t_2 - t_1}{t_2} - \frac{1}{B t_2} \tag{11.41}$$

Let us note that if $t_2 < t_1$, then from the above equation it follows that $\rho < 0$. Thus, it must hold that

$$\boxed{t_2 > t_1}. \tag{11.42}$$

In other words, the lifetime of the upper level (2) must be larger than the lifetime of the lower level (1). However, in the case we are currently examining it holds that $\rho > 0$, hence

$$\boxed{R > \frac{1}{B t_0 (t_2 - t_1) \frac{h\nu}{V} F(\nu)} := R_c} \tag{11.43}$$

The quantity R_c is called **critical pumping**. Apparently, for $R_c > 0 \Leftrightarrow$ Eq. 11.42. Thus, ρ can be written as

$$\boxed{\rho = \frac{AR}{BR_c} - \frac{A}{B}} \tag{11.44}$$

From Eqs. 11.38, 11.43, 11.44, it occurs that

$$\boxed{N_2 = t_1 R + (t_2 - t_1) R_c} \tag{11.45}$$

Let the case be (C2), i.e., $\rho = 0$. Then, Eq. 11.37 yields $R = AN_2$. Therefore,

$$\boxed{N_2 = t_2 R} \tag{11.46}$$

To wrap this up, in the steady state, the solutions to Eqs. 11.32, 11.33, 11.35 are

$$\boxed{N_1 = t_1 R, \quad \forall\, R} \tag{11.47}$$

$$\boxed{N_2 = \begin{cases} t_2 R, & \forall\, R \leq R_c \\ t_1 R + (t_2 - t_1) R_c, & \forall\, R \geq R_c \end{cases}} \tag{11.48}$$

$$\boxed{\rho = \begin{cases} 0, & \forall\, R \leq R_c \\ \dfrac{AR}{BR_c} - \dfrac{A}{B} = \dfrac{1}{Bt_2 R_c} R - \dfrac{1}{Bt_2}, & \forall\, R \geq R_c \end{cases}} \tag{11.49}$$

Next, let us make some remarks.

Remark 1. The **population inversion** is defined as

$$\boxed{\Delta N := N_2 - N_1}, \tag{11.50}$$

hence, from Eqs. 11.47 and 11.48 we conclude that

$$\boxed{\Delta N = \begin{cases} (t_2 - t_1) R, & \forall\, R \leq R_c \\ (t_2 - t_1) R_c, & \forall\, R \geq R_c \end{cases}} \tag{11.51}$$

This way it becomes apparent that $\Delta N > 0 \Leftrightarrow t_2 > t_1$, i.e., in order for population inversion to occur, Eq. 11.42 must hold.

In Figure 11.5 a representation of Eqs. Eξ. 11.47, 11.48, 11.49, 11.51 is presented, which was realized using the Matlab program N1N2DNrho.m, which can be found in Appendix C. The parameter values are here purposely dimensionless and do not correspond to actual values. The reader may play withe these parameter values to obtain an understanding of Eqs. 11.47, 11.48, 11.49, 11.51.

Remark 2. According to Eq. 11.43, the critical pumping is defined as

$$R_c := \frac{1}{Bt_0 (t_2 - t_1) \frac{h\nu}{V} F(\nu)}.$$

Thus, increasing t_0 implies a decrease in R_c, which is reasonable, since, if we increase t_0, this means that the losses, i.e. ρ/t_0, are mitigated. Additionally, we remind that in order to get $R_c > 0$, Eq. 11.42 must hold, that is $t_2 > t_1$. Furthermore, if $t_2 >> t_1$, a very small R_c is obtained.

Remark 3. The relationship

$$\frac{A}{B} = \frac{8\pi h \nu^3}{c^3} \Leftrightarrow \frac{1}{B} = \frac{8\pi h t_2 \nu^3}{c^3}, \tag{11.52}$$

thus, Eq. 11.43 becomes

$$R_c = \frac{8\pi h t_2 \nu^3}{c^3 t_0 (t_2 - t_1) \frac{h\nu}{V} F(\nu)} \propto \nu^2. \tag{11.53}$$

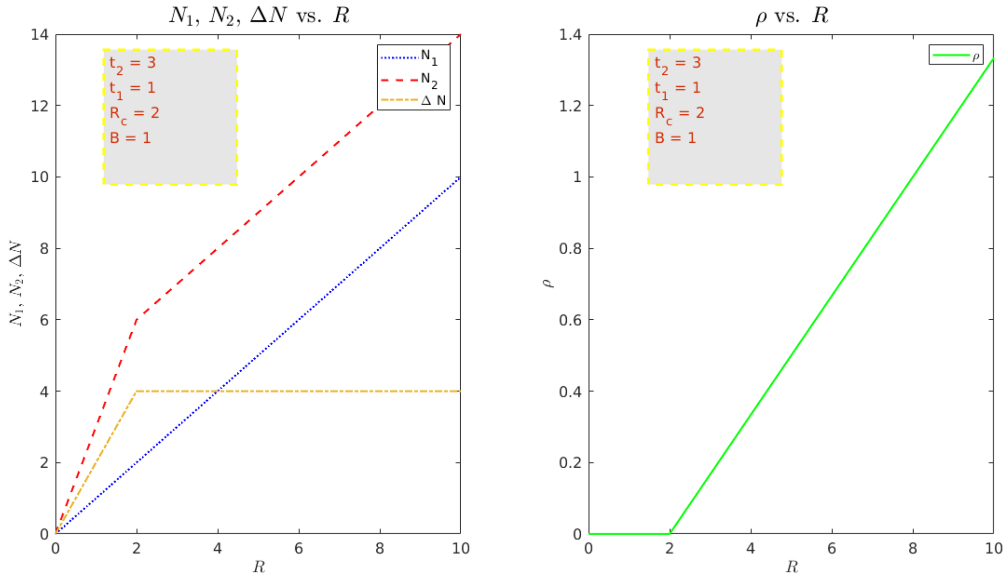

Figure 11.5: A representation of Eqs. 11.47, 11.48, 11.49, 11.51, realized using the Matlab program N1N2DNrho.m, which can be found in Appendix C.

Thus, e.g., R_c(microwaves) $<$ R_c(visible), i.e., it is easier to create a coherent beam in the microwaves than in the visible.

Remark 4. All the above make sense only if the transition from the upper level (2) to the lower level (1) with photon emission is allowed. In other words, as we discussed in Chapter 7, it must hold that $\vec{r}_{12} := \int dV \Phi_1^*(\vec{r})\, \vec{r}\, \Phi_2(\vec{r}) \neq 0$, i.e., $\vec{\mathscr{P}}_{12} := \int dV \Phi_1^*(\vec{r})\, (-e)\vec{r}\, \Phi_2(\vec{r}) \neq 0$.

Aiming to solve the rate equations numerically in the general case, we will make, initially, Eqs. 11.47, 11.48, 11.49, 11.51 dimensionless.

- First of all, let us complete the changes of variables we performed in Eqs. 11.26 and 11.27, i.e.,

$$n_i = \frac{N_i}{V}, \tag{11.54}$$

and

$$r = \frac{R}{V}, \tag{11.55}$$

by defining

$$r_c = \frac{R_c}{V}. \tag{11.56}$$

Then, Eqs. 11.47, 11.48, 11.49, 11.51 become

$$\boxed{n_1 = t_1 r, \quad \forall\ r} \tag{11.57}$$

$$\boxed{n_2 = \begin{cases} t_2 r, & \forall\ r \leq r_c \\ t_1 r + (t_2 - t_1) r_c, & \forall\ r \geq r_c \end{cases}} \tag{11.58}$$

$$\boxed{\rho = \begin{cases} 0, & \forall\ r \leq r_c \\ \dfrac{Ar}{Br_c} - \dfrac{A}{B} = \dfrac{1}{Bt_2 r_c} r - \dfrac{1}{Bt_2}, & \forall\ r \geq r_c \end{cases}} \tag{11.59}$$

$$\boxed{\Delta n := n_2 - n_1 = \begin{cases} (t_2 - t_1)r, & \forall\ r \leq r_c \\ (t_2 - t_1)r_c, & \forall\ r \geq r_c \end{cases}} \tag{11.60}$$

- Next, we make Eqs. 11.57, 11.58, 11.59, 11.60 dimensionless. To this end, we define the following quantities:

  $$n_0 := t_2 r_c \tag{11.61}$$

  with units $[n_0] = \frac{\text{s}}{\text{sm}^3} = 1/\text{m}^3$.

  $$\tau := \frac{t}{t_2}. \tag{11.62}$$

  In other words, we are counting time in units of the upper level's (2) lifetime, t_2, so that τ is dimensionless, $[\tau] = 1$.

  $$\tau_0 := \frac{t_0}{t_2} \tag{11.63}$$

  and

  $$\tau_1 := \frac{t_1}{t_2} \tag{11.64}$$

  which are dimensionless, as well $([\tau_0] = [\tau_1] = 1)$. We continue by defining

  $$r_N := \frac{r}{r_c}, \tag{11.65}$$

  which is the "dimensionless pumping", $[r_N] = 1$. Moreover,

  $$\varrho := Bt_2\rho, \tag{11.66}$$

  is the "dimensionless EM radiation density", $[\varrho] = \left[\frac{\text{m}^3}{\text{Js}^2}\,\text{s}\,\frac{\text{Js}}{\text{m}^3}\right] = 1$. We also define the "dimensionless populations for the levels (1) and (2)" as

  $$\nu_1 := \frac{n_1}{n_0}, \tag{11.67}$$

  $$\nu_2 := \frac{n_2}{n_0}, \tag{11.68}$$

  since $[\nu_1] = \frac{[t_1 r]}{[n_0]} = \frac{\text{sm}^3}{\text{sm}^3} = 1$ and, e.g., $[\nu_2] = \frac{[t_2 r]}{[n_0]} = \frac{\text{sm}^3}{\text{sm}^3} = 1$.

Based on the above definitions, Eqs. 11.57, 11.58, 11.59, 11.60 become

$$\boxed{\nu_1 = \tau_1 r_N, \quad \forall\ r_N} \tag{11.69}$$

$$\boxed{\nu_2 = \begin{cases} r_N, & \forall\ r_N \leq 1 \\ \tau_1 r_N + (1 - \tau_1), & \forall\ r_N \geq 1 \end{cases}} \tag{11.70}$$

$$\boxed{\varrho = \begin{cases} 0, & \forall\ r_N \leq 1 \\ r_N - 1, & \forall\ r_N \geq 1 \end{cases}} \tag{11.71}$$

$$\boxed{\Delta\nu := \nu_2 - \nu_1 = \begin{cases} (1 - \tau_1)r_N, & \forall\ r_N \leq 1 \\ (1 - \tau_1), & \forall\ r_N \geq 1 \end{cases}} \tag{11.72}$$

Remarks

- In Eqs. 11.69, 11.70, 11.71, 11.72, all quantities are dimensionless.
- $\nu_1, \nu_2, \Delta\nu$ depend only on τ_1 and r_N.
- ϱ depends only on r_N.

  For example, for $\tau_1 = 0.5$ and $r_N = 1.5$, it occurs that
  $\nu_1 = 0.5 \cdot 1.5 = 0.75$
  $\nu_2 = 0.5 \cdot 1.5 + (1 - 0.5) = 0.75 + 0.5 = 1.25$
  $\Delta\nu = 0.5$
  $\varrho = 1.5 - 1 = 0.5,$

  while, for $\tau_1 = 0.5$ and $r_N = 0.5$, it occurs that
  $\nu_1 = 0.5 \cdot 0.5 = 0.25$
  $\nu_2 = 0.5$
  $\Delta\nu = 0.25$
  $\varrho = 0.$

11.5 Numerical solution of rate equations in general case, i.e., at every instance.

We have already shown that the rate equations, i.e., Eqs. 11.18, 11.20, 11.22, can be written in the form of Eqs. 11.23, 11.24, 11.25

$$\frac{dn_1}{dt} = -\frac{n_1}{t_1} + B\rho(n_2 - n_1) + An_2$$

$$\frac{dn_2}{dt} = r + B\rho(n_1 - n_2) - An_2$$

$$\frac{d\rho}{dt} = -\frac{\rho}{t_0} + \left[B\rho(n_2 - n_1) + A'n_2\right]h\nu F(\nu)$$

where

$$n_i = \frac{N_i}{V},$$

$$r = \frac{R}{V},$$

while, above, we also defined

$$r_c = \frac{R_c}{V}.$$

Let us now make the rate equations dimensionless, using, as we did above, the definitions of Eqs. 11.61, 11.62, 11.63, 11.64, 11.65, 11.66, 11.67, 11.68. This way, the dimensionless Eqs. Eξ. 11.73, 11.74, 11.75 occur. For the latter, we also used Eq. 11.43, together with Eq. 11.56.

$$\boxed{\frac{d\nu_1}{d\tau} = -\frac{\nu_1}{\tau_1} + \varrho(\nu_2 - \nu_1) + \nu_2} \tag{11.73}$$

$$\boxed{\frac{d\nu_2}{d\tau} = r_N + \varrho(\nu_1 - \nu_2) - \nu_2} \tag{11.74}$$

$$\boxed{\frac{d\varrho}{d\tau} = -\frac{\varrho}{\tau_0} + \left[\varrho(\nu_2 - \nu_1) + \frac{A'}{A}\nu_2\right]\frac{1}{\tau_0(1 - \tau_1)}} \tag{11.75}$$

Remarks

- In Eqs. 11.73, 11.74, 11.75, all quantities are dimensionless.
- The solution of the differential equations 11.73, 11.74, 11.75 to obtain ν_1, ν_2, ϱ, depends only on τ_0, τ_1, r_N and $\frac{A'}{A}$.
- In the following Section we will solve them on Matlab using the programs laser.m and calllasercommands.m.

11.6 Simulation lab: practice on numerical solution of rate equations.

Eqs. 11.73, 11.74, 11.75, can be numerically solved with different ways and software. In this Section we solve them using Matlab, with the help of the two files presented below, in Codes 11.1 and 11.2. The result of running the program is presented in Figure 11.6.

Code 11.1: Το αρχείο matlab calllasercommands.m.

```
global tau1 tau0 arn AptoA
x0=[0 0 0];
tspan=[0,500];
[t,x]=ode45(@laser,tspan,x0)
plot(t,x)

%figure;
%plot(t,x(1),'k',t,x(2),'r',t,x(3),'g')
xlabel('\tau','FontSize',16)
ylabel('\nu_1, \nu_2, \rho','FontSize',16)
set(gca,'fontsize',16)
title('\nu_1, \nu_2, \rho vs. \tau','FontSize',16)
text(100,1.10,'\nu_1','Color','b','FontSize',16)
text(150,1.10,'\nu_2','Color','r','FontSize',16)
text(200,1.10,'\rho','Color',[1,0.5,0],'FontSize',16)
annotation('textbox',...
[0.6 0.54 0.25 0.22],...
'String',{['\tau_1 = ' num2str(tau1)],...
        ['\tau_0 = ' num2str(tau0)], ['r_N = ' num2str(arn)],...
        ['AptoA = ' num2str(AptoA)]},...
'FontSize',12,...
'FontName','Arial',...
'LineStyle','--',...
'EdgeColor',[1 1 0],...
'LineWidth',2,...
'BackgroundColor',[0.9 0.9 0.9],...
'Color',[0.84 0.16 0]);
```

Code 11.2: Το αρχείο matlab laser.m.

```
function xprime = laser(t,x);
global tau1 tau0 arn AptoA
%LASER: Computes the derivatives involved in solving the laser equations.
```

```
% nu1=x(1), nu2=x(2), rho=x(3)
tau1=0.5;
tau0=10;
arn=1.5; % normalized pumping
AptoA=10^(-9);
tautau=tau0*(1-tau1);
xprime=[x(2)+x(3)*(x(2)-x(1))-x(1)/tau1; arn+x(3)*(x(1)-x(2))-x(2);-x(3)/tau0+(AptoA*x(2)+x(3)*(x(2)-x(1)))*(1/tautau)];

% Observe that x is stored as x(1), y is stored as x(2), and z as stored as x(3).
% Additionally, xprime is a column vector,
% as is evident from the semicolon following the first appearance of x(2).
% If in the Command Window, we type
% >> x0=[-8 8 27];
% >> tspan=[0,20];
% >> [t,x]=ode45(@lorenz,tspan,x0)
```

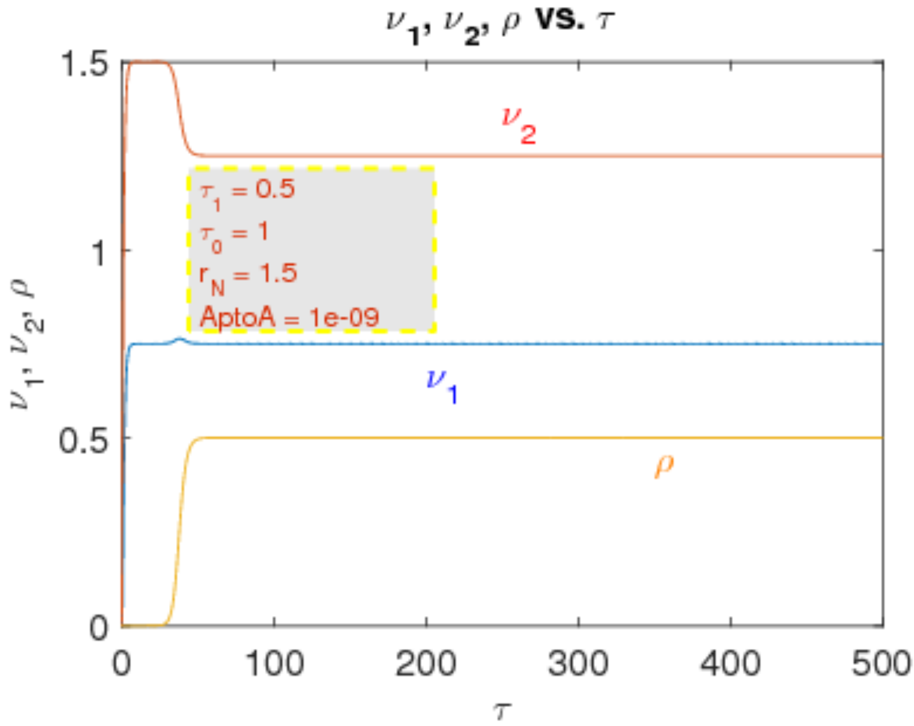

Figure 11.6: Graphical representation of ν_1, ν_2, ϱ as functions of τ, as it is obtained by the Matlab code. Note that the notation ρ in the panel is in fact the dimensionless ϱ of Eq. 11.75.

As an example, let us suppose that we want to determine the effect of changing r_N on the functions of ν_1, ν_2, ϱ versus τ. Let us keep $\tau_0 = 10$, $\frac{A'}{A} = 10^{-9}$ and $\tau_1 = 0.5$ constant, while we change r_N setting the values 0.5, 1.5, 2.0, 2.5. The results of the solution to our rate equations using our programs is presented in Figure 11.7. We initially observe that when the values of ν_1, ν_2, ϱ have finally stabilized, which means that we have reached the steady state, they coincide with the predictions of Eqs. 11.69, 11.70, 11.71. Furthermore, we should point out the reason why there is a difference in the time it takes for ϱ to become

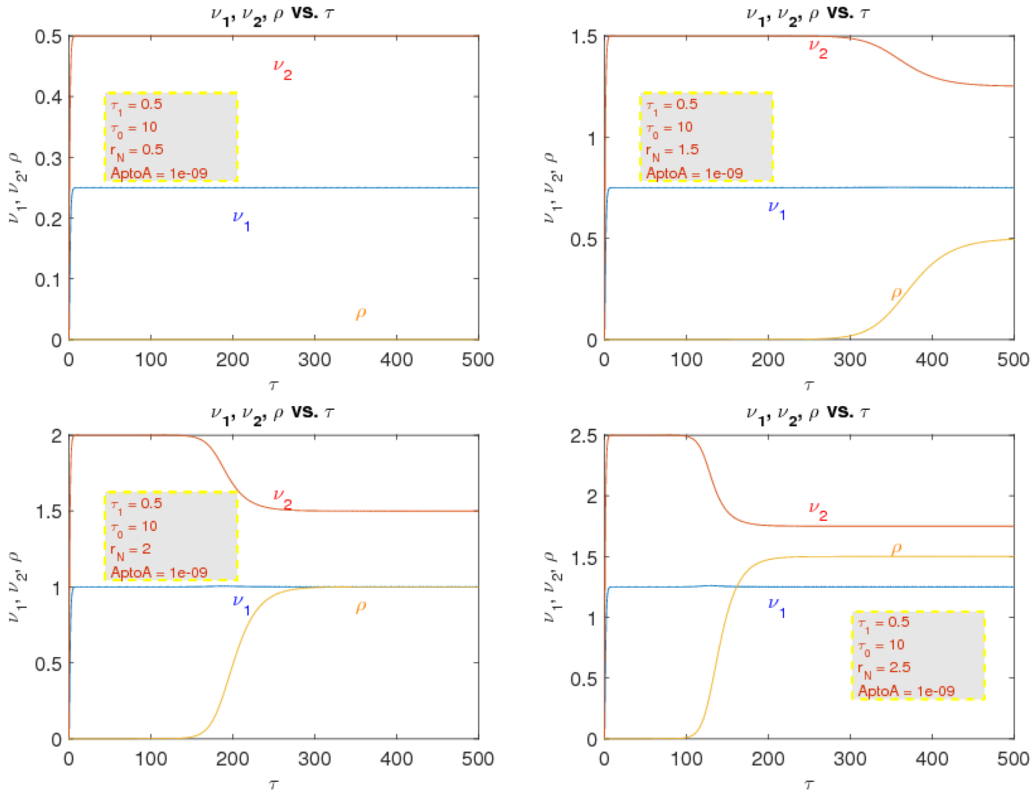

Figure 11.7: The effect of changing r_N on the functions of ν_1, ν_2, ϱ versus τ. We keep $\tau_0 = 10$, $\frac{A'}{A} = 10^{-9}$ and $\tau_1 = 0.5$ constant, while we change r_N setting the values 0.5, 1.5, 2.0, 2.5. Note that the notation ρ in the panels is in fact the dimensionless ϱ of Eq. 11.75.

perceivable. The reason is that when we increase the dimensionless pumping r_N, the term ν_2 is also increased due to Eq. 11.74, thus, in Eq. 11.75, the term $\frac{A'}{A}\nu_2$, which is the only one that leads to $\frac{d\varrho}{d\tau} > 0$ when ϱ is negligible, increases as well.

11.7 Standing EM waves inside a 3D cavity: Longitudinal modes and transverse modes.

Let us inspect standing electromagnetic waves in a 3D cavity more carefully. There are the so-called **longitudinal** and the so-called **transverse modes**. Let us begin with some general nomenclature. EM modes without an electric field in the direction of propagation are called **TE** (**Transverse Electric**). EM modes without a magnetic field in the direction of propagation are called **TM** (**Transverse Magnetic**). Finally, EM modes without an electric and a magnetic field in the direction of propagation are called **TEM** (**Transverse ElectroMagnetic**). Here, we will focus on TEM, considering the longest dimension of the cavity as the direction of propagation, i.e., using the choice we have made so far, the dimension parallel to the z-axis.

The **longitudinal modes** appeared when we solved the essentially one-dimensional (1D) problem, by putting mirrors in positions $z = 0$ and $z = L$, and assuming that the lateral component of $\vec{E}$ becomes zero on the mirrors (just like the perpendicular component of $\vec{B}$). So, we found that (Eq. 8.45)

$$k_m = \frac{m\pi}{L}, m \in \mathcal{N}^*.$$

We also found that (Eq. 8.50)

$$\omega_m = \frac{m\pi c}{L}, m \in \mathcal{N}^*.$$

Thus (Eq. 11.28),

$$\nu_m = \frac{mc}{2L}, m \in \mathscr{N}^*,$$

and

$$L = m\frac{\lambda_m}{2}, \tag{11.76}$$

as expected for standing waves between two mirrors in distance L (length). From Eq. 11.28, we concluded (Eq. 11.29) that the frequency distance of the longitudinal EM modes is

$$\Delta\nu_{m,m+1} = \frac{c}{2L}.$$

In this 1D problem, the solutions contain (Eq. 8.48)

$$Z_m(z) = \sqrt{\frac{2}{L}}\sin\left(\frac{m\pi z}{L}\right),$$

$m = 1, 2, 3, \ldots$. Thus, the number of nodes, i.e., where $Z_m(z)$ is constantly zero, is $m' = m - 1$. We could also solve the following 1D problems: in height (h) with $p = 1, 2, 3, \ldots$ and $p' = p - 1$ = number of nodes in the x-axis, or in width (w) with $q = 1, 2, 3, \ldots$ and $q' = q - 1$ = number of nodes in the y-axis.

However, a cavity is three-dimensional (3D), e.g. rectangular parallelepiped or cylindrical, as shown in Figure 11.8. In a rectangular parallelepiped cavity, commonly $L >> h, w$, where L = length, h = height, and w = width. In a cylindrical cavity, commonly $L >> r$, L = length, and r = radius. The **transverse modes** occur during solving the 3D problem and depend on the geometry of the cavity, e.g. whether it is rectangular parallelepiped or cylindrical. This subject has been discussed in Section 2.10. Let us assume that we examine an empty rectangular parallelepiped cavity with perfectly conducting walls and edges with height $h = a_x$, width $w = a_y$, and length $L = a_z$, along the x, y and z axes, respectively. Additionally, let us assume that the cavity lies on the first octant of the Cartesian coordinate system $Oxyz$, with a vertex on O. For the electric field, Eqs. 2.66, 2.67, 2.68 occur, i.e.,

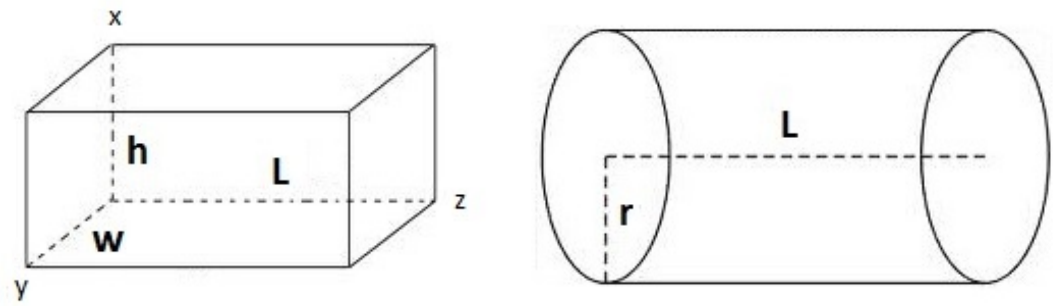

Figure 11.8: A rectangular parallelepiped and a cylindrical cavity.

$$E_x = E_{x0}\cos(k_x x)\sin\left(k_y y\right)\sin(k_z z)e^{-i\omega t} \Rightarrow \text{becomes zero for } y = 0 \text{ and } z = 0 \tag{11.77}$$

$$E_y = E_{y0}\sin(k_x x)\cos\left(k_y y\right)\sin(k_z z)e^{-i\omega t} \Rightarrow \text{becomes zero for } x = 0 \text{ and } z = 0 \tag{11.78}$$

$$E_z = E_{z0}\sin(k_x x)\sin\left(k_y y\right)\cos(k_z z)e^{-i\omega t} \Rightarrow \text{becomes zero for } x = 0 \text{ and } y = 0 \tag{11.79}$$

For the magnetic field, Eqs. 2.72, 2.73, 2.74 occur, i.e.,

$$B_x = \frac{i}{\omega}\left(E_{y0}k_z - E_{z0}k_y\right)\sin(k_x x)\cos\left(k_y y\right)\cos(k_z z)e^{-i\omega t} \tag{11.80}$$

$$B_y = \frac{i}{\omega}\left(E_{z0}k_x - E_{x0}k_z\right)\cos(k_x x)\sin\left(k_y y\right)\cos(k_z z)e^{-i\omega t} \tag{11.81}$$

$$B_z = \frac{i}{\omega}\left(E_{x0}k_y - E_{y0}k_x\right)\cos(k_x x)\cos\left(k_y y\right)\sin(k_z z)e^{-i\omega t} \tag{11.82}$$

Eq. 2.69 holds, as well:

$$k_x^2 + k_y^2 + k_z^2 = \frac{\omega^2}{c^2}$$

So does Eq. 2.70

$$k_x = \frac{m_x \pi}{a_x}, \quad k_y = \frac{m_y \pi}{a_y}, \quad k_z = \frac{m_z \pi}{a_z},$$

where $m_x, m_y, m_z \in \mathbb{Z}$. We can alternatively consider $m_x, m_y, m_z \in \mathbb{N}$, absorbing the sign change in E_{x0}, E_{y0}, E_{z0}, i.e., allowing E_{x0}, E_{y0}, E_{z0} to take positive or negative values, such that they agree with the boundary conditions. $m_x = p, m_y = q, m_z = m$, which are called **mode numbers**, are thus independent non-negative integers which obey to the constraint that no more than one of them can simultaneously become zero [4]. This constraint occurs since if two or three of m_x, m_y, m_z become zero, then the EM field in the cavity becomes zero as well, according to Eqs. 2.66, 2.67, 2.68 and Eqs. 2.72, 2.73, 2.74. Combining the above, we can write that the angular frequency and the frequency obey to the rule

$$\omega_{pqm} = 2\pi\nu_{pqm} = k_{pqm}c, \tag{11.83}$$

wherek_{pqm} is the norm of the vector with components k_x, k_y, k_z.

For a rectangular parallelepiped cavity, we have shown Eq. 2.76

$$\omega_{m_x,m_y,m_z} = \pi c\sqrt{\left(\frac{m_x}{a_x}\right)^2 + \left(\frac{m_y}{a_y}\right)^2 + \left(\frac{m_z}{a_z}\right)^2}, \quad \text{hence}$$

$$\nu_{m_x,m_y,m_z} = \frac{c}{2}\sqrt{\left(\frac{m_x}{a_x}\right)^2 + \left(\frac{m_y}{a_y}\right)^2 + \left(\frac{m_z}{a_z}\right)^2}$$

or

$$\omega_{pqm} = \pi c\sqrt{\left(\frac{p}{h}\right)^2 + \left(\frac{q}{w}\right)^2 + \left(\frac{m}{L}\right)^2}, \quad \text{hence}$$

$$\nu_{pqm} = \frac{c}{2}\sqrt{\left(\frac{p}{h}\right)^2 + \left(\frac{q}{w}\right)^2 + \left(\frac{m}{L}\right)^2}$$

If, however, we have a triagonal. cavity, with $h = w = a$, then

$$\omega_{pqm} = \pi c\sqrt{\frac{p^2+q^2}{a^2} + \frac{m^2}{L^2}},$$

$$\nu_{pqm} = \frac{c}{2}\sqrt{\frac{p^2+q^2}{a^2} + \frac{m^2}{L^2}}.$$

while, for a cubic cavity, with $h = w = L = a$,

$$\omega_{pqm} = \frac{\pi c}{a}\sqrt{p^2 + q^2 + m^2},$$
$$\nu_{pqm} = \frac{c}{2a}\sqrt{p^2 + q^2 + m^2}.$$

From Eqs. 2.66,2.67,2.68, 2.72,2.73,2.74, we obtain Table 11.1 (Table 2.2)

Table 11.1: Modes for a cubic cavity. The numbers of modes $m_x = p, m_y = q, m_z = m$ are independent, non-negative integers, subject to the constraint that no more than one of them can become zero simultaneously, or else the EM field in the cavity becomes zero.

$m_x = p$	$m_y = q$	$m_z = m$	$^{2a}/_{c}\nu$	EM field
0	0	0	0	0
0	0	1	1	0
0	1	1	$\sqrt{2}$	$\neq 0$
1	1	1	$\sqrt{3}$	$\neq 0$
2	0	0	2	0
2	1	0	$\sqrt{5}$	$\neq 0$

For the tetragonal cavity,

$$\nu_{pqm} = \frac{c}{2}\sqrt{\frac{p^2 + q^2}{a^2} + \frac{m^2}{L^2}} == \frac{c}{2}\frac{m}{L}\sqrt{1 + \frac{L^2}{a^2}\frac{p^2 + q^2}{m^2}} = \frac{mc}{2L}\sqrt{1 + x}, \tag{11.84}$$

where

$$x = \frac{L^2}{a^2}\frac{p^2 + q^2}{m^2}. \tag{11.85}$$

This x is very small in practice. For example, suppose a He-Ne LASER, with central wavelength $\lambda_0 \approx 632.8$ nm, $\nu_0 \approx 0.474$ PHz, and $L = 0.4$ m. Let us try to estimate the order of magnitude of m. If we had only longitudinal modes (1D problem), $\omega_m = \frac{m\pi c}{L} \Rightarrow \nu_m = \frac{mc}{2L} \sim \nu_0 = \frac{c}{\lambda_0} \Rightarrow m \sim \frac{2L}{\lambda_0} = \frac{0.8 \text{ m}}{632.8 \text{ nm}} \Rightarrow m \approx 1.264 \times 10^6$, hence $m^2 \approx 1.6 \times 10^{12}$. For $a \approx 1$ mm, $(^L/_a)^2 \approx 160000$, for $a \approx 2$ mm, $(^L/_a)^2 \approx 40000$, for $a \approx 4$ mm, $(^L/_a)^2 \approx 10000$, for $a \approx 10$ mm, $(^L/_a)^2 \approx 1600$. Thus, for small $p, q \approx 0, 1, 2, \ldots, x$ is small, so we can get, e.g., a Taylor expansion

$$\sqrt{1 + x} \approx 1 + \frac{x}{2} - \frac{x^2}{8} + \cdots \approx 1 + \frac{x}{2}, \tag{11.86}$$

which yields

$$\nu_{pqm} \approx \frac{mc}{2L} + \frac{cL}{4a^2}\frac{p^2 + q^2}{m}. \tag{11.87}$$

Thus

$$\nu_{00m} \approx \frac{mc}{2L} = \nu_m, \tag{11.88}$$

which are the frequencies of the longitudinal modes for the 1D problem (Eq. 11.28). Of course, in the 3D problem, if two of the numbers of modes become zero, the EM field in the cavity becomes zero, as well. The modes with $p \neq 0$ or $q \neq 0$ are called transverse modes. Thus, the frequency distance between two consecutive transverse modes, e.g., by changing p only for given q and m is

$$\Delta\nu_{p,p+1} \approx \frac{cL}{4a^2}\frac{(p+1)^2 + q^2}{m} - \frac{cL}{4a^2}\frac{p^2 + q^2}{m} = \frac{cL}{4a^2}\frac{2p + 1}{m}. \tag{11.89}$$

For example, for $L = 0.4$ m and $a = 4$ mm, $\Delta\nu_{p,p+1} \approx 1.5\,(2p+1)$ MHz, where we have estimated $m \approx 1.264 \times 10^6$. Let us remember, for comparison, that for $L = 0.4$ m, the frequency distance of longitudinal modes is $\Delta\nu_{m,m+1} = \frac{c}{2L} = 375$ MHz. For $p = 1$, it occurs that $\Delta\nu_{p,p+1} \approx 4.5$ MHz, hence the frequency distance of the transverse modes is rather smaller than the frequency distance of the longitudinal modes. Given this, the longitudinal and transverse modes in a rectangular parallelepiped cavity are qualitatively depicted [5] in Figure 11.9. We also took into account that, for the same m,

$$\begin{array}{ccc} p = 1, q = 0 \text{ or } p = 0, q = 1 & \Rightarrow & p^2 + q^2 = 1 \\ p = 1, q = 1 & \Rightarrow & p^2 + q^2 = 2 \\ p = 2, q = 0 \text{ or } p = 0, q = 2 & \Rightarrow & p^2 + q^2 = 4 \\ p = 2, q = 1 \text{ or } p = 1, q = 2 & \Rightarrow & p^2 + q^2 = 5 \end{array}$$

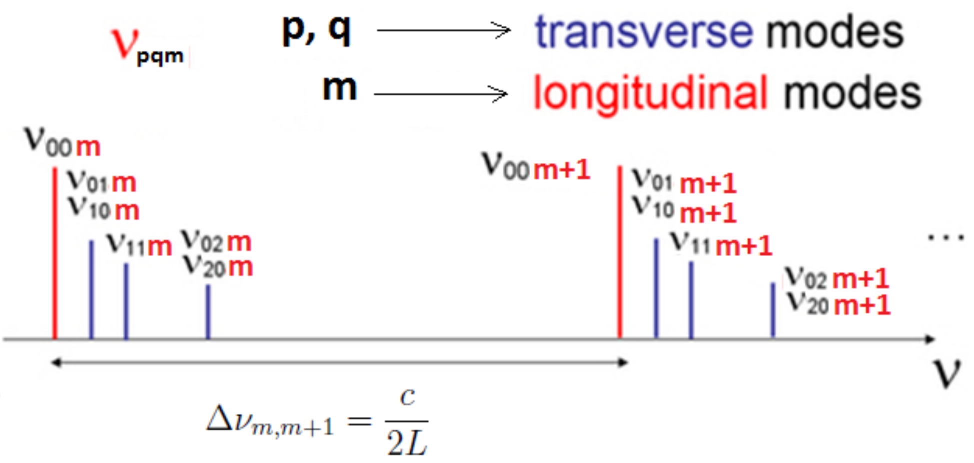

Figure 11.9: Longitudinal and transverse modes ν_{pqm} in a rectangular parallelepiped cavity.

11.8 Shape of TEM00 and TEMp'q' of higher order in rectangular parallelepiped and cylindrical cavities.

Usually, in nomenclature, the indices p', q' are used instead of p, q. These are defined as follows:

In a **rectangular parallelepiped cavity**, the indices in $\text{TEM}_{p'q'}$ mean:
p' = the number of nodes along the x-axis.
q' = the number of nodes along the y-axis.
For example, TEM_{02} means there there are no nodes along the x-axis and two nodes along the y-axis. The EM radiation intensity of the mode $\text{TEM}_{p'q'}$ is, in Cartesian coordinates, [6]

$$I_{p'q'}(x, y) = I_0 \left[H_{p'}\left(\frac{\sqrt{2}x}{w} \right) e^{-\frac{x^2}{w^2}} \right]^2 \left[H_{q'}\left(\frac{\sqrt{2}y}{w} \right) e^{-\frac{y^2}{w^2}} \right]^2 \tag{11.90}$$

On the left-hand side of Table 11.2, the Hermite polynomials, $H_n(x)$, involved in Eq. 11.90, are presented, while w is the spot size FWHM of the fundamental TEM_{00} mode. The shape of the TEM mode, as occurs from Eq. 11.90 is presented in Figure 11.10, left. Higher order modes have larger spatial extent. Therefore, by interposing an aperture the laser output we can prune these modes that have more extent than desired. Generally, the total form of the radiation intensity occurs as a superposition of all the modes in the cavity, although it is often desired to operate solely with the fundamental mode.

In a **cylindrical cavity**, the indices in $\text{TEM}_{p'q'}$ mean:
p' = the number of radial nodes.

Table 11.2: The first Hermite polynomials, which are related to the rectangular parallelepiped cavity, and the first Laguerre polynomials, which are related to the cylindrical cavity.

Hermite polynomials	**Laguerre polynomials**
$H_0(x) = 1$	$L_0(x) = 1$
$H_1(x) = 2x$	$L_1(x) = -x + 1$
$H_2(x) = 4x^2 - 2$	$L_2(x) = \frac{1}{2}(x^2 - 4x + 2)$
$H_3(x) = 8x^3 - 12x$	$L_3(x) = \frac{1}{6}(-x^3 + 9x^2 - 18x + 6)$
$H_4(x) = 16x^4 - 48x^2 + 12$	$L_4(x) = \frac{1}{24}(x^4 - 16x^3 + 72x^2 - 96x + 24)$
...	...

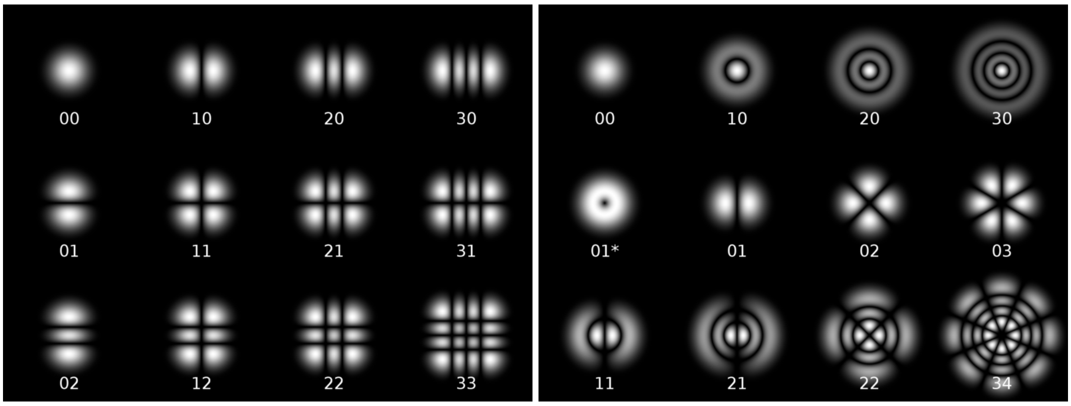

Figure 11.10: Left: Transverse TEM$_{p'q'}$ modes in a rectangular parallelepiped cavity [7]. Right: Transverse TEM$_{p'q'}$ modes in a cylindrical cavity [8]. TEM$_{00}$ is more concentrated close to the z-axis than higher order TEM$_{p'q'}$: as the values of the indices increase, the modes occupy a larger portion of the xy-plane.

q' = the number of nodes along half a periphery, i.e., in angular terms, within a π angle.
For example, TEM$_{02}$ means there there are no radial nodes and two nodes along half a periphery, i.e., within a π angle. The EM radiation intensity of the mode TEM$_{p'q'}$ is, in polar coordinates (r, φ), [6]

$$I_{p'q'}(\rho, \varphi) = I_0 \rho^{q'} \left[L_{p'}^{q'}(\rho) \right]^2 \cos^2(q'\varphi) e^{-\rho} \tag{11.91}$$

where $\rho = 2r^2/w^2$, w is the spot size FWHM of the fundamental mode, TEM$_{00}$, which coincides with the TEM$_{00}$ of the rectangular parallelepiped cavity, and $L_{p'}^{q'}$ is the associated Laguerre polynomial of order p' and index q'. On the right-hand side of Table 11.2, the Laguerre polynomials,

$$L_n(x) = \frac{e^x}{n!} \frac{d^n}{dx^n} \left(e^{-x} x^n \right), \tag{11.92}$$

are presented. These are used to construct the associated (or generalized) Laguerre polynomials, $L_n^a(x)$, which are involved in Eq. 11.91. Specifically, the Laguerre polynomials are the special, $a = 0$, case of the associated (or generalized) Laguerre polynomials, that is,

$$L_n^0(x) = L_n(x). \tag{11.93}$$

$$L_n^a(x) = \frac{x^{-a} e^x}{n!} \frac{d^n}{dx^n} \left(e^{-x} x^{n+a} \right). \tag{11.94}$$

The shape of the TEM mode, as occurs from Eq. 11.91 is presented in Figure 11.10, right.

In summary, the shape of the EM radiation intensity I, of the TEM$_{p'q'}$ in a rectangular parallelepiped cavity (left) and in a cylindrical cavity (right) is presented in Figure 11.10. In Table 11.2, we present the first Hermite polynomials, associated with the rectangular parallelepiped cavity (left), and the first Laguerre polynomials, associated with the cylindrical cavity (right).

11.9 Laser types - indicative applications.

The first LASER that produced visible light was the Ruby LASER, constructed in 1960 [9]. Today, there are really many types of LASER; most of these are used only for specialized research purposes. Their wavelengths vary from the ultraviolet, to the visible, the near infrared, the mid infrared, and the far infrared [10]. We will not go into much detail. As a matter of fact, this book focuses on quantum optics and not on the technical aspects of LASER, for which there is a vast literature in Greek, either translated or not [11, 12, 13, 14, 15, 16]. Therefore, we will not go into these subjects. In Table 11.3 the most important LASER types are presented, together with some representative members of each type. They are mainly classified with respect to the active medium and the pumping mechanism.

Today, LASER applications cover a very broad spectrum. Let us name some, indicatively: **research** (pumping for other LASER, interferometry, LASER cooling, various spectroscopies, lithography, confocal microscopy, etc), **medicine** (surgery, dentistry, tissue ablation, kinda stone treatment, dermatology, retinal phototherapy, etc), **cosmetics** (tattoo removal, wrinkle removal, etc), **telecommunications**, **holography**, **military**, **industry** (soldering, cutting, automotive lighting, lithography, engraving, etc), **everyday life** (printers, writing and reading Blu-ray discs, DVDs, CDs etc, projectors, pointers, optical scanners, detection of pollution, etc).

11.10 p-n junction LASER or diode LASER.

Most lasers are not tiny objects. For example, in He-Ne lasers, the length of the cavity is some dm and its thickness is some mm. However, we use lasers in portable audio and video reproduction devices (e.g., DVD players), to read product prices in shops with small barcode readers, in printers, in optical fiber communications and many more daily use items. Those tiny lasers are usually laser diodes - they are also called $p-n$ junction lasers. These are devices similar to LEDs (light-emitting diodes), the tiny light indicators used in various devices. The laser diodes were first constructed by Robert N. Hall in the 1960s [17]. Their tiny size and cheap price makes them the most widespread lasers today.

We have basically a bilayer semiconductor device, with one layer being a p-type semiconductor (with excess holes) and the other one being a n-type semiconductor (with excess electrons). A common $p-n$ diode conducts only in one direction, i.e., then the applied voltage has a forward bias. The inverse voltage is called reverse bias; the diode does not conduct in this case. In a LED or a laser diode there is electron-hole recombination, which takes place through the band gap and produces photons (phonons may participate in the process, as well). The most common semiconductors used in laser diodes are alloys such as $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$, $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}_y\mathrm{P}_{1-y}$. Depending on the size of the band gap, photons can have various visible colors or even ultraviolet or infrared wavelengths.

In laser diodes, pumping occurs by forward bias. The number of impurities (donors) in the n-type semiconductor and the number of impurities (acceptors) in the p-type semiconductor are large enough (of the order of $10^{18}\mathrm{cm}^{-3}$) that the Fermi level of the n-type semiconductor, F_n lies within the conduction band and the Fermi level of the p-type semiconductor lies within the valence band (Figure 11.12, top). Then the two layers contact, the large hole concentration in the p-type semiconductor and the large concentration of electron in the n-type semiconductor create flows from the side with large concentration to the side with small concentration: electrons are injected in the p-type layer and holes are injected in the n-type layer, hence, in the vicinity of the junction, the p-type layer is negatively charged and the n-type layer is

Table 11.3: Types of LASER and some members of each type. In the first column the active media are presented, and in the right column the wavelengths in nm.

Gas LASER	**pumping: electric discharge**
He-Ne	543.5, 593.9, 611.8, 632.8, 1152.3, 1520, 3391.3
Ar	351, 363.8, 454.6, 457.9, 465.8, 476.5, 472.7, 488.0, 514.5, 528.7
Kr	416, 530.9, 568.2, 647.1, 676.4, 752.5, 799.3
N	337.1
CO_2	9400, 10600
Chemical LASER	**pumping: chemical reaction**
HF	2700 - 2900
DF	3600 - 4200
O, I	1315
Dye LASER	**pumping: other lasers or flashlamps**
stilbene	390-435
coumarin	460-515
rhodamine	570-640
Metal vapor LASER	**pumping: electric discharge**
HeCd	441.6, 325
HeHg	567, 615
HeSe	red to UV
HeAg	224.3
Sr	430.5
Solid state LASER	**pumping: other lasers or flashlamps**
Ruby	694.3
Nd:YAG	1064, 1320
NdCrYAG	1064, 1320
Er:YAG	2940
Yb	1030
Ho:YAG	2100
Semiconductor LASER	**pumping: voltage or light**
GaN	400
InGaN	400-500
AlGaInP, AlGaAs	630-900
InGaAsP	1000-2100

positively charged; this causes thermodynamic equilibrium. Therefore, the Fermi levels coincide and the is no longer electron or hole flow from the p-type layer to the n-type layer and vice versa. This means that a potential energy barrier is created, of the order of 0.1 eV (Figure 11.12, middle). If an external voltage V is applied, then the Fermi levels are separated so that

$$\Delta F = F_n - F_p = eV. \tag{11.95}$$

The operating voltage of a laser diode is small, of the order of V, since ΔF is of the order of the semiconductor's band gap, E_g, which is close to eV. This is how population inversion is achieved in the vicinity of the junction (orange arrow in Figure 11.12, bottom). This means that there are enough electrons in the conduction band and enough holes in the valence band for lasing. Some of the electrons spontaneously drop from the conduction band to the available states of the valence band; in other words, we have spontaneous emission. These electrons are not, of course, coherent. The have a random phase. However, they

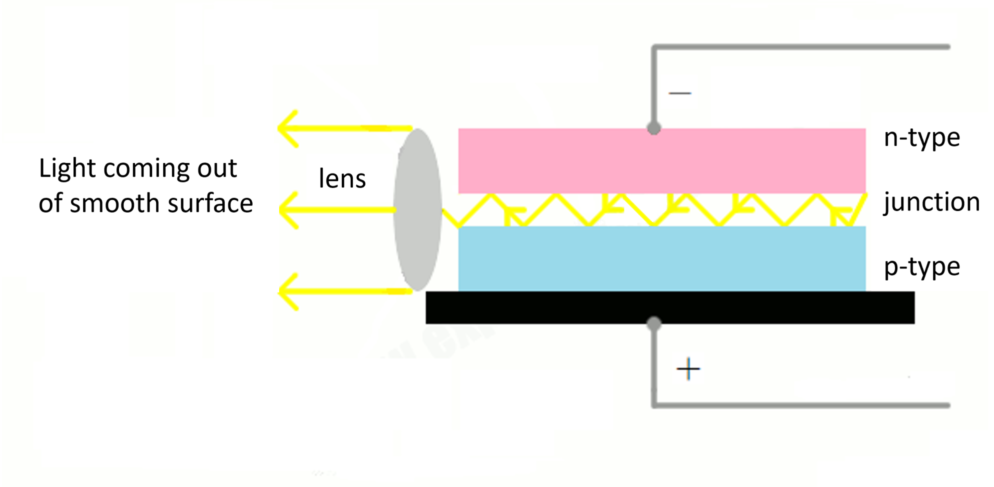

Figure 11.11: A laser diode device with two electrodes (+) and (−) in forward bias. The upper and lower surfaces, which are normal to the plane of the figure, have dimensions of the order of mm^2. The junction region, i.e. the "medium" layer is of the order of 100 nm, while the sides are of the order of 10-100 μm. In other words, this device is small enough to be used in various small everyday devices.

force other electrons in the conduction band to drop to the valence band by emitting photons; in other words, we have stimulated emission: emission of photons with the same energy, momentum, polarization, and phase. However, since these electrons do not drop from a level with small enough width (as it is the case, e.g., in a He-Ne laser), but rather from the occupied energy region of the conduction band to the empty energy region of the valence band, the emission line of the laser diode is broader than, e.g., the one of the He-Ne laser, of the order of 100 times [3].

Photons are forced to be reflected in the narrow region of the contact between the p- and n-type layers, thus creating standing waves. Therefore, photons are traveling inside the junction for a time long enough to achieve many stimulated emissions. Part of the amplified light comes out of a surface of the structure that has been flattened out, while the rest surfaces remain rough so that light is confined. This flattened surface must be exactly parallel to its opposite, for standing waves to occur in the cavity. These two surfaces may be also covered by mirrors or metallic coatings to amplify the generation of standing waves. In other words, a LED device can emit a laser beam if it has a resonance cavity [3].

11.11 Quantum dot LASER.

Another type of semiconductor laser is the quantum dot laser (Figure 11.13). It is a device the active medium of which is a collection of quantum dots (see Section 4.3). Due to the strong quantum confinement of the carriers in quantum dots, their electronic structure is similar the one of atoms. Actually, as we also mentioned in Section 4.3, this is the reason why quantum dots are also sometimes referred to as artificial atoms when they are single and as artificial molecules when they are coupled. Lasers constructed by such active media display properties similar to gas lasers and are superior to other semiconductor lasers, e.g., in terms of emission lines. Since the electronic structure of quantum dots is dependent on their size as well as of the type of -usually- semiconducting alloys used [18, 19], the active region can be constructed in a way such that the device can operate in several wavelengths, even in regions that were not possible for common semiconductor lasers. Quantum dot laser devices are used in commercial applications, medicine, screens, spectroscopy, telecommunications, etc. Some years ago, a quantum dot laser for use in optical telecommunication systems [20] in 10 Gbps = Giga bits per second, with operating wavelength 1.3 μm and operating temperatures 20 - 70 ^{o}C. Since then, this performance has been further improved.

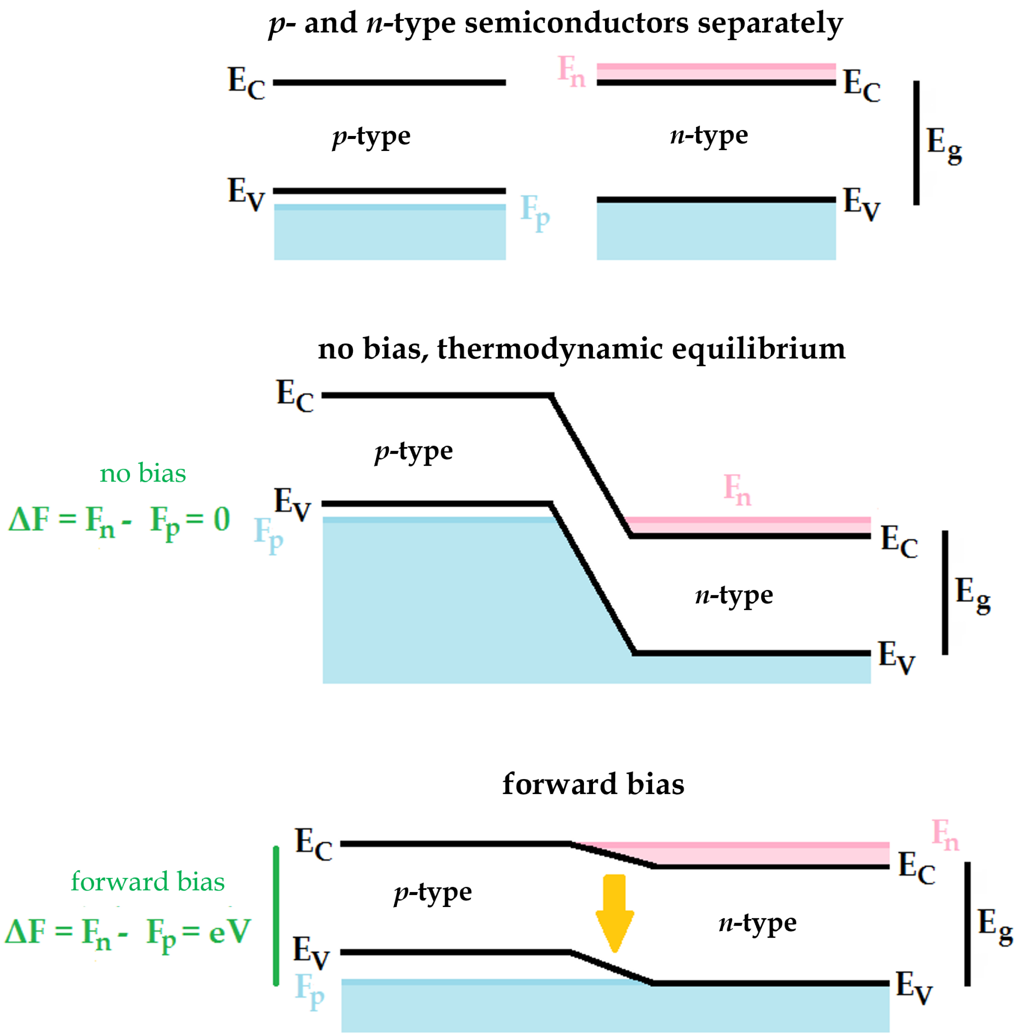

Figure 11.12: Operation principle of the p-n as a laser. Top: the p- and n-type semiconductors, separately. Middle: The structure without polarization, i.e., without external bias, in thermodynamic equilibrium. Bottom: The structure with forward bias, an external voltage V. When the structure has been formed, there are "three layers", since there is also the junction region (where the bands appear inclined). During forward bias, we have population inversion in the vicinity of the junction, which is denoted by an orange arrow. This means that in this region there are many electrons that, as they drop from the conduction band to the valence band through the band gap E_g, emit photons and are recombined with holes. These photons, in turn, force stimulated emission to other electrons of the junction region.

11.12 Isolation techniques for the TEM00 and of higher order TEMp'q'.

In Figure 11.10, the $\mathrm{TEM}_{p'q'}$ were presented. Here, let us consider the case of a rectangular parallelepiped cavity [7], which is presented again, for the facilitation of the readership, in Figure 11.14. We observe that TEM_{00} mode is more concentrated close to the z-axis (centered at the point $x = y = 0$) than higher order $\mathrm{TEM}_{p'q'}$: as the values of the indices increase, the modes occupy a larger portion of the xy-plane. The polarization of the light beam on the laser output depends on the mixture of polarizations of the $\mathrm{TEM}_{p'q'}$ modes it contains [21]. The polarization of the outgoing beam can be corrected using a window positioned at Brewster's angle, see, e.g., Sections 12.1 and 12.3. $\mathrm{TEM}_{p'q'}$ modes of higher order can be pruned by inserting an aperture in the way of the outgoing beam. This aperture ("iris" = hole of adjustable width) closes as much as it is needed so that higher order $\mathrm{TEM}_{p'q'}$, which have a larger spatial extent than

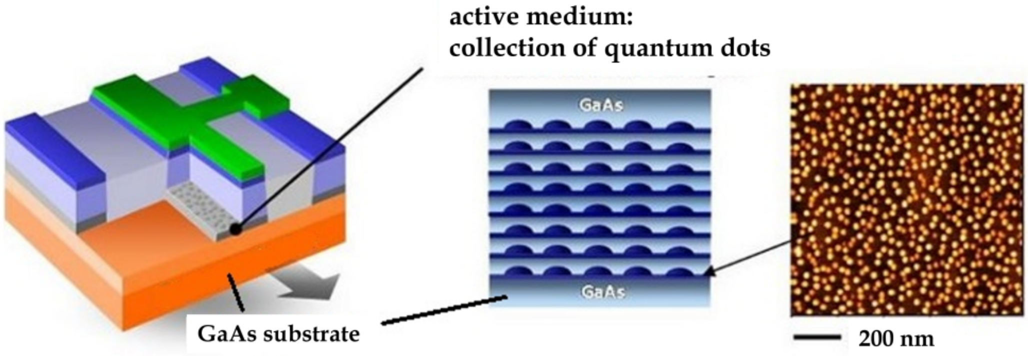

Figure 11.13: The body of a quantum dot laser device that transmits data in 25 Gbps. Modified image from the press conference by Fujitsu, 2010.

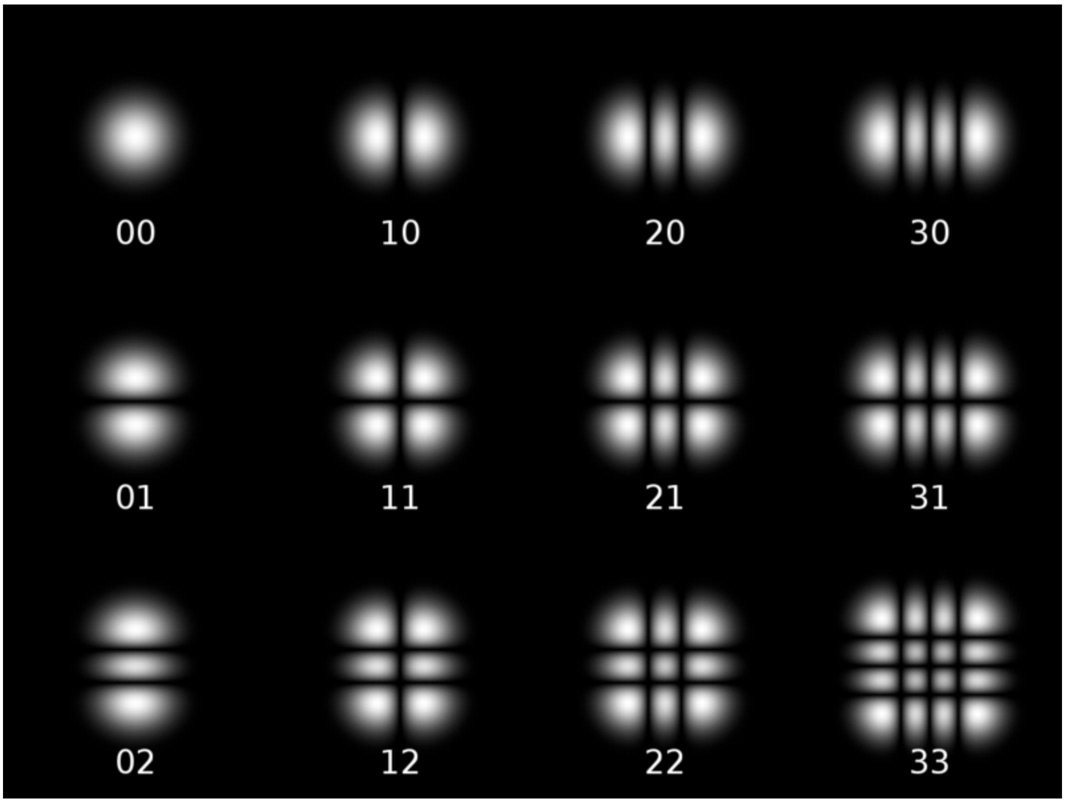

Figure 11.14: Transverse $\mathrm{TEM}_{p'q'}$ modes in a rectangular parallelepiped cavity [7]. TEM_{00} is more concentrated close to the z-axis than higher order $\mathrm{TEM}_{p'q'}$: as the values of the indices increase, the modes occupy a larger portion of the xy-plane.

the hole width, are not allowed to pass. Thus, we can even isolate a single dot, i.e., TEM_{00} mode. On the other hand, as the aperture width gets larger, higher order $\mathrm{TEM}_{p'q'}$ modes are also allowed to pass.

If the vertical thread is shifted a bit more, it will reach a position in which the field o 02 becomes zero. Similarly, if the horizontal thread is shifted a bit more, it will reach a position in which the field o 20 becomes zero. This new position will allow 02 (or, similarly, 20) to survive, since in this new position it will have zero intensity and thus will not have losses due to diffraction by the thin thread. On the other hand, 01 and 00 (or, similarly, 10 and 00) will be destroyed. $\mathrm{TEM}_{p'q'}$ modes of even higher order can be isolated in a similar fashion.

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CHAPTER 12

VARIOUS

In this Chapter:
We lay down some useful properties and elements. We analyze Fresnel equations and explain what the Brewster is and the total internal reflection. We discuss the polarized beam emission. We refer to the Poynting vector.
Prerequisite knowledge: Basic knowledge of Electromagnetism.

12.1 Fresnel equations. Brewster angle.

We recall (Section 2.4) that the Maxwell's equations in terms of total charge and current are, in *differential form* and *integral form*,

$$\begin{array}{rcl}
\textit{differential form} & & \textit{integral form}\\
\boxed{\vec{\nabla}\cdot\vec{E}=\frac{\rho}{\varepsilon_0}} & \Rightarrow & \boxed{\Phi_{E,S=\partial V}=\oint_{S=\partial V}\vec{E}\cdot d\vec{a}=\frac{q_{\text{enclosed in }V}}{\varepsilon_0}}\\
\boxed{\vec{\nabla}\cdot\vec{B}=0} & \Rightarrow & \boxed{\Phi_{B,S=\partial V}=\oint_{S=\partial V}\vec{B}\cdot d\vec{a}=0}\\
\boxed{\vec{\nabla}\times\vec{E}=-\frac{\partial\vec{B}}{\partial t}} & \Rightarrow & \boxed{\mathscr{E}_{\text{EMF}}=\oint_{L=\partial S}\vec{E}\cdot d\vec{\ell}=-\frac{\partial\Phi_{B,S}}{\partial t}}\\
\boxed{\vec{\nabla}\times\vec{B}=\mu_0\vec{J}+\mu_0\varepsilon_0\frac{\partial\vec{E}}{\partial t}} & \Rightarrow & \boxed{\oint_{L=\partial S}\vec{B}\cdot d\vec{\ell}=\mu_0 I_{\text{passing through }S}+\mu_0\varepsilon_0\frac{\partial\Phi_{E,S}}{\partial t}}
\end{array}$$

Constantinos Simserides (2023). «Quantum Optics».
Kallipos, Open Academic Editions. https://dx.doi.org/10.57713/kallipos-186

We moved from one formulation to the other using the Gauss's theorem and the Stokes' theorem

Gauss's theorem $$\oint_{S=\partial V} \vec{\Delta} \cdot d\vec{a} = \int_V \vec{\nabla} \cdot \vec{\Delta}\, dV$$

Stokes' theorem $$\oint_{L=\partial S} \vec{\Delta} \cdot d\vec{\ell} = \int_S \vec{\nabla} \times \vec{\Delta} \cdot d\vec{a}$$

We also recall that vectors $\vec{D}$ and $\vec{H}$ are connected with vectors $\vec{E}$ and $\vec{B}$, respectively, through the relations

$$\vec{D} = \varepsilon_0 \varepsilon \vec{E}, \tag{12.1}$$

$$\vec{B} = \mu_0 \mu \vec{H}. \tag{12.2}$$

Let us assume (Assumption 1) that ε, μ **are constant values and not tensors**.

Additionally, the Maxwell's equations in terms of free (f) charge and current are, in *differential form* and *integral form*,

differential form *integral form*

$$\boxed{\vec{\nabla} \cdot \vec{D} = \rho_f} \Rightarrow \boxed{\oint_{S=\partial V} \vec{D} \cdot d\vec{a} = q_{f,\,\text{enclosed in } V}} \tag{12.3}$$

$$\boxed{\vec{\nabla} \cdot \vec{B} = 0} \Rightarrow \boxed{\oint_{S=\partial V} \vec{B} \cdot d\vec{a} = 0} \tag{12.4}$$

$$\boxed{\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}} \Rightarrow \boxed{\mathscr{E}_{\text{EMF}} = \oint_{L=\partial S} \vec{E} \cdot d\vec{\ell} = -\frac{\partial \Phi_{B,S}}{\partial t}} \tag{12.5}$$

$$\boxed{\vec{\nabla} \times \vec{H} = \vec{J}_f + \frac{\partial \vec{D}}{\partial t}} \Rightarrow \boxed{\oint_{L=\partial S} \vec{H} \cdot d\vec{\ell} = I_{f,\text{passing through } S} + \frac{\partial \Phi_{D,S}}{\partial t}} \tag{12.6}$$

In the absence of free charges and currents, these equations become

$$\vec{\nabla} \cdot \vec{D} = 0 \qquad \oint_{S=\partial V} \vec{D} \cdot d\vec{a} = 0 \tag{12.7}$$

$$\vec{\nabla} \cdot \vec{B} = 0 \qquad \oint_{S=\partial V} \vec{B} \cdot d\vec{a} = 0 \tag{12.8}$$

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \qquad \oint_{R=\partial S} \vec{E} \cdot d\vec{\ell} = -\frac{\partial \Phi_{B,S}}{\partial t} \tag{12.9}$$

$$\vec{\nabla} \times \vec{H} = \frac{\partial \vec{D}}{\partial t} \qquad \oint_{R=\partial S} \vec{H} \cdot d\vec{\ell} = \frac{\partial \Phi_{D,S}}{\partial t} \tag{12.10}$$

In the case of an interface between two media, say 1 and 2, **repeating the procedure we followed in Section 2.5**, i.e. applying the Gauss's theorem in an elementary $S = \partial V$,

$$\oint_{S=\partial V} \vec{D} \cdot d\vec{a} = 0 \Rightarrow \cdots \Rightarrow$$

$$\boxed{D_{1\perp} = D_{2\perp}} \tag{12.11}$$

$$\oint_{S=\partial V} \vec{B} \cdot d\vec{a} = 0 \Rightarrow \cdots \Rightarrow$$

$$\boxed{B_{1\perp} = B_{2\perp}} \tag{12.12}$$

$D_{1\perp}, D_{2\perp}, B_{1\perp}, B_{2\perp}$ are the algebraic values of the components of $\vec{D}$ or $\vec{B}$ that are normal to the interface, on the side of medium 1 or 2. In other words, it occurs that $D_\perp$ and $B_\perp$ are continuous on the interface.

Applying the Stokes' theorem in an elementary $L = \partial S$

$$\oint_{L=\partial S} \vec{E} \cdot d\vec{\ell} = -\frac{\partial \Phi_{B,S}}{\partial t} \Rightarrow \cdots \Rightarrow$$

$$\boxed{E_{1\|} = E_{2\|}} \tag{12.13}$$

$$\oint_{L=\partial S} \vec{H} \cdot d\vec{\ell} = \frac{\partial \Phi_{D,S}}{\partial t} \Rightarrow \cdots \Rightarrow$$

$$\boxed{H_{1\|} = H_{2\|}} \tag{12.14}$$

$E_{1\|}, E_{2\|}, H_{1\|}, H_{2\|}$ are the algebraic values of the components of $\vec{E}$ or $\vec{H}$ that are parallel to the interface, on the side of medium 1 or 2. In other words, it occurs that $E_\|$ and $H_\|$ are continuous on the interface.

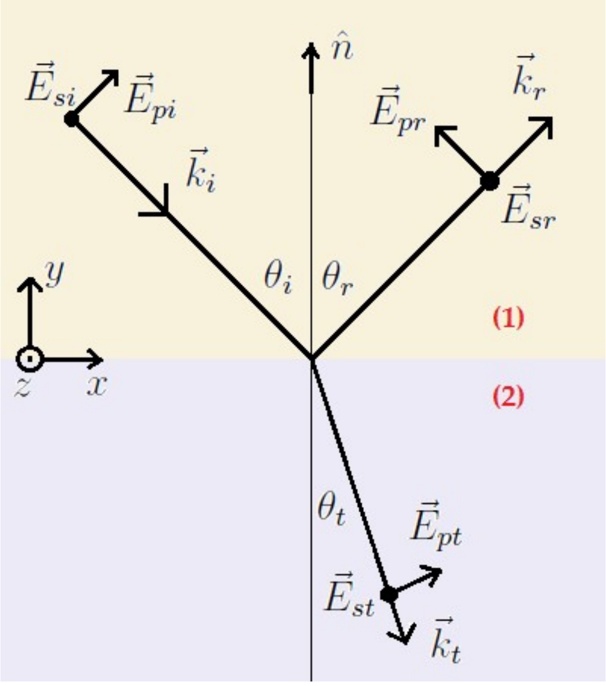

Figure 12.1: Incidence of EM wave at an interface between two media 1 and 2. Plane of incidence q is the plane defined by the incident wave vector $\vec{k}_i$ and the normal to the interface, at the point of incidence, unit vector $\hat{n}$, that is here plane xy. We observe the angles of incidence, reflection, refraction or transmission, $\theta_i, \theta_r, \theta_t$, respectively, as well as the s (perpendicular to q) and p (belonging to q) components of the incident, reflected, refracted or transmitted electric field $\vec{E}_{si}, \vec{E}_{pi}, \vec{E}_{sr}, \vec{E}_{pr}, \vec{E}_{st}, \vec{E}_{pt}$, respectively.

Let us now consider the incidence of an EM wave at an **interface** between two media, 1 and 2 (Figure 12.1), in the absence of free charges or currents, so that Eqs. 12.7, 12.8, 12.9, 12.10, as well as Eqs. 12.11, 12.12, 12.13, 12.14 hold. Furthermore, let us denote by q the plane of incidence, i.e. the plane defined by the incident wavevector $\vec{k}_i$ and the normal to the interface, at the point of incidence, unit vector $\hat{n}$, that is here plane xy. By the way, let us denote by $\vec{k}_r$ the reflected wavevector, and by $\vec{k}_t$ the transmitted or refracted wavevector. The polarization of an EM wave incident to an interface is characterized by the direction of $\vec{E}$ with respect to q. Specifically, the polarization is named s or p, after the German words senkrecht=perpendicular or parallel, respectively, depending on whether $\vec{E}$ is perpendicular or parallel to the plane q. Schematically, if we identify the plane of incidence with the plane of this page, then,

$$\begin{array}{lllll} \odot & \vec{E} & s \text{ polarization} & (\vec{E} \perp q) & \text{TE (transverse electric) polarization} \\ \nearrow & \vec{E} & p \text{ polarization} & (\vec{E} \in q) & \text{TM (transverse magnetic) polarization} \end{array}$$

Below, we will separately examine the incidence of EM wave in an interface between two materials for s or TE polarization and for p or TM polarization. Before we move on, we recall that $\vec{E} \times \vec{B} \parallel \vec{k}$. Also, the index $\perp$ denotes a field component perpendicular to the interface, while the index $||$ denotes a field component parallel to the interface.

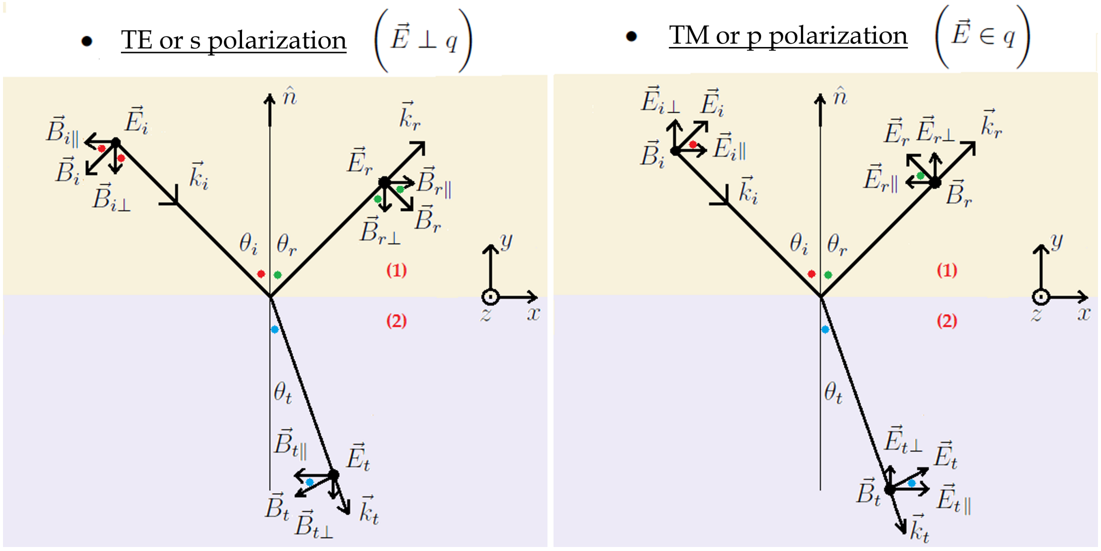

Figure 12.2: **Left:** TE or s polarization ($\vec{E} \perp q$). We observe $\vec{E}_i, \vec{E}_r, \vec{E}_t$, $\vec{B}_i, \vec{B}_{i\perp}, \vec{B}_{i\|}$, $\vec{B}_r, \vec{B}_{r\perp}, \vec{B}_{r\|}$, $\vec{B}_t, \vec{B}_{t\perp}, \vec{B}_{t\|}$. **Right:** TM or p polarization ($\vec{E} \in q$). We observe $\vec{B}_i, \vec{B}_r, \vec{B}_t$, $\vec{E}_i, \vec{E}_{i\perp}, \vec{E}_{i\|}$, $\vec{E}_r, \vec{E}_{r\perp}, \vec{E}_{r\|}$, $\vec{E}_t, \vec{E}_{t\perp}, \vec{E}_{t\|}$. The index $\perp$ denotes a field component perpendicular to the interface, while the index $||$ denotes a field component parallel to the interface. Colored dots denote equal angles.

In the left panel of Figure 12.2, we present the **TE or s polarization**, i.e. the situation in which $\vec{E} \perp q$. From Eq. 12.1, since $\vec{E} \perp q \Rightarrow \vec{D} \perp q$. Then,

$$\begin{array}{lll} \text{Continuity condition for } D_\perp \text{ (Eq. 12.11)} & \Rightarrow & \text{nothing } (\nexists \text{ such components for } s \text{ polarization}) \\ \text{Continuity condition for } B_\perp \text{ (Eq. 12.12)} & \Rightarrow & -B_i \sin\theta_i - B_r \sin\theta_r = -B_t \sin\theta_t \\ \text{Continuity condition for } E_\| \text{ (Eq. 12.13)} & \Rightarrow & E_r + E_i = E_t \\ \text{Continuity condition for } H_\| \text{ (Eq. 12.14)} & \Rightarrow & -\dfrac{B_i \cos\theta_i}{\mu_0\mu_1} + \dfrac{B_r \cos\theta_r}{\mu_0\mu_1} = -\dfrac{B_t \cos\theta_t}{\mu_0\mu_2} \end{array}$$

In the right panel of Figure 12.2, we present the **TM or p polarization**, i.e. the situation in which $\vec{B} \perp q$.

$$\begin{array}{lll} \text{Continuity condition for } D_\perp \text{ (Eq. 12.11)} & \Rightarrow & \varepsilon_1(E_i \sin\theta_i + E_r \sin\theta_r) = \varepsilon_2 E_t \sin\theta_t \\ \text{Continuity condition for } B_\perp \text{ (Eq. 12.12)} & \Rightarrow & \text{nothing } (\nexists \text{ such components for } p \text{ polarization}) \\ \text{Continuity condition for } E_\| \text{ (Eq. 12.13)} & \Rightarrow & E_i \cos\theta_i - E_r \cos\theta_r = E_t \cos\theta_t \\ \text{Continuity condition for } H_\| \text{ (Eq. 12.14)} & \Rightarrow & \dfrac{B_i}{\mu_0\mu_1} + \dfrac{B_r}{\mu_0\mu_1} = \dfrac{B_t}{\mu_0\mu_2} \end{array}$$

Let c_0 be the speed of light in vacuum, c the speed of light inside some material, and n the refraction index of this material. Then,

$$\left.\begin{aligned} \frac{E}{B} &= c \\ n &= \frac{c_0}{c} \end{aligned}\right\} \Rightarrow B = n\frac{E}{c_0}. \tag{12.15}$$

Let us assume that (Assumption 2) the frequency ν of the EM wave **remains unchanged during changing materials and during transmitting through the material**. Due to the fundamental law of wave mechanics,

$$c = \lambda\nu = \frac{2\pi}{k}\nu, \tag{12.16}$$

$$n = \frac{c_0}{c} = \frac{2\pi\nu|\vec{k}|}{|\vec{k}_0|2\pi\nu} \Rightarrow \left.\begin{aligned} |\vec{k}_i| &= n_i|\vec{k}_0| \\ |\vec{k}_r| &= n_r|\vec{k}_0| \\ |\vec{k}_t| &= n_t|\vec{k}_0| \\ n_1 = n_i &= n_r \\ n_2 &= n_t \end{aligned}\right\} \Rightarrow \boxed{\begin{aligned} |\vec{k}_i| &= n_1|\vec{k}_0| \\ |\vec{k}_r| &= n_1|\vec{k}_0| \\ |\vec{k}_t| &= n_2|\vec{k}_0| \end{aligned}} \tag{12.17}$$

If the amplitudes are constant then, in TE polarization, the continuity of $E_{||}$, i.e. the relationship $E_r + E_i = E_t$, implies that

$$\left.\begin{aligned} E_{0r}e^{i(\vec{k}_r\cdot\vec{r}-\omega_r t)} + E_{0i}e^{i(\vec{k}_i\cdot\vec{r}-\omega_i t)} &= E_{0t}e^{i(\vec{k}_t\cdot\vec{r}-\omega_t t)} \\ \forall\, t, \forall\, \vec{r} \text{ on the interface} \end{aligned}\right\} \Rightarrow$$

$$\boxed{\vec{k}_r\cdot\vec{r} - \omega_r t = \vec{k}_i\cdot\vec{r} - \omega_i t = \vec{k}_t\cdot\vec{r} - \omega_t t} \tag{12.18}$$

i.e. we arrive at a phase matching condition. Similarly, if the amplitudes are constant, then, in TM polarization, the continuity of $H_{||}$, i.e. the relationship $\frac{B_i}{\mu_0\mu_1} + \frac{B_r}{\mu_0\mu_1} = \frac{B_t}{\mu_0\mu_2}$ implies Eq. 12.18, as well. Taking Assumption 2 into account, if follows that $\omega_r = \omega_i = \omega_t$, hence,

$$\boxed{\vec{k}_r\cdot\vec{r} = \vec{k}_i\cdot\vec{r} = \vec{k}_t\cdot\vec{r}} \tag{12.19}$$

Let us look into Eq 12.2, and remember Eq. 12.17. Then, $\vec{k}_i\cdot\vec{r} = \vec{k}_r\cdot\vec{r} \Rightarrow$

$$|\vec{k}_i||\vec{r}|\cos\left(\frac{\pi}{2} - \theta_i\right) = |\vec{k}_r|\cdot|\vec{r}|\cos\left(\frac{\pi}{2} - \theta_r\right) \Rightarrow n_1|\vec{k}_0|\sin\theta_i = n_1|\vec{k}_0|\sin\theta_r \Rightarrow$$

$$\boxed{\theta_r = \theta_i}, \tag{12.20}$$

which is the **reflection law**. Furthermore,

$$\vec{k}_i\cdot\vec{r} = \vec{k}_t\cdot\vec{r} \Rightarrow |\vec{k}_i||\vec{r}|\cos\left(\frac{\pi}{2} - \theta_i\right) = |\vec{k}_t||\vec{r}|\cos\left(\frac{\pi}{2} - \theta_t\right) \Rightarrow n_1|\vec{k}_0|\sin\theta_i = n_2|\vec{k}_0|\sin\theta_t \Rightarrow$$

$$\boxed{n_i\sin\theta_i = n_t\sin\theta_t}, \tag{12.21}$$

which is the **refraction law**.

Let us examine TE polarization in more detail, using the equations we obtained above. We will assume that our materials are non-magnetic, i.e. that $\mu_1 = \mu_2 = 1$.

$$\left.\begin{aligned} E_r + E_i &= E_t \\ \frac{B_i \cos\theta_i}{\mu_0\mu_1} - \frac{B_r \cos\theta_r}{\mu_0\mu_1} &= \frac{B_t \cos\theta_t}{\mu_0\mu_2} \\ \mu_1 = \mu_2 &= 1 \\ B &= n\frac{E}{c_0} \end{aligned}\right\} \Rightarrow \left.\begin{aligned} E_r + E_i &= E_t \\ n_1 E_i \cos\theta_i - n_1 E_r \cos\theta_r &= n_2 E_t \cos\theta_t \\ n := \frac{n_2}{n_1} &\text{ (the relative refraction index)} \end{aligned}\right\} \Rightarrow$$

$$\left.\begin{aligned} E_r + E_i &= E_t \\ E_i \cos\theta_i - E_r \cos\theta_r &= nE_t \cos\theta_t \end{aligned}\right\} \overset{\theta_i=\theta_r}{\Rightarrow} \left.\begin{aligned} E_r + E_i &= E_t \\ E_i - E_r &= \frac{nE_t \cos\theta_t}{\cos\theta_i} \end{aligned}\right\} \Rightarrow$$

$$(\text{ adding by parts })\ 2E_i = E_t\left(1 + \frac{n\cos\theta_t}{\cos\theta_i}\right)$$

$$\boxed{t_{TE} := \frac{E_t}{E_i} = \frac{2\cos\theta_i}{\cos\theta_i + n\cos\theta_t} = \frac{2n_i\cos\theta_i}{n_i\cos\theta_i + n_t\cos\theta_t}}. \tag{12.22}$$

However,

$$n_i \sin\theta_i = n_t \sin\theta_t \text{ ή } \sin\theta_i = n\sin\theta_t$$

$$\text{while } \cos\theta_t = \sqrt{1-\sin^2\theta_t} = \sqrt{1-\frac{\sin^2\theta_i}{n^2}},$$

$$\text{thus, } t_{TE} = \frac{2\cos\theta_i}{\cos\theta_i + n\sqrt{1-\dfrac{\sin^2\theta_i}{n^2}}}.$$

Hence,

$$\boxed{t_{TE} = \frac{2\cos\theta_i}{\cos\theta_i + \sqrt{n^2 - \sin^2\theta_i}}}. \tag{12.23}$$

Moreover,

$$\left.\begin{aligned} E_t = E_i + E_r &= \frac{(E_i - E_r)\cos\theta_i}{n\cos\theta_t} \\ E_r\left(1 + \frac{\cos\theta_i}{n\cos\theta_t}\right) &= E_i\left(\frac{\cos\theta_i}{n\cos\theta_t} - 1\right) \end{aligned}\right\} \Rightarrow$$

$$\boxed{r_{TE} := \frac{E_r}{E_i} = \frac{\cos\theta_i - n\cos\theta_t}{\cos\theta_i + n\cos\theta_t} = \frac{n_i\cos\theta_i - n_t\cos\theta_t}{n_i\cos\theta_i + n_t\cos\theta_t}}. \tag{12.24}$$

Hence,

$$\boxed{r_{TE} = \frac{\cos\theta_i - \sqrt{n^2 - \sin^2\theta_i}}{\cos\theta_i + \sqrt{n^2 - \sin^2\theta_i}}}. \tag{12.25}$$

Therefore, Eqs. 12.23 and 12.25 lead to the conclusion that

$$\boxed{t_{TE} = r_{TE} + 1} \tag{12.26}$$

The quantities t_{TE} and r_{TE}, defined in Eqs. 12.22, 12.24 are just ratios of amplitudes and not transmittance (T) and reflectance (R). The latter two quantities are defined below, in Eqs. 12.53.

If we want no TE reflection, it must hold that $r_{TE} = 0$, hence, due to Eq. 12.24,

$$\left.\begin{array}{r} n_i\cos\theta_i = n_t\cos\theta_t \\ \text{however (Eq. 12.21)},\ n_i\sin\theta_i = n_t\sin\theta_t \end{array}\right\} \Rightarrow \left.\begin{array}{r} \tan\theta_i = \tan\theta_t \\ \theta_i, \theta_t \ \text{ are acute angles} \end{array}\right\} \Rightarrow \tag{12.27}$$

$$\boxed{\theta_t = \theta_i} \tag{12.28}$$

therefore, due to Eqs. 12.27, it follows that

$$\boxed{n_t = n_i}. \tag{12.29}$$

Eqs. 12.28 and 12.29 mean that the EM wave does not change propagation medium. In other words, this is a trivial solution, since in this case there is no interface. To conclude, it is not possible not to have reflected s polarization. Due to the above, Eq. 12.22 yields $t_{TE} = 1$. The values $r_{TE} = 0, t_{TE} = 1$ satisfy Eq. 12.26. See Figure 12.3.

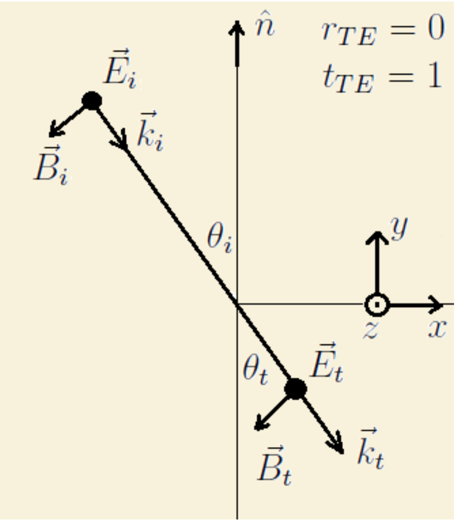

Figure 12.3: If we want no TE reflection (no reflected s polarization), then the EM wave does not change propagation medium. In other words, this is a trivial solution, since in this case there is no interface. **Conclusion:** It is not possible not to have reflected s polarization.

Let us examine TM polarization in more detail, using the equations we obtained above. We will assume that our materials are non-magnetic, i.e. that $\mu_1 = \mu_2 = 1$.

$$\left.\begin{aligned} E_i \cos\theta_i - E_r \cos\theta_r = E_t \cos\theta_t \\ \frac{B_i}{\mu_0\mu_1} + \frac{B_r}{\mu_0\mu_1} = \frac{B_t}{\mu_0\mu_2} \\ \mu_1 = \mu_2 = 1 \\ B = n\frac{E}{c_0} \end{aligned}\right\} \Rightarrow \left.\begin{aligned} E_i \cos\theta_i - E_r \cos\theta_r = E_t \cos\theta_t \\ n_1 E_i + n_1 E_r = n_2 E_t \\ n := \frac{n_2}{n_1} \text{ (the relative refraction index)} \end{aligned}\right\} \overset{\theta_i=\theta_r}{\Rightarrow}$$

$$\left.\begin{aligned} E_i - E_r = E_t\frac{\cos\theta_t}{\cos\theta_i} \\ E_i + E_r = nE_t \end{aligned}\right\} \Rightarrow \text{(adding by parts)}\ \ 2E_i = E_t\left(n + \frac{\cos\theta_t}{\cos\theta_i}\right) \Rightarrow$$

$$\boxed{t_{TM} := \frac{E_t}{E_i} = \frac{2\cos\theta_i}{n\cos\theta_i + \cos\theta_t} = \frac{2n_i\cos\theta_i}{n_t\cos\theta_i + n_i\cos\theta_t}}. \tag{12.30}$$

Alternatively,

$$t_{TM} = \frac{2\cos\theta_i}{n\cos\theta_i + \sqrt{1 - \dfrac{\sin^2\theta_i}{n^2}}} \Rightarrow$$

$$\boxed{t_{TM} = \frac{2n\cos\theta_i}{n^2\cos\theta_i + \sqrt{n^2 - \sin^2\theta_i}}}. \tag{12.31}$$

Moreover,

$$\left.\begin{aligned} E_t = \frac{n\cos\theta_i}{\cos\theta_t}(E_i - E_r) = (E_i + E_r) \\ E_i\left(\frac{n\cos\theta_i}{\cos\theta_t} - 1\right) = E_r\left(\frac{n\cos\theta_i}{\cos\theta_t} + 1\right) \end{aligned}\right\} \Rightarrow$$

$$\boxed{r_{TM} := \frac{E_r}{E_i} = \frac{n\cos\theta_i - \cos\theta_t}{n\cos\theta_i + \cos\theta_t} = \frac{n_t\cos\theta_i - n_i\cos\theta_t}{n_t\cos\theta_i + n_i\cos\theta_t}} \tag{12.32}$$

or

$$\boxed{r_{TM} = \frac{n^2\cos\theta_i - \sqrt{n^2 - \sin^2\theta_i}}{n^2\cos\theta_i + \sqrt{n^2 - \sin^2\theta_i}}}. \tag{12.33}$$

Hence,

$$\boxed{r_{TM} - nt_{TM} = -1} \tag{12.34}$$

The quantities t_{TM} and r_{TM}, defined in Eqs. 12.30, 12.32 are just ratios of amplitudes and not transmittance (T) and reflectance (R). The latter two quantities are defined below, in Eqs. 12.53.

If we want no TM reflection, it must hold that $r_{TM} = 0$, hence, due to Eq. Eξ. 12.32,

$$\left.\begin{array}{r} n_t \cos\theta_i = n_i \cos\theta_t \\ \text{however (Eq. 12.21), } n_t \sin\theta_t = n_i \sin\theta_i \end{array}\right\} \Rightarrow \left.\frac{\cos\theta_i}{\sin\theta_t} = \frac{\cos\theta_t}{\sin\theta_i}\right\} \Rightarrow \sin 2\theta_t = \sin 2\theta_i \tag{12.35}$$

$$\text{Hence,} \qquad \textbf{(1)} \quad 2\theta_t = 2\theta_i \qquad \text{or} \qquad \textbf{(2)} \quad 2\theta_t = \pi - 2\theta_i$$

Choice (1) yields

$$\boxed{\theta_t = \theta_i} \tag{12.36}$$

and, due to Eq. 12.21,

$$\boxed{n_t = n_i}. \tag{12.37}$$

Eqs. 12.36 and 12.37 mean that the EM wave does not change propagation medium. In other words, this is a trivial solution, since in this case there is no interface. To conclude, it is not possible not to have reflected s polarization. Due to the above, Eq. 12.30 yields $t_{TM} = 1$. The values $r_{TM} = 0, t_{TM} = 1$, due to Eq. 12.37, satisfy Eq. 12.34. See Figure 12.4, left.

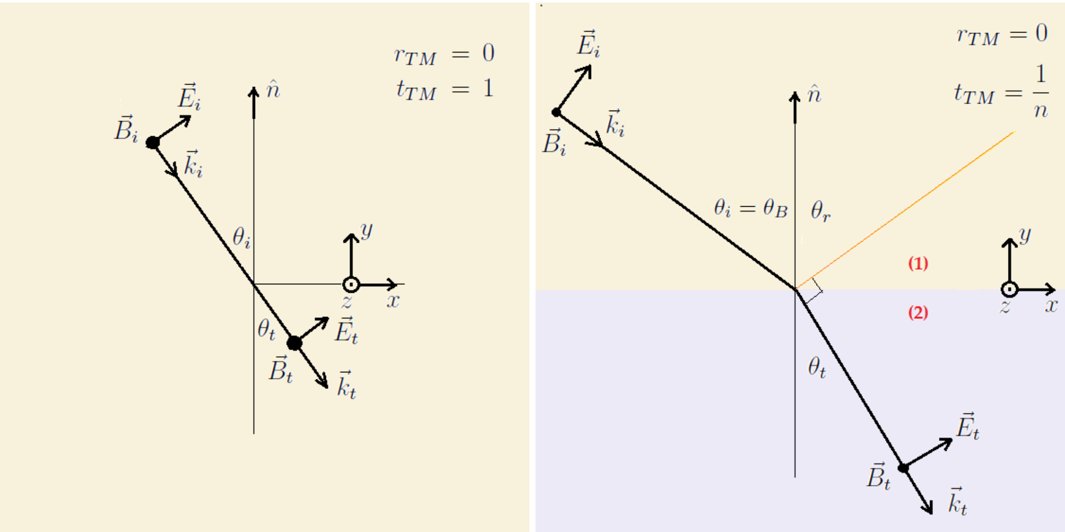

Figure 12.4: **Left**: If we want no TE reflection (no reflected p polarization), one case (**choice (1)**) is that the EM wave does not change propagation medium. In other words, this is a trivial solution, since in this case there is no interface. The values $r_{TM} = 0, t_{TM} = 1$, due to Eq. 12.37, satisfy Eq. 12.34, i.e. $r_{TM} - nt_{TM} = -1$. **Right**: If we want no TE reflection (no reflected p polarization), the other case (**choice (2)**) is that the reflected beam is perpendicular to the refracted beam. However, the reflected beam, denoted here by the orange line, refers to TE polarization. It holds that $n = n_t/n_i = \tan\theta_i$, and the angle θ_i which satisfies this relationship is called the **Brewster angle,** θ_B. That is, $\tan\theta_B = n_t/n_i = n$. The values $r_{TM} = 0, t_{TM} = 1/n$ satisfy Eq. 12.34, i.e. $r_{TM} - nt_{TM} = -1$. **Conclusion:** It is possible not to have reflected p polarization, and this happens when $\theta_i = \theta_B$.

Choice (2) yields $\theta_t = \dfrac{\pi}{2} - \theta_i$ or $\theta_i + \theta_t = \dfrac{\pi}{2}$, which, due to the reflection law (Eq. 12.20), leads to $\theta_r + \theta_t = \dfrac{\pi}{2}$. If we denote by $\sphericalangle$ the angle between the reflected and refracted beams, it holds that $\theta_r + \sphericalangle + \theta_t = \pi$. Therefore, $\sphericalangle = \dfrac{\pi}{2}$, i.e. the reflected beam is perpendicular to the refracted beam. See Figure 12.4, right.

$$\left.\begin{array}{l} \text{Due to the refraction law (Eq. 12.21),} \quad n_t \sin\theta_t = n_i \sin\theta_i \\ \text{and choice (2),} \quad \theta_t = \dfrac{\pi}{2} - \theta_i \end{array}\right\} \Rightarrow$$

$$n_t \sin\left(\frac{\pi}{2} - \theta_i\right) = n_i \sin\theta_i \Rightarrow \frac{n_t}{n_i} = \frac{\sin\theta_i}{\cos\theta_i} \Rightarrow$$

$$\boxed{n = \frac{n_t}{n_i} = \tan\theta_i} \tag{12.38}$$

The angle θ_i which satisfies Eq. 12.38 is called the **Brewster angle**, θ_B. (The same conclusions can be drawn from $n_t \cos\theta_i = n_i \cos\theta_t$ of Eqs. 12.35, as well). Then, Eq. 12.30 becomes

$$t_{TM} = \frac{2n_i \cos\theta_i}{n_t \cos\theta_i + n_i \cos\theta_t} = \frac{2n_i \cos\theta_i}{n_t \cos\theta_i + n_i \sin\theta_i} = \frac{2}{n + \tan\theta_i} = \frac{2}{2n} \Rightarrow$$

$$\boxed{t_{TM} = \frac{1}{n}} \tag{12.39}$$

The values $r_{TM} = 0, t_{TM} = \dfrac{1}{n}$ satisfy Eq. 12.34. See Figure 12.4, right. To conclude, it is possible not to have reflected p polarization, and this happens when $\theta_i = \theta_B$.

Eqs. 12.22, 12.24, 12.30, 12.32, as well as their equivalents, are called the **Fresnel equations**. They are summarized below:

$$\boxed{t_{TE} := \frac{E_t}{E_i} = \frac{2n_i \cos\theta_i}{n_i \cos\theta_i + n_t \cos\theta_t}} \tag{12.40}$$

$$\boxed{r_{TE} := \frac{E_r}{E_i} = \frac{n_i \cos\theta_i - n_t \cos\theta_t}{n_i \cos\theta_i + n_t \cos\theta_t}} \tag{12.41}$$

$$\boxed{t_{TM} := \frac{E_t}{E_i} = \frac{2n_i \cos\theta_i}{n_t \cos\theta_i + n_i \cos\theta_t}} \tag{12.42}$$

$$\boxed{r_{TM} := \frac{E_r}{E_i} = \frac{n_t \cos\theta_i - n_i \cos\theta_t}{n_t \cos\theta_i + n_i \cos\theta_t}} \tag{12.43}$$

12.2 Total internal reflection.

Let us assume that $n_i > n_t$ and use the refraction law (Eq. 12.21).

$$\left.\begin{array}{r} \text{refraction law } n_i \sin\theta_i = n_t \sin\theta_t \\ n_i > n_t \Rightarrow \ n = \dfrac{n_t}{n_i} < 1 \end{array}\right\} \Rightarrow \left.\begin{array}{r} \sin\theta_i < \sin\theta_t \\ \theta_i, \theta_t \text{ are acute angles} \end{array}\right\} \Rightarrow \theta_i < \theta_t \tag{12.44}$$

However, increasing θ_i increases θ_t as well, since, due to the refraction law (Eq. 12.21), $\nearrow\ \theta_i \Rightarrow \nearrow \sin\theta_i \Rightarrow \nearrow \sin\theta_t \Rightarrow \nearrow \theta_t$. This, increasing θ_i, θ_t is also increasing, remaining at the same time larger than θ_i (Eq. 12.44). Hence, when θ_t reaches the value $\dfrac{\pi}{2}$, the value of θ_i in called critical angle, i.e. $\theta_i^{cr} = \theta_i$. Then, it holds that $n_i \ \sin\theta_i^{cr} = n_t \sin(\pi/2)$. Hence,

$$\boxed{\sin\theta_i^{cr} = \frac{n_t}{n_i} = n}, \tag{12.45}$$

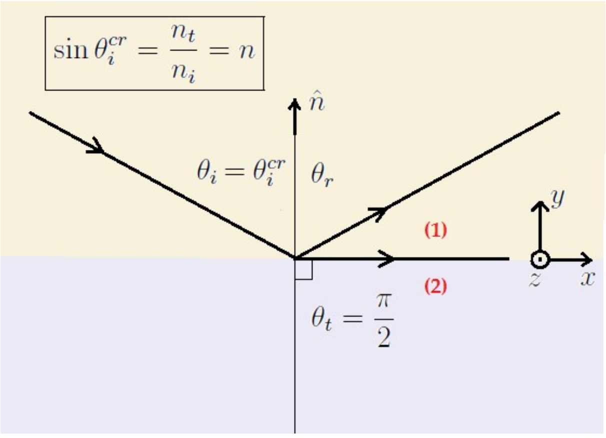

Figure 12.5: Total internal reflection: the refracted ray is tangent to the interface, i.e. it essentially does not get into the other material, $\theta_t = \frac{\pi}{2}$. The value of θ_i at which this happens is called critical angle, i.e. $\theta_i^{cr} = \theta_i$. Then, it holds that $\sin\theta_i^{cr} = \frac{n_t}{n_i} = n$.

This situation, in which the refracted ray is tangent to the interface, i.e. it essentially does not get into the other material is called **total internal reflection** (see Figure 12.5). Then,

$$t_{TE} = \frac{2n_i\cos\theta_i}{n_i\cos\theta_i + n_t\cos\theta_t} = \frac{2n_i\cos\theta_i^{cr}}{n_i\cos\theta_i^{cr} + n_t\cos\left(\frac{\pi}{2}\right)} = 2$$

$$r_{TE} = \frac{n_i\cos\theta_i - n_t\cos\theta_t}{n_i\cos\theta_i + n_t\cos\theta_t} = \frac{n_i\cos\theta_i^{cr} - n_t\cos\left(\frac{\pi}{2}\right)}{n_i\cos\theta_i^{cr} + n_t\cos\left(\frac{\pi}{2}\right)} = 1$$

We observe that Eq. 12.26, $t_{TE} = r_{TE} + 1$, holds, since $2 = 1 + 1$.

$$t_{TM} = \frac{2n_i\cos\theta_i}{n_t\cos\theta_i + n_i\cos\theta_t} = \frac{2n_i\cos\theta_i^{cr}}{n_t\cos\theta_i^{cr} + n_i\cos\left(\frac{\pi}{2}\right)} = \frac{2}{n}$$

$$r_{TM} = \frac{n_t\cos\theta_i - n_i\cos\theta_t}{n_t\cos\theta_i + n_i\cos\theta_t} = \frac{n_t\cos\theta_i^{cr} - n_i\cos\left(\frac{\pi}{2}\right)}{n_t\cos\theta_i^{cr} + n_i\cos\left(\frac{\pi}{2}\right)} = 1$$

We observe that Eq. 12.34, $r_{TM} - nt_{TM} = -1$, holds, since $1 - n\frac{2}{n} = -1$.

12.3 Emission of polarized beam.

According to what we saw in Section 12.1, When the angle of incidence is equal to the Brewster angle $(\theta_i = \theta_B)$, then an unpolarized incident beam results in a fully polarized reflected beam and a partially polarized refracted beam. These are depicted in Figure 12.6. Hence, if we put on the output of a laser device a material such that the outgoing beam is incident to it at an angle $\theta_i = \theta_B$, then we can exploit either the fully polarized reflected beam or the partially polarized refracted beam. Technical details vary in different kinds of lasers [1], [2], [3].

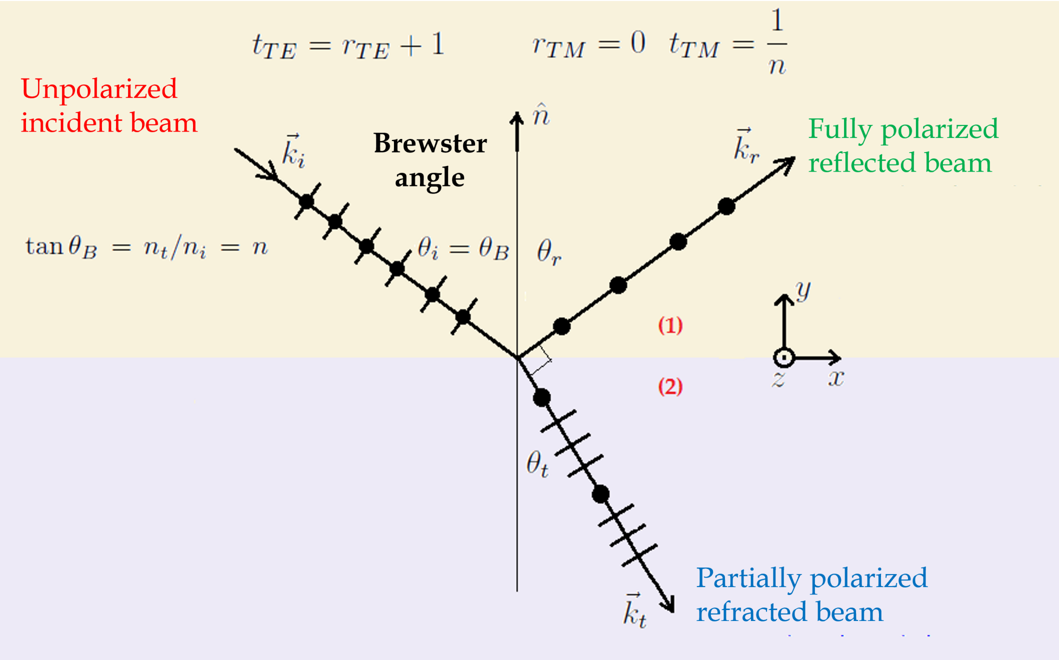

Figure 12.6: When the angle of incidence is equal to the Brewster angle ($\theta_i = \theta_B$), then an unpolarized incident beam results in a fully polarized reflected beam and a partially polarized refracted beam.

12.4 Poynting vector.

The Poynting vector is defined as

$$\boxed{\vec{S} := \vec{E} \times \vec{H}}, \tag{12.46}$$

and, in terms of units,

$$[\vec{S}] = [\vec{E}][\vec{H}] = \frac{\mathrm{VA}}{\mathrm{mm}} = \frac{\mathrm{VC}}{\mathrm{m^2 s}} = \frac{\mathrm{J}}{\mathrm{m^2 s}} = \frac{\mathrm{W}}{\mathrm{m^2}}.$$

Therefore, the Poynting vector describes power per unit surface. Its norm is

$$|\vec{S}| = |\vec{E}||\vec{H}| = \frac{|\vec{E}||\vec{B}|}{\mu\mu_0} = \frac{|\vec{E}|^2 n}{\mu\mu_0 c_0} = |\vec{E}|^2 \sqrt{\frac{\varepsilon\cancel{\mu}\varepsilon_0\cancel{\mu_0}}{\mu^{\cancel{2}}\mu_0^{\cancel{2}}}} \Rightarrow$$

$$\boxed{|\vec{S}| = |\vec{E}|^2 \sqrt{\frac{\varepsilon\varepsilon_0}{\mu\mu_0}}}, \tag{12.47}$$

where we have used the relation

$$\left.\begin{array}{l} \dfrac{|\vec{E}|}{|\vec{B}|} = c \\ n = \dfrac{c_0}{c} \end{array}\right\} \Rightarrow |\vec{B}| = \frac{|\vec{E}|n}{c_0}.$$

Additionally, as we might remember,

$$\left.\begin{array}{l} c_0 = \dfrac{1}{\sqrt{\varepsilon_0\mu_0}} \\ c = \dfrac{1}{\sqrt{\varepsilon\varepsilon_0\mu\mu_0}} \end{array}\right\} \Rightarrow n := \frac{c_0}{c} = \sqrt{\frac{\varepsilon\varepsilon_0\mu\mu_0}{\varepsilon_0\mu_0}} \Rightarrow \boxed{n = \sqrt{\varepsilon\mu}}.$$

Let us now calculate the norms of the Poynting vectors for the incident, reflected and refracted beams, using Eq. 12.47:

$$|\vec{S}_i| = |\vec{E}_i|^2\sqrt{\frac{\varepsilon_i\varepsilon_0}{\mu_i\mu_0}} = |\vec{E}_i|^2\sqrt{\frac{\varepsilon_1\varepsilon_0}{\mu_1\mu_0}} \tag{12.48}$$

$$|\vec{S}_r| = |\vec{E}_r|^2\sqrt{\frac{\varepsilon_r\varepsilon_0}{\mu_r\mu_0}} = |\vec{E}_r|^2\sqrt{\frac{\varepsilon_1\varepsilon_0}{\mu_1\mu_0}} \tag{12.49}$$

$$|\vec{S}_t| = |\vec{E}_t|^2\sqrt{\frac{\varepsilon_t\varepsilon_0}{\mu_t\mu_0}} = |\vec{E}_t|^2\sqrt{\frac{\varepsilon_2\varepsilon_0}{\mu_2\mu_0}} \tag{12.50}$$

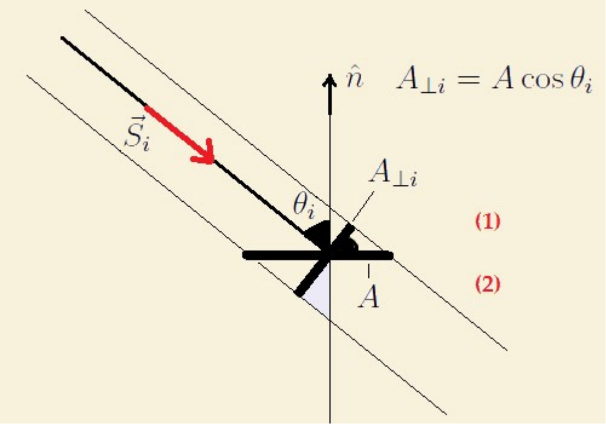

Figure 12.7: The Poynting vector of the incident beam, $\vec{S}_i$, a part of the interface, A, and its projection, $A_{\perp i}$, normal to $\vec{S}_i$. $A_{\perp i} = A\cos\theta_i$.

In Figure 12.7 we observe the Poynting vector of the incident beam, $\vec{S}_i$, a part of the interface, A, and its projection, $A_{\perp i}$, normal to $\vec{S}_i$. From this Figure, it is evident that $A_{\perp i} = A\cos\theta_i$. The situation is similar for the reflected and refracted beams. Concisely,

$$A_{\perp i} = A\cos\theta_i,$$
$$A_{\perp r} = A\cos\theta_r,$$
$$A_{\perp t} = A\cos\theta_t.$$

Let us denote by $P_i(A_{\perp i})$ the power incident to surface $A_{\perp i}$ and so forth, and recall that the Poynting vector describes power per unit surface. Then,

$$|\vec{S}_i| = \frac{P_i(A_{\perp i})}{A_{\perp i}} \Rightarrow P_i(A_{\perp i}) = |\vec{S}_i|A_{\perp i} \Rightarrow P_iA_{\perp i} = |\vec{S}_i|A\cos\theta_i,$$
$$\text{similarly, } \Rightarrow P_rA_{\perp r} = |\vec{S}_r|A\cos\theta_r,$$
$$\text{similarly, } \Rightarrow P_tA_{\perp t} = |\vec{S}_t|A\cos\theta_t.$$

However, if the materials do not absorb energy, then the incident power is equal to the reflected power plus the refracted power. That is,

$$P_i(A_{\perp i}) = P_r(A_{\perp r}) + P_t(A_{\perp t}). \tag{12.51}$$

Hence,

$$|\vec{S}_i|A\cos\theta_i = |\vec{S}_r|A\cos\theta_r + |\vec{S}_t|A\cos\theta_t \Rightarrow 1 = \frac{|\vec{S}_r|}{|\vec{S}_i|} + \frac{|\vec{S}_t|\cos\theta_t}{|\vec{S}_i|\cos\theta_i} \Rightarrow$$

$$1 = \frac{|\vec{E}_r|^2}{|\vec{E}_i|^2} + \frac{|\vec{E}_t|^2}{|\vec{E}_i|^2}\sqrt{\frac{\varepsilon_2\mu_1}{\varepsilon_1\mu_2}}\frac{\cos\theta_t}{\cos\theta_i},$$

where we have used Eqs. 12.48, 12.49, 12.50. In other words,

$$\boxed{1 = R + T}, \tag{12.52}$$

where we have defined

$$\boxed{\begin{aligned} R &:= \frac{|\vec{E}_r|^2}{|\vec{E}_i|^2} && \text{(reflectance)} \\ T &:= \frac{|\vec{E}_t|^2}{|\vec{E}_i|^2}\sqrt{\frac{\varepsilon_2\mu_1}{\varepsilon_1\mu_2}}\frac{\cos\theta_t}{\cos\theta_i} && \text{(transmittance)} \end{aligned}} \tag{12.53}$$

The quantities r and t (e.g. Eqs. 12.40, 12.41, 12.42, 12.43) have been defined as ratios of amplitudes. Therefore, we can write

$$1 = r^2 + t^2\sqrt{\frac{\varepsilon_2\mu_1}{\varepsilon_1\mu_2}}\frac{\cos\theta_t}{\cos\theta_i} \tag{12.54}$$

$$R = r^2 \tag{12.55}$$

$$T = t^2\sqrt{\frac{\varepsilon_2\mu_1}{\varepsilon_1\mu_2}}\frac{\cos\theta_t}{\cos\theta_i} \tag{12.56}$$

For non-magnetic materials, i.e. when $\mu_1 = \mu_2 = 1$, if follows that $T = \frac{|\vec{E}_t|^2}{|\vec{E}_i|^2}\frac{n_2}{n_1}\frac{\cos\theta_t}{\cos\theta_i} = t^2 n \frac{\cos\theta_t}{\cos\theta_i}$.

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APPENDIX A

EXERCISES

A.1 Exercises for Chapter 1: Overview.

There are no exercises in this chapter.

A.2 Exercises for Chapter 2: The quantum nature of light.

- **Exercise 1.** Conventionally, the far infrared (FIR) part of the electromagnetic spectrum corresponds to wavelengths 25 μm < λ < 1000 μm. Find the x (Eq. 2.8) to which FIR corresponds for temperature (a) 300 K, i.e., approximately the temperature of an animal, (b) 6000 K, i.e., approximately the effective temperature of the Sun's photosphere, and (c) 6 K.

- **Exercise 2.** Conventionally, the ultraviolet (UV) part of the electromagnetic spectrum corresponds to wavelengths 10 nm < λ < 400 nm. Find the x (Eq. 2.8) to which UV corresponds for temperature (a) 300 K, i.e., approximately the temperature of an animal, (b) 6000 K, i.e., approximately the effective temperature of the Sun's photosphere, and (c) 6 K.

- **Exercise 3.** Conventionally, the far infrared (FIR) part of the electromagnetic spectrum corresponds to wavelengths 25 μm < λ < 1000 μm. For the upper and the lower limit of the FIR region, find the temperature of a black body at which the Wien's prediction, ρ_W becomes half the experimental value ρ, which is also predicted by the Planck's law. In other words, we are looking for the temperature regime at which we have problem at lower frequencies.

  Solution of Exercise 3.
  We demand that the relationship $\rho_W = 0.5\rho$ is satisfied. Thus, according to Eqs. 2.11 and 2.12, we have

$$\rho_0 \frac{x^3}{e^x} = 0.5\rho_0 \frac{x^3}{e^x - 1} \Rightarrow e^x - 1 = 0.5e^x \Rightarrow e^x = 2 \Rightarrow x = \ln 2 \approx 0.693.$$

$$x = \frac{h\nu}{k_B T} \overset{c=\lambda\nu}{\Longleftrightarrow} \lambda = \frac{hc}{x k_B T}. \tag{A.1}$$

The ratio

$$\frac{hc}{k_B} \approx 14.404 \times 10^{-3} \mathrm{mK}. \tag{A.2}$$

Hence, between the upper and lower limits of the FIR region, the following inequality holds:

$$\begin{gathered}
25\ \mu\mathrm{m} < \frac{hc}{x k_B T} < 1000\ \mu\mathrm{m} \Rightarrow \\
\frac{hc}{x k_B\, 1000\ \mu\mathrm{m}} < T < \frac{hc}{x k_B\, 25\ \mu\mathrm{m}} \Rightarrow \\
21\ \mathrm{K} \lesssim T \lesssim 831\ \mathrm{K}.
\end{gathered}$$

- **Exercise 4.** Find when the Rayleigh-Jeans law prediction, ρ_{RJ}, becomes exactly equal to the experimental value, ρ, which is also predicted by the Planck's law.

  Solution of Exercise 4.
  We demand that equality $\rho_{RJ} = \rho$ holds. Using Eqs. 2.10 and 2.12, it occurs that

  $$\rho_0 x^2 = \rho_0 \frac{x^3}{e^x - 1}.$$

  Hence, for $x \neq 0$, $x = e^x - 1 \Rightarrow e^x = 1 + x \Rightarrow x = 0$, which is **absurd**. Therefore, the Rayleigh-Jeans law never coincides with the Planck's law.

- **Exercise 5** Find the temperature T_Δ at which, in the UV limit, i.e., for $\lambda = 400$ nm, the prediction of the Rayleigh-Jeans law, ρ_{RJ}, becomes twice the experimental value, ρ, which is also predicted by the Planck's law.

  Solution of Exercise 5.
  We demand that the condition $\rho_{RJ} = 2\rho$ holds. From Eqs. 2.10 and 2.12, it occurs that

  $$\rho_0 x^2 = 2\rho_0 \frac{x^3}{e^x - 1}.$$

  Hence, for $x \neq 0$, $2x = e^x - 1 \Rightarrow e^x = 1 + 2x$. From a graphical solution of the above equation, we have $x_\Delta = 1.25645 \approx \frac{5}{4}$. From Eq. 2.8, we have

  $$x_\Delta = \frac{h\nu}{k_B T_\Delta} \overset{c=\lambda\nu}{\Longleftrightarrow} T_\Delta = \frac{hc}{k_B \lambda x_\Delta}. \tag{A.3}$$

  Substitution of numerical values leads to $T_\Delta \approx 28800$ K. This temperature only corresponds to surface temperature of stars with very large mass (e.g. 30 times the mass of Sun). Hence, we realize that the term "UV catastrophe" is misleading.

- **Exercise 6.** Examine the behavior of Planck's law in the following limits: (a) zero frequency, and (b) infinite frequency. Also, prove that (c) at very low frequencies, Planck's law is identical to the Rayleigh-Jeans law, while, (d) at very high frequencies, it is identical to Wien's law.

Solution of Exercise 6.
For $\nu \rightarrow 0 \Rightarrow x \rightarrow 0:$

$$\lim_{x\rightarrow 0} \rho = \rho_0 \lim_{x\rightarrow 0} \left(\frac{x^3}{e^x - 1}\right) = \rho_0 \lim_{x\rightarrow 0} \left(\frac{3x^2}{e^x}\right) = 0$$

For $\nu \rightarrow \infty \Rightarrow x \rightarrow \infty:$

$$\lim_{x\rightarrow \infty} \rho = \rho_0 \lim_{x\rightarrow \infty} \left(\frac{x^3}{e^x - 1}\right) \overset{\text{τελικά}}{=\!=\!=} \rho_0 \lim_{x\rightarrow \infty} \left(\frac{6}{e^x}\right) = 0$$

For low frequencies, i.e., for small x $(x \downarrow\downarrow)$:

$$f(x) = f(0) + f'(0)\frac{x}{1!} + f''(0)\frac{x^2}{2!} + ... \tag{A.4}$$

thus

$$e^x - 1 = 1 + 1\frac{x}{1!} + 1\frac{x^2}{2!} + \cdots - 1 \approx x \quad \text{(1st order approximation)}. \tag{A.5}$$

Hence,

$$\rho = \rho_0 \frac{x^3}{e^x - 1} \simeq \rho_0 \frac{x^3}{x} = \rho_0 x^2 = \rho_{\mathrm{RJ}}. \tag{A.6}$$

For high frequencies, i.e., for large x $(x \uparrow\uparrow)$:

$$e^x - 1 \simeq e^x \Rightarrow \rho = \rho_0 \frac{x^3}{e^x - 1} \simeq \rho_0 \frac{x^3}{e^x} = \rho_{\mathrm{W}} \tag{A.7}$$

- **Exercise 7.** Prove that $\rho_{\mathrm{W}} \neq \rho_{\mathrm{RJ}}$ for small and large x.

Solution of Exercise 7.
For large x $(x \uparrow\uparrow)$:

$$\lim_{x\rightarrow \infty} \rho_{\mathrm{RJ}} = \rho_0 \lim_{x\rightarrow \infty} x^2 = \infty \neq \lim_{x\rightarrow \infty} \rho_{\mathrm{W}} = \rho_0 \lim_{x\rightarrow \infty} \frac{x^3}{e^x} = 0. \tag{A.8}$$

For small x $(x \downarrow\downarrow)$, although for $x \rightarrow 0$ both vanish:

$$\lim_{x\rightarrow 0} \rho_{\mathrm{RJ}} = \rho_0 \lim_{x\rightarrow 0} x^2 = 0 = \lim_{x\rightarrow 0} \rho_{\mathrm{W}} = \rho_0 \lim_{x\rightarrow 0} \frac{x^3}{e^x} = 0, \tag{A.9}$$

they still remain unequal. Indeed, using the expansion

$$f(x) = f(0) + f'(0)\frac{x}{1!} + f''(0)\frac{x^2}{2!} + ... \tag{A.10}$$

we realize that

$$e^x = 1 + 1\frac{x}{1!} + 1\frac{x^2}{2!} + \cdots \approx 1 + x \quad \text{(1st order approximation)}, \tag{A.11}$$

hence,

$$\rho_{\mathrm{W}} = \rho_0 \frac{x^3}{e^x} \approx \rho_0 \frac{x^3}{1 + x} \neq \rho_0 x^2 = \rho_{\mathrm{RJ}}. \tag{A.12}$$

- **Exercise 8.** For temperatures (a) 300 K, (b) 6000 K, and (c) 6 K: Calculate the wavelength, λ_{tw}, at which the prediction of the Rayleigh-Jeans law, ρ_{RJ}, becomes twice the value of the experimental value, ρ, also predicted by Planck's law. In which region of the EM spectrum does λ_{tw} belong each time?

- **Exercise 9.** Prove that the following substitution of a position vector

$$\vec{r} \quad \rightarrow \quad \vec{r'} = -\vec{r} \tag{A.13}$$

is equivalent, in spherical coordinates, with the substitutions

$$\begin{array}{ccc} r & \rightarrow & r' = r \\ \theta & \rightarrow & \theta' = \pi - \theta \\ \phi & \rightarrow & \phi' = \pi + \phi \end{array} \tag{A.14}$$

Exercise 10. The Γ function [1] is an extension of the factorial function to real and complex numbers with its argument shifted by -1. It can be finally proven that

$$\Gamma(n) = (n-1)! \quad \text{for} \quad n = 1, 2, 3, \ldots \quad \textit{factorial form} \tag{A.15}$$

The Γ function is defined for all complex numbers except for negative integers and zero $(0, -1, -2, \ldots)$. If the complex number z has a positive real part, i.e., if $Real(z) > 0$, then it is defined by the relation

$$\Gamma(z) := \int_0^\infty e^{-t} t^{z-1} dt \quad \textit{Euler form} \tag{A.16}$$

This definition can be extended to all complex numbers, except non-positive integers, in a manner that does not concern us here. The Γ function is mainly used in probabilities and statistics. The notation $\Gamma(z)$ is attributed to Legendre. There are also *other forms*

$$\Gamma(z) = 2\int_0^\infty e^{-t^2} t^{2z-1} dt \tag{A.17}$$

$$\Gamma(z) = \int_0^1 [\ln(1/t)]^{z-1} dt. \tag{A.18}$$

(a) Starting from the Euler form, prove that

$$\begin{aligned} \Gamma(z+1) &= z\Gamma(z) && \text{(A.19)} \\ \Gamma(1) &= 1 && \text{(A.20)} \\ \Gamma(n) &= (n-1)! && \text{(A.21)} \\ \Gamma(1/2) &= \sqrt{\pi} && \text{(A.22)} \end{aligned}$$

The Gaussian integral is given:

$$\int_0^\infty e^{-ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}. \tag{A.23}$$

(b) Prove that

$$I = \int_0^\infty e^{-\gamma r} r^n dr = \gamma^{-(n+1)} n! \tag{A.24}$$

where $n = 1, 2, 3, \ldots$ and $\gamma > 0$.

- **Exercise 11.** Check the following [2, 1]:
  (a) Assuming as known that $\int_0^{\infty} \frac{\sin^2(ax)}{x^2} dx = \frac{\pi}{2}|a|$, prove that for $t > 0$, $\int_{-\infty}^{\infty} \frac{\sin^2(xt/2)}{x^2} dx = \frac{\pi t}{2}$.
  (b) $e^{\pm i(\phi+\pi)} = -e^{\pm i\phi}$.
  (c) $\int_0^{2\pi} e^{i\phi} d\phi = 0$.
  (d) In the first order approximation, $\sqrt{c+x} \approx \sqrt{c} + \frac{x}{2\sqrt{c}}$.

  Solution of Exercise 11.
  The first three questions are simple. The Taylor expansion of a real or complex function, $f(x)$, of a real or complex variable, x, that is infinitely differentiable at a real or complex number, a, is the power series

$$f(x) = f(a) + \frac{f'(a)}{1!}(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \frac{f^{(3)}(a)}{3!}(x-a)^3 + \cdots = \sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!}(x-a)^n, \quad \text{(A.25)}$$

  where, $n!$ is the factorial of n and $f^{(n)}(a)$ is the n-th derivative of f at the point a. The zeroth order derivative of f is, by definition, f itself, $(x-a)^0 := 1$ and $0! := 1$. For $a = 0$, this power series is also called Maclaurin series, i.e.,

$$f(x) = f(0) + \frac{f'(0)}{1!}x + \frac{f''(0)}{2!}x^2 + \frac{f^{(3)}(0)}{3!}x^3 + \cdots = \sum_{n=0}^{\infty} \frac{f^{(n)}(0)}{n!}x^n. \quad \text{(A.26)}$$

  In the first order approximation,

$$f(x) \approx f(0) + \frac{f'(0)}{1!}x. \quad \text{(A.27)}$$

  Thus, for $f(x) = \sqrt{c+x}$, it is implied that $f'(x) = \frac{1}{2\sqrt{c+x}} \Rightarrow f'(0) = \frac{1}{2\sqrt{c}}$, while $f(0) = \sqrt{c}$. Hence, $f(x) \approx \sqrt{c} + \frac{x}{2\sqrt{c}}$.

- **Exercise 12.** Assume that the EM energy of a resonator with frequency ν inside a black-body cavity can only take discrete values (i.e., it is "quantized") and, specifically, has the form

$$E_n = h\nu\left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, 3, \ldots \quad \text{(A.28)}$$

  instead of the form $E_n = h\nu n, n = 0, 1, 2, 3, \ldots$ that Planck assumed. Find how is the energy density per unit frequency of EM black-body radiation at thermal equilibrium, $\rho(\nu, T)$ (units $\frac{\mathrm{J}}{\mathrm{m^3 Hz}}$), is modified relative to the Planck's law (Eq. 2.7).

- **Exercise 13.** Calculate the wavelength, λ_0, at which the Planck's law in the form $\rho(\lambda, T)$ displays a maximum, assuming that we can approximate as black bodies: (1) the human body with temperature $\theta \approx 36.6\ ^\circ\mathrm{C}$, (2) the Sun's photosphere, with "effective temperature" $T \approx 5800$ K, and (3) the photosphere of the Altair star, with "effective temperature" $T \approx 7000$ - 8500 K.

  Solution of Exercise 13.
  (1) $\lambda_0 \approx 9355.2$ nm $\approx 9.3552\ \mu$m, i.e., in the infrared (IR).
  (2) $\lambda_0 \approx 500$ nm, i.e., in green, while yellow is in ≈ 570-590 nm.
  (3) $\lambda_0 \approx 414$ έως 341 nm, i.e., in the violet - ultraviolet.

- **Exercise 14.** Assume that instead of Planck's law in the form $\rho(\lambda, T)$ of Eq. 2.18, the -1 in the denominator was missing, i.e., we had the respective Wien's law. Prove that in such case, the Wien's displacement law would be $\lambda_0 T = \frac{hc}{5k_B}$.
- **Exercise 15.** For the λ_0 and ν_0 or Eqs. 2.101 and 2.98, prove that $\lambda_0\nu_0 \approx 0.568c$, while, if instead of the Planck's law in the forms $\rho(\nu, T)$ and $\rho(\lambda, T)$, the Wien's expressions held, i.e., if -1 in the denominator was missing, we would have $\lambda_0\nu_0 = \frac{3}{5}c$.
- **Exercise 16.** From the distribution of Planck's law, $\rho(\nu, T)$, derive the distribution $\rho(\omega, T)$, where $\omega = 2\pi\nu$ is the angular frequency, i.e., prove that

$$\rho(\omega, T) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\frac{\hbar\omega}{k_B T}} - 1}. \tag{A.29}$$

- **Exercise 17.** Prove Eqs. 2.66, 2.67, 2.68, as well as Eq. 2.69, which result by separating the variables $x, y, z,$ of $\vec{r}$. These proofs were omitted in the main text, for brevity.

Solution of Exercise 17. We separate the variables $x, y, z,$ of $\vec{r}$. In Eq. 2.65

$$\nabla^2 \vec{E}_{\vec{r}} + \frac{\omega^2}{c^2}\vec{E}_{\vec{r}} = \vec{0}$$

we look for solutions of the form

$$\vec{E}_{\vec{r}}(x, y, z) = X(x)Y(y)Z(z)\hat{e},$$

where $\hat{e}$ defines the polarization, i.e., the orientation of $\vec{E}$. Thus,

$$YZ\frac{d^2X}{dx^2} + XZ\frac{d^2Y}{dy^2} + XY\frac{d^2Z}{dz^2} + \frac{\omega^2}{c^2}XYZ = 0 \Rightarrow$$

$$\underbrace{\frac{1}{X}\frac{d^2X}{dx^2}}_{f(x)} + \underbrace{\frac{1}{Y}\frac{d^2Y}{dy^2}}_{g(y)} + \underbrace{\frac{1}{Z}\frac{d^2Z}{dz^2}}_{h(z)} + \frac{\omega^2}{c^2} = 0$$

We find that three functions which depend on different variables have a constant sum. Hence, we can assume that each one of them is equal to a constant. We denote these constants by $-k_x^2$, $-k_y^2$, $-k_z^2$, respectively. Thus, Eq. 2.69 occurs

$$k_x^2 + k_y^2 + k_z^2 = \frac{\omega^2}{c^2},$$

but also

$$\frac{1}{X}\frac{d^2X}{dx^2} \overset{\text{we set}}{=} -k_x^2 \qquad \frac{1}{Y}\frac{d^2Y}{dy^2} \overset{\text{we set}}{=} -k_y^2 \qquad \frac{1}{Z}\frac{d^2Z}{dz^2} \overset{\text{we set}}{=} -k_z^2 \Rightarrow$$

$$\frac{d^2X}{dx^2} + k_x^2 X = 0 \qquad \frac{d^2Y}{dy^2} + k_y^2 Y = 0 \qquad \frac{d^2Z}{dz^2} + k_z^2 Z = 0$$

Hence, we have solutions of the form

$$\begin{aligned} X(x) &= A_1\sin(k_x x) + B_1\cos(k_x x) \quad \boxed{1} \\ Y(y) &= A_2\sin\left(k_y y\right) + B_2\cos\left(k_y y\right) \quad \boxed{2} \\ Z(z) &= A_3\sin(k_z z) + B_3\cos(k_z z) \quad \boxed{3} \end{aligned}$$

Consequently,

$$\vec{E}_{\vec{r}}(x,y,z) = (\hat{e}_x + \hat{e}_y + \hat{e}_z)$$

$$[A_1\sin(k_x x) + B_1\cos(k_x x)][A_2\sin\left(k_y y\right) + B_2\cos\left(k_y y\right)][A_3\sin(k_z z) + B_3\cos(k_z z)].$$

$\hat{e}$ has generally a random orientation, so we analyze its componentis in the x, y, z axes, i.e., $\hat{e} = \hat{e}_x + \hat{e}_y + \hat{e}_z$. Thus,

E_x will be some first combination of the $\sin$ and $\cos$ contained in $\boxed{1}, \boxed{2}, \boxed{3}$

E_y will be some second combination of the $\sin$ and $\cos$ contained in $\boxed{1}, \boxed{2}, \boxed{3}$, and

E_z will be some third combination of the $\sin$ and $\cos$ contained in $\boxed{1}, \boxed{2}, \boxed{3}$

These combinations must be such, that

$$\begin{aligned} &E_x \text{ becomes zero for } y = 0 \text{ and } z = 0 \\ &E_y \text{ becomes zero for } x = 0 \text{ and } z = 0 \\ &E_z \text{ becomes zero for } x = 0 \text{ and } y = 0. \end{aligned}$$

So, Eqs. 2.66, 2.67, and 2.68 occur.

$$\begin{aligned} E_x &= E_{x0}\cos(k_x x)\sin\left(k_y y\right)\sin(k_z z)e^{-i\omega t} \Rightarrow \text{becomes zero for } y = 0 \text{ and } z = 0 \\ E_y &= E_{y0}\sin(k_x x)\cos\left(k_y y\right)\sin(k_z z)e^{-i\omega t} \Rightarrow \text{becomes zero for } x = 0 \text{ and } z = 0 \\ E_z &= E_{z0}\sin(k_x x)\sin\left(k_y y\right)\cos(k_z z)e^{-i\omega t} \Rightarrow \text{becomes zero for } x = 0 \text{ and } y = 0 \end{aligned}$$

- **Exercise 18.** Prove Eq. 2.71 as well as Eqs. 2.72, 2.73, 2.74. These proofs were omitted in the main text, for brevity.

Solution of Exercise 18. From the (1st') Maxwell's equation, we have

$$\vec{\nabla}\cdot\vec{E} = 0 \Rightarrow \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)\cdot(E_x, E_y, E_z) = 0 \Rightarrow \frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} = 0 \Rightarrow$$

$$\begin{aligned} &-E_{x0}k_x\sin(k_x x)\sin\left(k_y y\right)\sin(k_z z)e^{-i\omega t} + \\ &-E_{y0}k_y\sin(k_x x)\sin\left(k_y y\right)\sin(k_z z)e^{-i\omega t} + \\ &-E_{z0}k_z\sin(k_x x)\sin\left(k_y y\right)\sin(k_z z)e^{-i\omega t} = 0 \Rightarrow \\ &k_x E_{x0} + k_y E_{y0} + k_z E_{z0} = 0, \text{which is Eq. 2.71.} \end{aligned}$$

From the (3rd') Maxwell's equation, $\vec{\nabla}\times\vec{E} = -\dfrac{\partial\vec{B}}{\partial t} \Rightarrow$

$$\begin{vmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ \dfrac{\partial}{\partial x} & \dfrac{\partial}{\partial y} & \dfrac{\partial}{\partial z} \\ [E_{x0}\cos(k_x x) & [E_{y0}\cos\left(k_y y\right) & [E_{z0}\cos(k_z z) \\ \sin\left(k_y y\right)\sin(k_z z)] & \sin(k_x x)\sin(k_z z)] & \sin(k_x x)\sin\left(k_y y\right)] \end{vmatrix} e^{-i\omega t} = -\left(\frac{\partial B_x}{\partial t}, \frac{\partial B_y}{\partial t}, \frac{\partial B_z}{\partial t}\right) \Rightarrow$$

$$-\frac{\partial B_x}{\partial t} = [k_y E_{z0}\cos(k_z z)\sin(k_x x)\cos\left(k_y y\right) - k_z E_{y0}\cos\left(k_y y\right)\sin(k_x x)\cos(k_z z)]e^{-i\omega t} \Rightarrow$$

$$-\frac{\partial B_x}{\partial t} = [k_y E_{z0} - k_z E_{y0}]\sin(k_x x)\cos\left(k_y y\right)\cos(k_z z)e^{-i\omega t} \Rightarrow$$

$$B_x = \frac{[k_y E_{z0} - k_z E_{y0}]}{i\omega}\sin(k_x x)\cos\left(k_y y\right)\cos(k_z z)e^{-i\omega t} \Rightarrow$$

$$B_x = \frac{i}{\omega}[k_z E_{y0} - k_y E_{z0}]\sin(k_x x)\cos\left(k_y y\right)\cos(k_z z)e^{-i\omega t} \quad \text{which is Eq. 2.72.}$$

Similar considerations hold to obtain Eqs. 2.73 and 2.74. Being somewhat "creative", in the temporal integration, for $t = 0$, we set $\vec{B}(0) = \vec{0}$.

- **Exercise 19.** Check whether $\vec{B}$ (Eq. 2.72, 2.73, 2.74) satisfies the SBC* on the walls, as well as what does occur from the (2nd') Maxwell's equation, $\vec{\nabla}\cdot\vec{B} = 0$, and the (4th') Maxwell's equation, $\vec{\nabla}\times\vec{B} = \varepsilon_0\mu_0\frac{\partial\vec{E}}{\partial t}$.

- **Exercise 20 (Essentially this is a review of the theory)** Assuming the Plank's law as known

$$\rho(\nu, T) = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{\frac{h\nu}{k_B T}} - 1},$$

prove the two formulations of the Stefan-Boltzmann law
(a) for the energy density, $\varrho(T)$, and
(b) for the intensity of radiation, I.
(c) Prove Planck's law in the form $\rho(\lambda, T)$.
(d) What are the SI units of $\rho(\nu, T)$, $\rho(\lambda, T)$, $\varrho(T)$, I?

It is given that $\int\limits_0^\infty \frac{x^3}{e^x - 1}dx = \frac{\pi^4}{15}$.

A.3 Exercises for Chapter 3:Interaction mechanisms between a photon and a two-levelsystem (2LS)

- **Exercise 1.** Let us consider the (Stimulated) Absorption and focus on the consumption of energy and momentum. Additionally, let us suppose that the atom is initially motionless. In which wavelength λ region does the kinetic energy of the atom, after absorbing the photon, become large enough (let us say, equal to 0.05 of the absorbed photon energy) so that it could not be ignored in the energy balance? Consider as given: the proton mass $m_p = 1.672621777(74)\times 10^{-27}$ kg, the Planck's constant $h = 6.62606957(29)\times 10^{-34}$ Js, the speed of light in vacuum $c = 2.99792458\times 10^8$ m/s. Assume, for simplicity, that the atomic mass $m_{\text{at}} \approx Zm_p + Nm_n + Zm_e \approx Am_p$.

- **Exercise 2.** Let us compare the probabilites for spontaneous emission and stimulated emission. Do we need small or large frequencies, small or large temperatures, if increased coherence is desired? Judging by the comparison of the above, is it easier to create a coherent beam in the radiowaves or in the infrared?

- **Exercise 3.** We want the probability for spontaneous emission to be equal to the probability for stimulated emission. In what temperature is this possible in the FM radiowaves (e.g., in frequency 100 MHz) and in the ultraviolet (e.g., in wavlength 200 nm)?

- **Exercise 4.** The dalton (Da) or unified atomic mass unit, $u = 1.660538921\ (073) \times 10^{-27}$ kg, is defined as the 1/12 of the atomic mass of the most common carbon isotope ($^{12}_{6}$C). Let us consider the $^{12}_{6}$C atom, which contains 6 protons, 6 neutrons and 6 electrons. Consider as given: $m_p = 1.007276466812(90)\ u$, $m_n = 1.00866491600(43)\ u$, $m_e = 5.4857990946(22) \times 10^{-4}\ u$. If we add 6 m_p + 6 m_n + 6 m_e, we find approximately 12.099 u, and not 12 u. This is due to the "mass defect", i.e., the fact that a part of the resting mass is used to bind the protons, neutrons and electrons together to form the atom. Let us consider the (Stimulated) Absorption and focus on the conservation of energy and momentum. Additionally, let us suppose that the atom is initially motionless. In which wavelength λ region does the kinetic energy of the atom, after absorbing the photon, become large enough (let us say, a tenth of the absorbed photon energy) so that it could not be ignored in the energy balance? $h = 6.62606957(29) \times 10^{-34}$ Js, $c = 2.99792458 \times 10^{8}$ m/s are also given.

- **Exercise 5.** Suppose an ensemble of hydrogen atoms in thermodynamic equilibrium and that the eigenenergies of each atom are given by the well-known Bohr's relationship $E_n \approx \frac{-13.6\text{ eV}}{n^2}$. Assume that the temperature is (a) 4.2 K and (b) 300 K. The Boltzmann constant is $k_B = 1.3806488(13) \times 10^{-23}$ J/K = $8.6173324(78) \times 10^{-5}$ eV/K.
  (A) Compare the number of atoms in the 1st Bohr orbit with the number of atoms in the 2nd orbit. Continue in pairs up to the 5th orbit (the pairs are 1st-2nd, 2nd-3rd, 3rd-4th, 4th-5th).
  (B) Compare the number of atoms that jump from the 1st to the 2nd orbit in time dt with a stimulated process, $dN^{\text{st}}_{1\to2}$, with the number of atoms the drop from the 2nd to the 1st orbit in time dt with a stimulated process, $dN^{\text{st}}_{2\to1}$. Continue in pairs up to the 5th orbit (the pairs are 1st-2nd, 2nd-3rd, 3rd-4th, 4th-5th). Suppose that $B_{12} = B_{21}$.

- **Exercise 6.** Consider a quantum dot of rectangular parallelepiped shape with a core of GaAs with dimensions $8 \times 4 \times 4$ nm and a shell of Al$_x$Ga$_{1-x}$As, where the molar fraction of Al, x, is such that the discontinuity of the conduction bands between the two materials is $V_b = 224$ meV. Consider the conduction band effective mass as approximately equal to the one of GaAs, i.e., $m^* \approx 0.067 m_e$.
  (A) How many energy levels does this quantum dot possess? If you cannot prove the above, consider as known that a quantum well of width L contains $n = 1 + \text{Int}\left[\sqrt{\frac{2m^* V_b L^2}{\pi^2 \hbar^2}}\right]$ bound energy states [3]. Int[ξ] is the integer part of ξ.
  (B) What is the wavelength to which the jump from the ground to the first excited level of this quantum dot corresponds?
  (C) Furthermore, assume a large ensemble of such quantum dots with one electron at each, and that the Boltzmann statistics with equal statistical weights is adequate to describe the energy level populations. The temperature is (a) 4.2 K and (b) 300 K. Compare the number of quantum dots at which the electron is on the ground level with the number of quantum dots at which the electron is on the first excited level.
  (D) Now, consider that all this ensemble of quantum dots is subject to an appropriate external EM field. Compare the number of quantum dots with electrons that jump from the ground to the first excited level in time dt with a stimulated process, $dN^{\text{st}}_{1\to2}$, with the number of quantum dots with electrons that drop from the first excited level to the ground level with a stimulated process, $dN^{\text{st}}_{2\to1}$. The reduced Planck's constant Planck $\hbar = 1.054571726(47) \times 10^{-34}$ Js, the elementary charge $e = 1.602176565(35) \times 10^{-19}$ C, the electron mass $m_e = 9.10938291(40) \times 10^{-31}$ kg, the Boltzmann constant $k_B = 1.3806488(13) \times 10^{-23}$ J/K= $8.6173324(78) \times 10^{-5}$ eV/K, and, generally, any physical constant you might need, are given.

- **Exercise 7.** Vindicate Figure 3.7, where the Maxwell - Boltzmann (MB), Fermi - Dirac (FD), and

Bose - Einstein (BE) statistics are compared. In other words, draw the concise Equation 3.20. Study the functions, their important points, their limits $x \longrightarrow \pm\infty$ and $x \longrightarrow 0^{\pm}$ etc. We have defined the continuous variable $x = \beta(E - \mu)$ and we are interested in the average number of particles $\overline{n}$ as a function of x.

- **Exercise 8.** (α') Show that in room temperature, $T = 300$ K, the quantum concentration, n_Q, is $\approx 1000\,\mathrm{nm}^{-3}$ for protons and $\approx 0.015\,\mathrm{nm}^{-3}$ for electron. (β') The density of copper is $\approx 9\,\mathrm{g\,cm}^{-3}$, its atomic mass is ≈ 63.5, and in its solid form, each copper atom has one "free electron". Show that the copper atoms cannot be described classically, since their concentration, n, is much larger than the quantum concentration, n_Q.

A.4 Exercises for Chapter 4: Continuous and discrete spectrum.

- **Exercise 1.** Prove that in the case of quasi-one-dimensional electron gas, with free states along the direction x and bound states along the directions y, z, the envelope functions are given by the expression

$$\varphi_{i,j,k_x}(\vec{r}) = \frac{1}{\sqrt{L_x}}\, e^{ik_x x} v_j(y)\zeta_i(z) \tag{A.30}$$

and the relevant eigenenergies by the expression

$$E_{i,j,k_x} = E_i + E_j + \frac{\hbar^2 k_x^2}{2m^*}, \tag{A.31}$$

where k_x is «continuous» and i, j are discrete indices.

- **Exercise 2.** Prove that in the case of three-dimensional electron gas, with free states along all directions x, y, z, the envelope functions are given by the expression

$$\varphi_{i,j,k_x}(\vec{r}) = \frac{1}{\sqrt{V}}\, e^{ik_x x} e^{ik_y y} e^{ik_z z}, \tag{A.32}$$

where $V = L_x L_y L_z$, and the relevant eigenenergies by the expression

$$E_{k_x,k_y,k_z} = \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m^*} = \frac{\hbar^2 k^2}{2m^*}, \tag{A.33}$$

where k_x, k_y, k_z are «continuous» indices.

A.5 Exercises for Chapter 5: Semiclassical approximation I.

- **Exercise 1.** Consider the equations occurring by the Rabi equations after the Rotating Wave Approximation (RWA), i.e.,

$$\dot{C}_1(t) = C_2(t)\frac{iE_0\mathscr{P}}{2\hbar}e^{-i(\Omega-\omega)t}$$

$$\dot{C}_2(t) = C_1(t)\frac{iE_0\mathscr{P}}{2\hbar}e^{i(\Omega-\omega)t}$$

We want to solve them under the initial conditions $C_1(0) = 1, C_2(0) = 0$.
(a') Perform the transformation

$$C_1(t) = \mathscr{C}_1(t)e^{-\frac{i(\Omega-\omega)t}{2}}$$

$$C_2(t) = \mathscr{C}_2(t)e^{\frac{i(\Omega-\omega)t}{2}}$$

and prove that the following system of differential equations occurs:

$$\begin{bmatrix} \dot{\mathscr{C}}_1(t) \\ \dot{\mathscr{C}}_2(t) \end{bmatrix} = \begin{bmatrix} -\frac{i\Delta}{2} & \frac{i\Omega_{\mathrm{R}}}{2} \\ \frac{i\Omega_{\mathrm{R}}}{2} & \frac{i\Delta}{2} \end{bmatrix} \begin{bmatrix} \mathscr{C}_1(t) \\ \mathscr{C}_2(t) \end{bmatrix}.$$

We have defined the detuning as $\Delta := \omega - \Omega$ and the Rabi frequency as $\Omega_{\mathrm{R}} := \frac{E_0\mathscr{P}}{\hbar}$.
(b') Define the vector

$$\vec{x}(t) = \begin{bmatrix} \mathscr{C}_1(t) \\ \mathscr{C}_2(t) \end{bmatrix}$$

and the matrix

$$\tilde{\mathscr{A}} = \begin{bmatrix} -\frac{i\Delta}{2} & \frac{i\Omega_{\mathrm{R}}}{2} \\ \frac{i\Omega_{\mathrm{R}}}{2} & \frac{i\Delta}{2} \end{bmatrix} = -i\mathrm{A} = -i\begin{bmatrix} \frac{\Delta}{2} & -\frac{\Omega_{\mathrm{R}}}{2} \\ -\frac{\Omega_{\mathrm{R}}}{2} & -\frac{\Delta}{2} \end{bmatrix}$$

so that the system of differential equations becomes

$$\dot{\vec{x}}(t) = \tilde{\mathscr{A}}\vec{x}(t)$$

Try solutions of the form

$$\vec{x}(t) = \vec{v}e^{\tilde{\lambda}t},$$

and show that, after all, we have to solve the eigenvalue problem

$$\mathrm{A}\vec{v} = \lambda\vec{v}$$

όπου $\tilde{\lambda} = -i\lambda$.
(c') Solve the problem for $\Delta = 0$.
(d') Solve the problem for $\Delta \neq 0$.
(e') Compare the maximum transfer percentage and the period of the oscillations that occur for $\Delta = 0$ and $\Delta \neq 0$.

- **Exercise 2.** Consider the case in which Eq. 5.103 holds, and specifically that the probability to find the electron at the upper level is

$$P_2(t) = |C_2(t)|^2 = \frac{\Omega_{\mathrm{R}}^2}{4}\frac{\sin^2\left(\frac{\Delta t}{2}\right)}{\left(\frac{\Delta t}{2}\right)^2}t^2.$$

Given the definition of the Rabi frequency, $\Omega_{\mathrm{R}} = \frac{\mathscr{P}\mathscr{E}_0}{\hbar}$ (see Eq. 5.50) and assuming we are at resonance, estimate the time needed so that $P_2(t) = 1$. The magnitude of the dipole moment, $\mathscr{P}$, is of the order of ea_0, where e is the elementary charge $\approx 1.602 \times 10^{-19}$ C and $a_0 \approx 0.529$ Å is the Bohr radius. Consider three cases for the magnitude of the electric field; in specific, 10^3, 10^5 and 10^8 V/m. The reduced Planck's constant is known: $\hbar \approx 1.054 \times 10^{-34}$ Js.

Solution of Exercise 2.
If we are at resonance, when $\Delta := \omega - \Omega = 0$, and we want the probability to become equal to

unity, then, if we set $x := \frac{\Delta t}{2} \Rightarrow x = 0 \Rightarrow \frac{\sin^2 x}{x^2} \longrightarrow 1$. Thus, it is implied that $t = \frac{2\hbar}{\mathscr{P}\mathscr{E}_0}$. In particular,

$$\mathrm{E}_0 = 10^3\,\mathrm{V/m} \Rightarrow \quad t = \frac{2 \times 1.054 \times 10^{-34}\,\mathrm{Js}}{1.6 \times 10^{-19}\,\mathrm{C} \quad 0.529 \times 10^{-10}\,\mathrm{m} \quad 10^3\,\mathrm{V/m}} \approx 2.5 \times 10^{-8}\,\mathrm{s} = \quad 25\,\mathrm{ns}$$

$$\mathrm{E}_0 = 10^5\,\mathrm{V/m} \Rightarrow \quad t = \frac{2 \times 1.054 \times 10^{-34}\,\mathrm{Js}}{1.6 \times 10^{-19}\,\mathrm{C} \quad 0.529 \times 10^{-10}\,\mathrm{m} \quad 10^5\,\mathrm{V/m}} \approx 2.5 \times 10^{-10}\,\mathrm{s} = 0.25\,\mathrm{ns}$$

$$\mathrm{E}_0 = 10^8\,\mathrm{V/m} \Rightarrow \quad t = \frac{2 \times 1.054 \times 10^{-34}\,\mathrm{Js}}{1.6 \times 10^{-19}\,\mathrm{C} \quad 0.529 \times 10^{-10}\,\mathrm{m} \quad 10^8\,\mathrm{V/m}} \approx 2.5 \times 10^{-13}\,\mathrm{s} = 0.25\,\mathrm{ps}$$

- **Exercise 3.** Using the program Oscillations.m (Code C.8 in Appendix C), create a graphical representation of oscillations for a two-level system for which it holds that $|\Delta| = 3\Omega_\mathrm{R}$.

- **Exercise 4.** Create a program analogous to Oscillations.m (Code C.8 in Appendix C) for a three-level system, and create a graphical representation of oscillations within it in the case $\Omega_\mathrm{R} = \Omega'_\mathrm{R} = 1, \Delta = 0$.

- **Exercise 5.** Two-level system in the semiclassical approach and dipole approximation. The following equations, before the rotating wave approximation, are given

$$\dot{C}_1(t) = C_2(t)\frac{i\Omega_\mathrm{R}}{2}\left[e^{i\Delta t} + e^{-i\Sigma t}\right], \tag{A.34}$$

$$\dot{C}_2(t) = C_1(t)\frac{i\Omega_\mathrm{R}}{2}\left[e^{-i\Delta t} + e^{i\Sigma t}\right]. \tag{A.35}$$

(a) Explain and define the symbols, Ω_R, Δ, Σ, $C_1(t)$, $C_2(t)$.
(b) Let's suppose that the magnitude of the perturbation is large so that Δ and Σ are negligible compared to Ω_R. How will Eqs. (A.34)-(A.35) be simplified?
For the simplified equations:
(c) Find $C_1(t), C_2(t)$ with initial conditions $C_1(0) = 1, C_2(0) = 0$.
(d) Calculate the probabilities of electron presence at the levels, $P_1(t)$ and $P_2(t)$, as well as the period, T_R, and the maximum transfer percentage, A_R, of the Rabi oscillations.
(e) Calculate the mean transfer rate, $k = \frac{\langle P_2(t)\rangle}{t_{2,\mathrm{mean}}}$, where $\langle P_2(t)\rangle$ is the mean value of the electron presence probability at level 2, and $t_{2,\mathrm{mean}}$ is the required time so that $P_2(t)$ reaches for the first time its mean value, having initially placed the electron at level 1.

- **Exercise 6.** Quantum dot and the variables are separable. Along axes x and y we have quantum wells which hold only one level, whereas, along the z axis we have a simple harmonic oscillator, whose levels are energetically equidistant at separation $\hbar\Omega$. We focus on the lower three levels, let's call them $k = 1, 2, 3$ ($n = 0, 1, 2$). Thus, we have a three-level system. Suppose semiclassical approach with electric field along the z axis. The eigenfunctions along the z axis are

$$Z_n(z) = u_n(z)\exp\left(-\frac{z^2}{2a^2}\right), \tag{A.36}$$

where $a = \left(\frac{\hbar}{m\Omega}\right)^{1/2}$ and the following are given

$$u_0(z) = \left(\frac{1}{a\sqrt{\pi}}\right)^{1/2}, \tag{A.37}$$

$$u_1(z) = \left(\frac{1}{a\sqrt{\pi}}\right)^{1/2}\left[2\left(\frac{z}{a}\right)\right], \tag{A.38}$$

$$u_2(z) = \left(\frac{1}{8a\sqrt{\pi}}\right)^{1/2}\left[2-4\left(\frac{z}{a}\right)^2\right]. \tag{A.39}$$

Prove that the (cyclic) Rabi frequencis, Ω_R and Ω_R' as well as the off-diagonal dipole moment matrix elements $\mathscr{P}$ and $\mathscr{P}'$, between levels 12 and 23, respectively, satisfy

(a)

$$\mathscr{P} = -\frac{2ea}{\sqrt{\pi}}\int_{-\infty}^{\infty} d\mu\, \mu^2\, e^{-\mu^2}, \tag{A.40}$$

(b)

$$\mathscr{P}' = -\frac{\sqrt{2}ea}{\sqrt{\pi}}\int_{-\infty}^{\infty} d\mu\, \mu^2\, e^{-\mu^2} + \frac{\sqrt{2}ea}{\sqrt{\pi}}\, 2\int_{-\infty}^{\infty} d\mu\, \mu^4\, e^{-\mu^2}, \tag{A.41}$$

and because it is given that

$$\int_{-\infty}^{\infty} d\mu\, \mu^2\, e^{-\mu^2} = \frac{\sqrt{\pi}}{2} \tag{A.42}$$

$$\int_{-\infty}^{\infty} d\mu\, \mu^4\, e^{-\mu^2} = \frac{3\sqrt{\pi}}{4} \tag{A.43}$$

we have finally

(c)

$$\left|\frac{\Omega_R}{\Omega_R'}\right| = \left|\frac{\mathscr{P}}{\mathscr{P}'}\right| = \frac{1}{\sqrt{2}}. \tag{A.44}$$

A.6 Exercises for Chapter 6: Semiclassical approximation II.

There are no exercises in this chapter.

A.7 Exercises for Chapter 7: Allowed and forbidden optical transitions.

- **Exercise 1.** Prove that, e.g. at the Hydrogen atom, the electric force is much larger than the gravitational force. Find, actually, how many orders of magnitude larger it is.

- **Exercise 2.** Find the quantum number n that characterizes the movement of the Earth around the Sun, within the Bohr's model. Consider as known: Earth's mass, $M = 6 \cdot 10^{24}$ kg, orbital radius of Earth, $R = 1.5 \cdot 10^{11}$ m, linear velocity of Earth, $v = 3 \cdot 10^4$ m/s.

- **Exercise 3.** Show that the constant A in the azimuthal function $\Phi_{m_\ell}(\phi) = Ae^{im_\ell\phi}$ can be chosen as $\frac{1}{\sqrt{2\pi}}$ so that the function is normalized. Moreover, show that for $m_\ell' \neq m_\ell$, the functions $\Phi_{m_\ell}(\phi)$ and $\Phi_{m_\ell'}(\phi)$ are orthogonal.

- **Exercise 4.** Show that $\Theta_{20}(\theta) = \frac{\sqrt{10}}{4}(3\cos^2\theta - 1)$ solves the polar equation 7.25 and that it is normalized.

- **Exercise 5.** Consider as given the function $R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-\frac{r}{a_0}}$ and Eq. 7.26 and find the energy E_1 of hydrogen.

- **Exercise 6.** Show that $R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r} a_0$ and $R_{21} = \frac{1}{2\sqrt{6}a_0^{3/2}} \frac{r}{a_0} e^{-\frac{r}{2a_0}}$ solve the radial equation (7.26) and that they are normalized. Consider as known:
$$\int_0^\infty \mathrm{d}\rho \rho^n e^{-}\gamma\rho = \gamma^{-(n+1)} n!,\ n = 1, 2, 3, \dots, \gamma > 0.$$

- **Exercise 7.** Compare the probability densities to find the electron in the $1s$ orbital of the hydrogen atom at distances $\frac{3a_0}{0}$, a_0 and $\frac{a_0}{2}$.

- **Exercise 8.** Find the distance at which the probability density to find the electron at the $1s$ orbital of the hydrogen atom becomes maximum.

- **Exercise 9.** Find the average distance of the electron in the $1s$ orbital of hydrogen. Consider as known:
$$\int_0^\infty \mathrm{d}\rho \rho^n e^{-}\gamma\rho = \gamma^{-(n+1)} n!,\ n = 1, 2, 3, \dots, \gamma > 0.$$

- **Exercise 10.** Show that the substitution $\vec{r} \longrightarrow -\vec{r}$ of a position vector is equivalent, in spherical coordinates, to the substitutions $r \longrightarrow r, \theta \longrightarrow \pi - \theta, \varphi \longrightarrow \pi + \varphi$, which were used in Section 7.7.

  Solution of Exercise 10:

  Let us consider, without any loss of generality, the point marked in Figure 7.9, which lies on the first octant. Thus, $\theta \in [0, \pi/2], \varphi \in [0, \pi/2]$.

  The substitution $\vec{r} \longrightarrow -\vec{r} \equiv r'$ is equivalent to
$$\begin{aligned} x' &= -x \Leftrightarrow r' \sin\theta' \cos\varphi' = -r \sin\theta \cos\varphi, \\ y' &= -y \Leftrightarrow r' \sin\theta' \sin\varphi' = -r \sin\theta \sin\varphi, \\ z' &= -z \Leftrightarrow r' \cos\theta' = -r \cos\theta. \end{aligned}$$

  However,
$$r' = \sqrt{x'^2 + y'^2 + z'^2} = \sqrt{(-x)^2 + (-y)^2 + (-z)^2} = \sqrt{x^2 + y^2 + z^2}$$

  Thus, $\boxed{r' = r}$, and the above relations become
$$\begin{aligned} \sin\theta' \cos\varphi' &= -\sin\theta \cos\varphi, \\ \sin\theta' \sin\varphi' &= -\sin\theta \sin\varphi, \\ \cos\theta' &= -\cos\theta. \end{aligned}$$

  From the third relation, given that $\theta, \theta' \in [0, \pi]$, it follows that $\boxed{\theta' = \pi - \theta}$. Additionally, dividing the first two relations by parts yields
$$\tan\varphi' = \tan\varphi$$

  Hence, given that $\varphi, \varphi' \in [0, 2\pi]$, the two possible solutions are $\varphi' = \varphi$ and $\varphi' = \pi + \varphi$. However, substituting the former solution to any of the first two relations, it follows that $\sin\theta' = -\sin\theta$, which, for $\theta, \theta' \in [0, \pi]$ is *absurd*. Therefore, $\boxed{\varphi' = \pi + \varphi}$.

- **Exercise 11.** Show that the below expression for the position vector,

$$\vec{r} = \frac{r}{2}\sin\theta[(\hat{e}_x - i\hat{e}_y)e^{i\varphi} + (\hat{e}_x + i\hat{e}_y)e^{-i\varphi}] + r\cos\theta\,\hat{e}_z,$$

which was used in Section 7.7, holds.

Solution of Exercise 11:

$$\begin{aligned}
&(\hat{e}_x - i\hat{e}_y)e^{i\varphi} = (\hat{e}_x - i\hat{e}_y)(\cos\varphi + i\sin\varphi) = \hat{e}_x\cos\varphi + \cancel{\hat{e}_x i\sin\varphi} - \cancel{i\hat{e}_y\cos\varphi} + \hat{e}_y\sin\varphi\\
&(\hat{e}_x + i\hat{e}_y)e^{-i\varphi} = (\hat{e}_x + i\hat{e}_y)(\cos\varphi - i\sin\varphi) = \hat{e}_x\cos\varphi - \cancel{\hat{e}_x i\sin\varphi} + \cancel{i\hat{e}_y\cos\varphi} + \hat{e}_y\sin\varphi\\
&\Rightarrow [\dots] = 2\hat{e}_x\cos\varphi + 2\hat{e}_y\sin\varphi \Rightarrow \frac{r}{2}\sin\theta[\dots] + r\cos\theta\hat{e}_z =\\
&= r\cos\varphi\sin\theta\hat{e}_x + r\sin\varphi\sin\theta\hat{e}_y + r\cos\theta\hat{e}_z = x\hat{e}_x + y\hat{e}_y + z\hat{e}_z = \vec{r}
\end{aligned}$$

- **Exercise 12.** Given that the Einstein coefficients are given by Eqs. 5.99, 5.100, 5.101

$$B_{12} = \frac{\mathscr{P}^2\pi}{6\hbar^2\varepsilon_0},$$

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3},$$

$$B_{12} = B_{21},$$

calculate them for the atomic transitions 100 → 210 and 100 → 21 ± 1 of the hydrogen atom. Assume that we are at resonance.

Solution of Exercise 12:
Calculations in Section 7.7 show that

$$\vec{\mathscr{P}}_{100210} = -\frac{2^{15/2}}{3^5}ea_0\hat{e}_z \qquad \Rightarrow |\vec{\mathscr{P}}_{100210}| = \frac{2^{15/2}}{3^5}ea_0$$

$$\vec{\mathscr{P}}_{10021\pm1} = -\frac{2^7}{3^5}(\hat{e}_x \pm i\hat{e}_y)ea_0 \qquad \Rightarrow |\vec{\mathscr{P}}_{10021\pm1}| = \frac{2^{15/2}}{3^5}ea_0$$

Hence, we can compactly write

$$\mathscr{P} = \frac{2^{15/2}}{3^5}ea_0.$$

Therefore, $\mathscr{P} \approx \frac{2^{15/2}}{3^5}\,1.602\times10^{-19}\text{C}\cdot0.529\times10^{-10}\,\text{m} \approx 0.6313\times10^{-29}\,\text{Cm}$, since the elementary charge $e \approx 1.602\times10^{-19}$ C and the Bohr radius $a_0 \approx 0.529$ Å. Hence,

$$B = B_{12} = B_{21} \approx 0.02121\times10^{22}\frac{\text{m}^3}{\text{Js}^2}$$

The vacuum permittivity is $\varepsilon_0 \approx 8.854\times10^{-12}$ F/m and the reduced Planck constant is $\hbar \approx 1.054\times10^{-34}$ Js.

Since we are at resonance, $\Delta := \omega - \Omega = 0 \Rightarrow \omega = \Omega$. So, let us calculate Ω. For the hydrogen energy levels, we have $E_n = -13.6\ eV/n^2$. Thus, $E_1 = -13.6$ eV, $E_2 = -3.4$ eV $\Rightarrow E_2 - E_1 = 10.2$ eV $\Rightarrow \Omega = \dfrac{E_2 - E_1}{\hbar} \approx 15.5 \times 10^{15}$ Hz $= 15.5$ PHz

$$A_{21} = \frac{8\pi h \nu^3}{c^3} B = \frac{8\pi \hbar^3 \omega^3}{h^2 c^3} B = \frac{2\hbar \Omega^3}{\pi c^3} B \approx \frac{\Omega^3 \mathscr{P}^2}{3c^3 \hbar \varepsilon_0} \approx 1.963 \times 10^9 \text{ Hz}$$

- **Exercise 13.** Calculate the matrix elements and simple overlaps $\langle 100|\vec{r}|100\rangle$ and $\langle 100|100\rangle$, $\langle 100|\vec{r}|200\rangle$ and $\langle 100|200\rangle$, $\langle 200|\vec{r}|200\rangle$ and $\langle 200|200\rangle$, of Section 7.7.

Solution of Exercise 13:

$$\langle 100|\vec{r}|100\rangle = (\pi a_0^3)^{-1/2}(\pi a_0^3)^{-1/2} \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} r^2 \sin\theta dr d\theta d\phi\, e^{-\frac{2r}{a_0}}\, r\left\{\frac{\sin\theta}{2}\left[(\hat{e}_x - i\hat{e}_y)e^{i\phi} + (\hat{e}_x + i\hat{e}_y)e^{-i\phi}\right] + \hat{e}_z \cos\theta\right\}$$

$$= \frac{a_0^4}{\pi a_0^3} \int_0^{\infty} \left(\frac{r}{a_0}\right)^3 e^{-\frac{2r}{a_0}} d\left(\frac{r}{a_0}\right) \int_0^{\pi}\int_0^{2\pi} \sin\theta d\theta d\phi \left\{\frac{\sin\theta}{2}\left[(\hat{e}_x - i\hat{e}_y)e^{i\phi} + (\hat{e}_x + i\hat{e}_y)e^{-i\phi}\right] + \hat{e}_z \cos\theta\right\}$$

$$= \frac{a_0}{\pi} \int_0^{\infty} q^3 e^{-2q} dq \left\{\int_0^{\pi} d\theta \frac{\sin^2\theta}{2} \int_0^{2\pi} d\phi \left[(\hat{e}_x - i\hat{e}_y)e^{i\phi} + (\hat{e}_x + i\hat{e}_y)e^{-i\phi}\right] + \int_0^{\pi} d\theta \sin\theta\cos\theta\, \hat{e}_z \int_0^{2\pi} d\phi\right\}$$

$$\int_0^{\infty} \underbrace{q^3 e^{-2q}}_{\gamma=2, n=3} dq = 2^{-(3+1)} 3! = \frac{2\cdot 3}{2^4} = \frac{3}{2^3} = \frac{3}{8}$$

$$\int_0^{2\pi} d\phi [\dots] = (\hat{e}_x - i\hat{e}_y)\int_0^{2\pi} d\phi\, e^{i\phi} + (\hat{e}_x + i\hat{e}_y)\int_0^{2\pi} d\phi\, e^{-i\phi}$$

$$\int_0^{2\pi} d\phi\, e^{\pm i\phi} = \int_0^{2\pi} d\phi \cos(\pm\phi) + i\int_0^{2\pi} d\phi \sin(\pm\phi) = \cancelto{0}{\int_0^{2\pi} d\phi \cos\phi} \pm i \cancelto{0}{\int_0^{2\pi} d\phi \sin\phi} = 0$$

$$\int_0^{\pi} d\theta \frac{\sin^2\theta}{2} = \frac{1}{2}\int_0^{\pi} \frac{1 - \cos 2\theta}{2} d\theta = \frac{1}{4}\left\{\pi - \int_0^{\pi} \cos 2\theta\right\} = \frac{\pi}{4}$$

$$\int_0^{\pi} d\theta \sin\theta\cos\theta = \frac{1}{2}\int_0^{\pi} d\theta \sin 2\theta = \frac{1}{2}\left[\frac{-\cos 2\theta}{2}\right]_0^{\pi} = 0$$

Thus, $\langle 100|\vec{r}|100\rangle = \dfrac{a_0}{\pi}\dfrac{3}{2^3}\left\{\dfrac{\pi}{4}\cdot 0 + 0 \cdot 2\pi\right\} = 0$, expected, since

$$\langle 100|\vec{r}|100\rangle = \int (\text{even})(\text{odd})(\text{even}) = 0.$$

While, $\langle 100|100\rangle = (\pi a_0^3)^{-1} \displaystyle\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} r^2 \sin\theta dr d\theta d\phi\, e^{-\frac{2r}{a_0}}$

$$
\begin{aligned}
&= \frac{a_0^3}{\pi a_0^3} \int_0^{\infty} d\left(\frac{r}{a_0}\right)\left(\frac{r}{a_0}\right)^2 e^{-\frac{2r}{a_0}} \int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\phi \\
&= \frac{1}{\pi} \int_0^{\infty} dq \, \underbrace{q^2 e^{-2q}}_{\gamma=2, n=2} \Big[-\cos\theta\Big]_0^{\pi} \cdot 2\pi = \frac{1}{\pi} 2^{-(2+1)} 2!(1+1) \cdot 2\pi = \frac{2^3}{2^3} = 1
\end{aligned}
$$

This is expected, since $\Phi_{100}(\vec{r})$ is normalized.

$$
\begin{aligned}
\langle 100|\vec{r}|200\rangle &= (\pi a_0^3)^{-1/2}(32\pi a_0^3)^{-1/2} \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} r^2 \sin\theta dr d\theta d\phi \, e^{-\frac{r}{a_0}} \left(2-\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} r \\
&\qquad \left\{\frac{\sin\theta}{2}\Big[(\hat{e}_x - i\hat{e}_y)e^{i\phi} + (\hat{e}_x + i\hat{e}_y)e^{-i\phi}\Big] + \hat{e}_z \cos\theta\right\} \\
&= \frac{a_0^4}{\pi a_0^3 4\sqrt{2}} \int_0^{\infty} d\left(\frac{r}{a_0}\right)\left(\frac{r}{a_0}\right)^3 e^{-\frac{3r}{2a_0}} \left(2-\frac{r}{a_0}\right) \int_0^{\pi}\int_0^{2\pi} \sin\theta d\theta d\phi \left\{\frac{\sin\theta}{2}\Big[\ldots\Big] + \hat{e}_z\cos\theta\right\}
\end{aligned}
$$

$$
\begin{aligned}
\int_0^{\infty} dq \, q^3 e^{-\frac{3q}{2}}\left(2-q\right) &= 2\int_0^{\infty} dq \, \underbrace{q^3 e^{-\frac{3q}{2}}}_{\gamma=\frac{3}{2}, n=3} - \int_0^{\infty} dq \, \underbrace{q^4 e^{-\frac{3q}{2}}}_{\gamma=\frac{3}{2}, n=4} = 2\left(\frac{3}{2}\right)^{-(3+1)} 3! - \left(\frac{3}{2}\right)^{-(4+1)} 4! \\
&= \frac{2\cdot 2^4}{3^4} 2\cdot 3 - \frac{2^5}{3^5} 2\cdot 3\cdot 2^2 = \frac{2^6}{3^3} - \frac{2^8}{3^4} = \left(\frac{4}{3}\right)^3 - \left(\frac{4}{3}\right)^4
\end{aligned}
$$

$$
\begin{aligned}
\int_0^{\pi} d\theta \frac{\sin^2\theta}{2} \int_0^{2\pi} d\phi \Big[(\hat{e}_x - i\hat{e}_y)e^{i\phi} + (\hat{e}_x + i\hat{e}_y)e^{-i\phi}\Big] + \int_0^{\pi} d\theta \sin\theta\cos\theta \, \hat{e}_z \int_0^{2\pi} d\phi \\
= \frac{\pi}{4} \cdot 0 + 0 \cdot 2\pi = 0
\end{aligned}
$$

$$
\begin{aligned}
\text{Thus, } \langle 100|\vec{r}|200\rangle &= \frac{a_0}{\pi 4\sqrt{2}}\left(\left(\frac{4}{3}\right)^3 - \left(\frac{4}{3}\right)^4\right) \cdot 0 = 0, \text{ expected, since} \\
\langle 100|\vec{r}|200\rangle &= \int (\text{even})(\text{odd})(\text{even}) = 0.
\end{aligned}
$$

$$
\begin{aligned}
\text{While, } \langle 100|200\rangle &= (\pi a_0^3)^{-1/2}(32\pi a_0^3)^{-1/2} \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} r^2 \sin\theta dr d\theta d\phi \, e^{-\frac{r}{a_0}} \left(2-\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \\
&= \frac{a_0^3}{\pi a_0^3 4\sqrt{2}} \int_0^{\infty} d\left(\frac{r}{a_0}\right)\left(\frac{r}{a_0}\right)^2 e^{-\frac{3r}{2a_0}} \left(2-\frac{r}{a_0}\right) \int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\phi \\
&= \frac{1}{\cancel{4\pi}\sqrt{2}} \int_0^{\infty} dq \, q^2 e^{-\frac{3q}{2}} \left(2-q\right)\cancel{4\pi} \\
&= \frac{1}{\sqrt{2}}\left\{2\int_0^{\infty} dq \, \underbrace{q^2 e^{-\frac{3q}{2}}}_{\gamma=\frac{3}{2}, n=2} - \int_0^{\infty} dq \, \underbrace{q^3 e^{-\frac{3q}{2}}}_{\gamma=\frac{3}{2} \; n=3}\right\} = \frac{1}{\sqrt{2}}\left\{2\left(\frac{3}{2}\right)^{-(2+1)} 2! - \left(\frac{3}{2}\right)^{-(3+1)} 3!\right\}
\end{aligned}
$$

$$= \frac{1}{\sqrt{2}}\left\{\frac{2^5}{3^3} - \frac{2^5}{3^3}\right\} = 0$$

This is expected, since $\Phi_{100}(\vec{r})$ and $\Phi_{200}(\vec{r})$ are orthogonal.

$$\begin{aligned}\langle 200|\vec{r}|200\rangle &= (32\pi a_0^3)^{-1/2}(32\pi a_0^3)^{-1/2}\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} r^2\sin\theta dr d\theta d\phi\, e^{-\frac{r}{a_0}}\left(2-\frac{r}{a_0}\right)^2 r \\ &\qquad \left\{\frac{\sin\theta}{2}\left[(\hat{e}_x - i\hat{e}_y)e^{i\phi} + (\hat{e}_x + i\hat{e}_y)e^{-i\phi}\right] + \hat{e}_z\cos\theta\right\} \\ &= \frac{a_0^4}{32\pi a_0^3}\int_0^{\infty} d\left(\frac{r}{a_0}\right)\left(\frac{r}{a_0}\right)^3 e^{-\frac{r}{a_0}}\left(2-\frac{r}{a_0}\right)^2\int_0^{\pi}\int_0^{2\pi}\sin\theta d\theta d\phi \\ &\qquad \left\{\frac{\sin\theta}{2}\left[\,\dots\,\right] + \hat{e}_z\cos\theta\right\}\end{aligned}$$

$$\begin{aligned}\int_0^{\infty} dq\, q^3\,(2-q)^2\,e^{-q} &= \int_0^{\infty} dq\, q^3\,(4+q^2-4q)\,e^{-q} = \\ &= 4\int_0^{\infty} dq\ \underbrace{q^3\,e^{-q}}_{\gamma=1,n=3} + \int_0^{\infty} dq\ \underbrace{q^5\,e^{-q}}_{\gamma=1,n=5} - 4\int_0^{\infty} dq\ \underbrace{q^4\,e^{-q}}_{\gamma=1,n=4} \\ &= 4\cdot 1^{-(3+1)}3! + 1^{-(5+1)}5! - 4\cdot 1^{-(4+1)}4! = 4! + 4!5 - 4!4 = \\ &= 4!(1+5-4) = 2\cdot 4!\end{aligned}$$

$$\frac{1}{2}\int_0^{\pi} d\theta\ \sin^2\theta\int_0^{2\pi} d\phi\left[(\hat{e}_x - i\hat{e}_y)\cancelto{0}{e^{i\phi}} + (\hat{e}_x + i\hat{e}_y)\cancelto{0}{e^{-i\phi}}\right] + \int_0^{\pi} d\theta\ \sin\theta\cos\theta\,\hat{e}_z\int_0^{2\pi} d\phi$$

$$\int_0^{\pi} d\theta\ \sin^2\theta = \int_0^{\pi}\frac{1-\cos 2\theta}{2}d\theta = \frac{\pi}{2} - \left[\frac{sin2\theta}{2\cdot 2}\right]_0^{\pi} = \frac{\pi}{2}$$

$$\int_0^{\pi} d\theta\ \sin\theta\ \cos\theta = \int_0^{\pi}\sin\theta\, d(\sin\theta) = 0$$

Thus, $\langle 200|\vec{r}|200\rangle = \frac{a_0}{32\pi}2\cdot 4!\left\{\frac{\pi}{2}\cdot 0 + 0\cdot 2\pi\right\} = 0$. This is expected, since

$$\langle 200|\vec{r}|200\rangle = \int(\text{even})(\text{odd})(\text{even}) = 0.$$

$$\begin{aligned}\text{Thus, } \langle 200|200\rangle &= \frac{1}{32\pi a_0^3}\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} r^2\sin\theta dr d\theta d\phi\left(2-\frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}} \\ &= \frac{\cancel{a_0^3}}{32\pi\cancel{a_0^3}}\int_0^{\infty} d\left(\frac{r}{a_0}\right)\left(\frac{r}{a_0}\right)^2\left(2-\frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}}\underbrace{\int_0^{\pi}\int_0^{2\pi}\sin\theta d\theta d\phi}_{4\pi\ \text{(total solid angle)}} \\ &= \frac{1}{8}\left\{\int_0^{\infty} dq\, q^2\left(4+q^2-4q\right)e^{-q}\right\}\end{aligned}$$

$$= \frac{1}{8}\Big\{4\int_0^\infty dq\ \underbrace{q^2\,e^{-q}}_{\gamma=1,n=2} + \int_0^\infty dq\ \underbrace{q^4\,e^{-q}}_{\gamma=1,n=4} - 4\int_0^\infty dq\ \underbrace{q^3\,e^{-q}}_{\gamma=1,n=3}\Big\}$$

$$= \frac{1}{8}\Big\{4\cdot 1^{-(2+1)}2! + 1^{-(4+1)}4! - 4\cdot 1^{-(3+1)}3!\Big\} = \frac{8+4!-4!}{8} = 1$$

This is expected, since $\Phi_{200}(\vec{r})$ is normalized.

- **Exercise 14.** For the hydrogen atom:

  1. Check the parity of $2s, 2p_z, 3d_{xz}$.
  2. Find how many and which nodal surfaces each of the above functions has.
  3. Check whether the transitions $1s \leftrightarrow 2p_z$, $1s \leftrightarrow 3p_z$, $2s \leftrightarrow 3p_z$ are allowed or fobidden within the dipole approximation and whether the selection rules $\Delta\ell = \pm 1$, $\Delta m_\ell = 0, \pm 1$ hold.
  4. Compare the strengths of transitions $1s \leftrightarrow 2p_z$, $1s \leftrightarrow 3p_z$ within the dipole approximation.
  5. The dipole moment matrix elements are

  $$\vec{\mathscr{P}}_{k_1 k_2} := \int_{\text{everywhere}} dV \Phi^*_{k_1}(\vec{r})\,(-e)\vec{r}\,\Phi_{k_2}(\vec{r})$$

     Explain why there is no such optical transition if this matrix element becomes zero.
  6. Find the energy, frequency, and wavelength at which the transitions $1s \leftrightarrow 2p_z$, $1s \leftrightarrow 3p_z$, $2s \leftrightarrow 3p_z$ correspond. Which of these transitions could be used for a visible laser?

- **Exercise 15.** Consider a 1D infinite quantum well of width L, with walls places at positions $x = -L/2$ and $x = L/2$. Its eigenfunctions are

$$\Psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}}\cos\left(\frac{n\pi x}{L}\right), & n = 1, 3, 5, \ldots \\ \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right), & n = 2, 4, 6, \ldots \\ 0, & \text{outside} \end{cases} .$$

The identities $\cos^2\theta = \frac{1+\cos(2\theta)}{2}$, $\sin^2\theta = \frac{1-\cos(2\theta)}{2}$ can be used. Show that the optical transitions $3 \leftrightarrow 1$ and $2 \leftrightarrow 4$ are forbidden, while $1 \leftrightarrow 2$ and $2 \leftrightarrow 3$ are allowed.

Show the same thing, this time considering a 1D infinite quantum well with walls at positions $x = 0$ and $x = L$, i.e., with eigenfunctions

$$\Psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right),\ n = 1, 2, 3, \ldots .$$

- **Exercise 16.** We give the atomic orbitals (notation $n\ell m$) of the hydrogen atom 210 ($2p_z$) and 32±2 (with proper sum and difference of which $3d_{x^2-y^2}$ and $3d_{xy}$ are constructed)

$$\psi_{210}(r,\theta,\varphi) = \left(32\pi a_0^3\right)^{-1/2}\ \frac{r}{a_0}\ \cos\theta\ \exp\left(-\frac{r}{2a_0}\right), \tag{A.45}$$

$$\psi_{32\pm2}(r,\theta,\varphi) = \left(26244\pi a_0^3\right)^{-1/2} \left(\frac{r}{a_0}\right)^2 \sin^2\theta \ \exp\left(\pm 2i\varphi\right) \ \exp\left(-\frac{r}{3a_0}\right). \qquad (A.46)$$

(a) Find and justify the parity and the number of nodal surfaces of these atomic orbitals.
(b) Is the transition 210 ↔ 32±2 allowed within the dipole approximation? Are the rules $\Delta\ell = \pm 1$ and $\Delta m = 0, \pm 1$ satisfied?
We give that $(\mathbf{r} \rightarrow \mathbf{r}' = -\mathbf{r}) \Leftrightarrow (r' = r, \theta' = \pi - \theta, \varphi' = \varphi + \pi)$.

A.8 Exercises for Chapter 8: Quantum mechanical approach I.

- **Exercise 1.** The index m of the EM mode is omitted for simplicity.
  (A) Determine the action of the terms $\hat{a}^\dagger\hat{a}$, $\hat{a}\hat{a}^\dagger$, $\hat{S}_+\hat{S}_-$, $\hat{S}_-\hat{S}_+$, $\hat{S}_+\hat{a}^\dagger$, $\hat{S}_+\hat{a}$, $\hat{S}_-\hat{a}^\dagger$, $\hat{S}_-\hat{a}$, act on the states $|\downarrow, n\rangle$ and $|\uparrow, n\rangle$.
  (B) Calculate $\langle\hat{a}^\dagger\hat{a}\rangle$, $\langle\hat{a}\hat{a}^\dagger\rangle$, $\langle\hat{S}_+\hat{S}_-\rangle$, $\langle\hat{S}_-\hat{S}_+\rangle$, $\langle\hat{S}_+\hat{a}^\dagger\rangle$, $\langle\hat{S}_+\hat{a}\rangle$, $\langle\hat{S}_-\hat{a}^\dagger\rangle$, $\langle\hat{S}_-\hat{a}\rangle$, for the states $|\downarrow, n\rangle$ and $|\uparrow, n\rangle$.

Solution of Exercise 1:
(A)

$$\hat{a}^\dagger\hat{a}\,|\uparrow, n\rangle = \hat{a}^\dagger\sqrt{n}\,|\uparrow, n-1\rangle = \sqrt{n}\sqrt{n}\,|\uparrow, n\rangle = n\,|\uparrow, n\rangle\,,$$
$$\hat{a}^\dagger\hat{a}\,|\downarrow, n\rangle = \hat{a}^\dagger\sqrt{n}\,|\downarrow, n-1\rangle = \sqrt{n}\sqrt{n}\,|\downarrow, n\rangle = n\,|\downarrow, n\rangle\,.$$

$$\hat{a}\hat{a}^\dagger\,|\uparrow, n\rangle = \hat{a}\sqrt{n+1}\,|\uparrow, n+1\rangle = \sqrt{n+1}\sqrt{n+1}\,|\uparrow, n\rangle = (n+1)\,|\uparrow, n\rangle\,,$$
$$\hat{a}\hat{a}^\dagger\,|\downarrow, n\rangle = \hat{a}\sqrt{n+1}\,|\downarrow, n+1\rangle = \sqrt{n+1}\sqrt{n+1}\,|\downarrow, n\rangle = (n+1)\,|\downarrow, n\rangle\,.$$

$\hat{S}_+\hat{S}_-\,|\uparrow, n\rangle = \hat{S}_+\,|\downarrow, n\rangle = |\uparrow, n\rangle = 1\,|\uparrow, n\rangle$, eigenstate with eigenvalue 1
$\hat{S}_+\hat{S}_-\,|\downarrow, n\rangle = \hat{S}_+\,|0, n\rangle = |0, n\rangle = 0\,|\downarrow, n\rangle$, eigenstate with eigenvalue 0[1].

$\hat{S}_-\hat{S}_+\,|\uparrow, n\rangle = \hat{S}_-\,|0, n\rangle = |0, n\rangle = 0\,|\uparrow, n\rangle$, eigenstate with eigenvalue 0[2].
$\hat{S}_-\hat{S}_+\,|\downarrow, n\rangle = \hat{S}_-\,|\uparrow, n\rangle = |\downarrow, n\rangle = 1\,|\downarrow, n\rangle$, eigenstate with eigenvalue 1.

$$\hat{S}_+\hat{a}^\dagger\,|\uparrow, n\rangle = \sqrt{n+1}\,|0, n+1\rangle,$$
$$\hat{S}_+\hat{a}^\dagger\,|\downarrow, n\rangle = \sqrt{n+1}\,|\uparrow, n+1\rangle.$$

$$\hat{S}_+\hat{a}\,|\uparrow, n\rangle = \sqrt{n}\,|0, n-1\rangle,$$
$$\hat{S}_+\hat{a}\,|\downarrow, n\rangle = \sqrt{n}\,|\uparrow, n-1\rangle.$$

$$\hat{S}_-\hat{a}^\dagger\,|\uparrow, n\rangle = \sqrt{n+1}\,|\downarrow, n+1\rangle,$$
$$\hat{S}_-\hat{a}^\dagger\,|\downarrow, n\rangle = \sqrt{n+1}\,|0, n+1\rangle.$$

$$\hat{S}_-\hat{a}\,|\uparrow, n\rangle = \sqrt{n}\,|\downarrow, n-1\rangle,$$
$$\hat{S}_-\hat{a}\,|\downarrow, n\rangle = \sqrt{n}\,|0, n-1\rangle.$$

---

[1] since $0\begin{bmatrix}0\\1\end{bmatrix} = \begin{bmatrix}0\\0\end{bmatrix}$.

[2] since $0\begin{bmatrix}1\\0\end{bmatrix} = \begin{bmatrix}0\\0\end{bmatrix}$

(B)

$$\langle \hat{a}^\dagger \hat{a}\rangle_{|\uparrow,n\rangle} = \langle \uparrow, n|\hat{a}^\dagger \hat{a}|\uparrow, n\rangle = n\,\langle \uparrow, n|\uparrow, n\rangle = n,$$
$$\langle \hat{a}^\dagger \hat{a}\rangle_{|\downarrow,n\rangle} = \langle \downarrow, n|\hat{a}^\dagger \hat{a}|\downarrow, n\rangle = n\,\langle \downarrow, n|\downarrow, n\rangle = n.$$

$$\langle \hat{a}\hat{a}^\dagger\rangle_{|\uparrow,n\rangle} = \langle \uparrow, n|\hat{a}\hat{a}^\dagger|\uparrow, n\rangle = (n+1)\,\langle \uparrow, n|\uparrow, n\rangle = n+1,$$
$$\langle \hat{a}\hat{a}^\dagger\rangle_{|\downarrow,n\rangle} = \langle \downarrow, n|\hat{a}\hat{a}^\dagger|\downarrow, n\rangle = (n+1)\,\langle \downarrow, n|\downarrow, n\rangle = n+1.$$

$$\langle \hat{S}_+\hat{S}_-\rangle_{|\uparrow,n\rangle} = \langle \uparrow, n|\hat{S}_+\hat{S}_-|\uparrow, n\rangle = \langle \uparrow, n|\uparrow, n\rangle = 1,$$
$$\langle \hat{S}_+\hat{S}_-\rangle_{|\downarrow,n\rangle} = \langle \downarrow, n|\hat{S}_+\hat{S}_-|\downarrow, n\rangle = \langle \downarrow, n|0, n\rangle = 0.$$

$$\langle \hat{S}_-\hat{S}_+\rangle_{|\uparrow,n\rangle} = \langle \uparrow, n|\hat{S}_-\hat{S}_+|\uparrow, n\rangle = \langle \uparrow, n|0, n\rangle = 0,$$
$$\langle \hat{S}_-\hat{S}_+\rangle_{|\downarrow,n\rangle} = \langle \downarrow, n|\hat{S}_-\hat{S}_+|\downarrow, n\rangle = \langle \downarrow, n|\downarrow, n\rangle = 1.$$

$$\langle \hat{S}_+\hat{a}^\dagger\rangle_{|\uparrow,n\rangle} = \langle \uparrow, n|\hat{S}_+\hat{a}^\dagger|\uparrow, n\rangle = \sqrt{n+1}\,\langle \uparrow, n|0, n+1\rangle = 0,$$
$$\langle \hat{S}_+\hat{a}^\dagger\rangle_{|\downarrow,n\rangle} = \langle \downarrow, n|\hat{S}_+\hat{a}^\dagger|\downarrow, n\rangle = \sqrt{n+1}\,\langle \downarrow, n|\uparrow, n+1\rangle = 0.$$

$$\langle \hat{S}_+\hat{a}\rangle_{|\uparrow,n\rangle} = \langle \uparrow, n|\hat{S}_+\hat{a}|\uparrow, n\rangle = \sqrt{n}\,\langle \uparrow, n|0, n-1\rangle = 0,$$
$$\langle \hat{S}_+\hat{a}\rangle_{|\downarrow,n\rangle} = \langle \downarrow, n|\hat{S}_+\hat{a}|\downarrow, n\rangle = \sqrt{n}\,\langle \downarrow, n|\uparrow, n-1\rangle = 0.$$

$$\langle \hat{S}_-\hat{a}^\dagger\rangle_{|\uparrow,n\rangle} = \langle \uparrow, n|\hat{S}_-\hat{a}^\dagger|\uparrow, n\rangle = \sqrt{n+1}\,\langle \uparrow, n|\downarrow, n+1\rangle = 0,$$
$$\langle \hat{S}_-\hat{a}^\dagger\rangle_{|\downarrow,n\rangle} = \langle \downarrow, n|\hat{S}_-\hat{a}^\dagger|\downarrow, n\rangle = \sqrt{n+1}\,\langle \downarrow, n|0, n+1\rangle = 0.$$

$$\langle \hat{S}_-\hat{a}\rangle_{|\uparrow,n\rangle} = \langle \uparrow, n|\hat{S}_-\hat{a}|\uparrow, n\rangle = \sqrt{n}\,\langle \uparrow, n|\downarrow, n-1\rangle = 0,$$
$$\langle \hat{S}_-\hat{a}\rangle_{|\downarrow,n\rangle} = \langle \downarrow, n|\hat{S}_-\hat{a}|\downarrow, n\rangle = \sqrt{n}\,\langle \downarrow, n|0, n-1\rangle = 0.$$

♣ Electrons obey to anticommutation relations (Eq. 9.17). Among others, we have shown (Eq. 8.119) that

$$\{\widehat{S}_+, \widehat{S}_-\} = \widehat{S}_+\widehat{S}_- + \widehat{S}_-\widehat{S}_+ = \hat{\mathbf{I}} \Rightarrow \widehat{S}_-\widehat{S}_+ = \hat{\mathbf{I}} - \widehat{S}_+\widehat{S}_- \Rightarrow \langle \widehat{S}_-\widehat{S}_+\rangle = \langle \hat{\mathbf{I}}\rangle - \langle \widehat{S}_+\widehat{S}_-\rangle$$

If a state $|\kappa\rangle = \begin{bmatrix} a \\ b \end{bmatrix}$ is normalized, then $\langle \hat{\mathbf{I}}\rangle_{|\kappa\rangle} = \langle \kappa|\hat{\mathbf{I}}|\kappa\rangle = \langle \kappa|\kappa\rangle = \begin{bmatrix} a^* & b^* \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = |a|^2 + |b|^2 = 1.$ Hence, $\langle \widehat{S}_-\widehat{S}_+\rangle = 1 - \langle \widehat{S}_+\widehat{S}_-\rangle$, which is in agreement with the above.

♠ Photons obey to commutation relations (Eq. 9.15). Among others, we have shown that $[\hat{a}_m, \hat{a}_\ell^\dagger] = \delta_{m\ell} \Rightarrow [\hat{a}_m, \hat{a}_m^\dagger] = 1 \Rightarrow \hat{a}_m\hat{a}_m^\dagger - \hat{a}_m^\dagger\hat{a}_m = 1 \Rightarrow \hat{a}_m\hat{a}_m^\dagger = 1 + \hat{a}_m^\dagger\hat{a}_m \Rightarrow \langle \hat{a}_m\hat{a}_m^\dagger\rangle = 1 + \langle \hat{a}_m^\dagger\hat{a}_m\rangle$, which is in agreement with the above.

- **Exercise 2.** Prove the following relationships:

(I) $[\hat{N}, \hat{a}] = -\hat{a}$
(II) $[\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger$
(III) $\hat{N}(\hat{a}\,|n\rangle) = (n-1)(\hat{a}\,|n\rangle)$
(IV) $\hat{N}(\hat{a}^\dagger\,|n\rangle) = (n+1)(\hat{a}^\dagger\,|n\rangle)$

where $\hat{N} = \hat{a}^\dagger \hat{a}$ is the photon number operator, $\hat{a}^\dagger$ is the photon creation operator, and $\hat{a}$ is the photon annihilation operator.

- **Exercise 3.** Starting from Eq. 8.81, and using Eqs. 8.97, 8.98 and 8.99, prove Eq. 8.100.

- **Exercise 4.** Consider electron raising and lowering between the energy levels of a two-level system (2LS).
  (a) Define the spinors that describe the electron at each of the two levels of the 2LS as well as the vacuum, in the form of column vectors.
  (b) Define the raising and lowering operators, $\hat{S}_+$ και $\hat{S}_-$, in matrix form. Show the result of their action on the spinors.
  (c) Find $\hat{S}_+ + \hat{S}_-$ and $\hat{S}_+\hat{S}_- + \hat{S}_-\hat{S}_+$.
  (d) Show that the Hamiltonian describing the 2LS is $\hat{H}_{2\text{LS}} = E_2\hat{S}_+\hat{S}_- + E_1\hat{S}_-\hat{S}_+$ and show how the relationship $H_{2\text{LS}} = \hbar\Omega\hat{S}_+\hat{S}_-$ occurs.
  (e) Show that

  $$\{\hat{S}_+, \hat{S}_+^\dagger\} = \hat{\mathbf{I}} \quad \{\hat{S}_-, \hat{S}_-^\dagger\} = \hat{\mathbf{I}} \quad \{\hat{S}_+, \hat{S}_+\} = \hat{\mathbf{0}} \quad \{\hat{S}_-, \hat{S}_-\} = \hat{\mathbf{0}}$$

  $\hat{\mathbf{I}}$ is the identity 2×2 matrix, and $\hat{\mathbf{0}}$ is the zero 2×2 matrix.

  (f) Let us now remember the Pauli matrices $\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z$:

  $$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

  Show that

  $$[\hat{\sigma}_x, \hat{\sigma}_y] = 2i\hat{\sigma}_z.$$

  an so on, cyclically.
  (g) Also show that the Pauli matrices anticommute.
  (h) Finally, show that

  $$\left.\begin{aligned} \hat{S}_+ + \hat{S}_- &= \hat{\sigma}_x \\ \hat{S}_+ - \hat{S}_- &= i\hat{\sigma}_y \end{aligned}\right.\,.$$

- **Exercise 5.**
  (a) For the Jaynes-Cummings Hamiltonian of one EM mode, calculate $\langle\hat{\alpha}^\dagger\hat{\alpha}\rangle$, $\langle\hat{\alpha}\hat{\alpha}^\dagger\rangle$, $\langle\hat{S}_+\hat{S}_-\rangle$, $\langle\hat{S}_-\hat{S}_+\rangle$, $\langle\hat{S}_+\hat{\alpha}\rangle$, $\langle\hat{S}_+\hat{\alpha}^\dagger\rangle$, $\langle\hat{S}_-\hat{\alpha}^\dagger\rangle$, $\langle\hat{S}_-\hat{\alpha}\rangle$, for the state

  $$|\psi_\text{A}(t)\rangle = \frac{e^{i\phi}}{\sqrt{2}}|\downarrow, 2\rangle + \frac{e^{i\theta}}{\sqrt{2}}|\uparrow, 1\rangle, \tag{A.47}$$

  where ϕ and θ are arbitrary angles.
  (b) Find to which system of differential equations is then equivalent the time-dependent Schrödinger equation.

A.9 Exercises for Chapter 9: Quantum mechanical approach II.

There are no exercises in this chapter.

A.10 Exercises for Chapter 10: Density matrix and operator.

- **Exercise 1.** Prove that, if the Hamiltonian is time-independent, then Eq. 10.31 has a solution of the form
$$\hat{\rho}(t) = e^{-i\hat{H}t/\hbar}\hat{\rho}(0)e^{i\hat{H}t/\hbar}.$$

- **Exercise 2.** Starting from Eq. 10.39, prove Eq. 10.35.

  Solution of Exercise 2: From Eq. 10.39 we have
$$\begin{aligned} i\hbar\dot{\hat{\rho}}_{nm} &= [\hat{H},\hat{\rho}]_{nm} = \langle n|\hat{H}\hat{\rho}|m\rangle - \langle n|\hat{\rho}\hat{H}|m\rangle \\ &= \sum_{\ell}\langle n|\hat{H}|\ell\rangle\langle\ell|\hat{\rho}|m\rangle - \sum_{\ell}\langle n|\hat{\rho}|\ell\rangle\langle\ell|\hat{H}|m\rangle \\ &= \sum_{\ell}(H_{n\ell}\rho_{\ell m} - \rho_{n\ell}H_{\ell m}), \end{aligned}$$
  which is Eq. 10.35.

- **Άσκηση 3.** Defining the Matrix 10.47, using Eqs. 10.51 and 10.52, and assuming that $U_{\mathscr{E}21}(t) = U_{\mathscr{E}12}(t)$, prove that the time evolution of the density matrix with decay mechanisms is given by Eq. 10.53.

A.11 Exercises for Chapter 11: Laser.

- **Exercise 1.** Create graphical representations of ν_1, ν_2, ϱ versus τ, changing $\tau_1 = 0.25$ or 0.5 or 0.75 or 1.0 or 1.5 and keeping $r_N = 1.5$, $A'/A = 10^{-9}$, $\tau_0 = 10$ constant, and explain them using Eqs. 11.73, 11.74, 11.75.

- **Exercise 2.** Consider the dimensionless form of the laser rate equations
$$\frac{d\nu_1}{d\tau} = \nu_2 + \varrho(\nu_2 - \nu_1) - \frac{\nu_1}{\tau_1}$$
$$\frac{d\nu_2}{d\tau} = r_N + \varrho(\nu_1 - \nu_2) - \nu_2$$
$$\frac{d\varrho}{d\tau} = -\frac{\varrho}{\tau_0} + \left\{\frac{A'}{A}\nu_2 + \varrho(\nu_2 - \nu_1)\right\}\frac{1}{\tau_0(1-\tau_1)}.$$
  Prove that when $\frac{A'}{A} << 1$, then in the steady state, the following equations hold:
$$\nu_1 = \tau_1 r_N, \quad \forall\ r_N$$
$$\nu_2 = \begin{cases} r_N, & \forall\ r_N < 1 \\ \tau_1 r_N + (1-\tau_1), & \forall\ r_N > 1 \end{cases}$$
$$\varrho = \begin{cases} 0, & \forall\ r_N < 1 \\ r_N - 1, & \forall\ r_N > 1 \end{cases}$$

- **Exercise 3.** The panels of Figure A.1 represent the solution of Eqs. 11.73, 11.74, 11.75, for changing $\tau_0 = 10$ or 5.0 or 1.0, and keeping $\tau_1 = 0.5$, $r_N = 1.5$, $A'/A = 10^{-9}$ constant.
  (a') What is the ratio of the lifetimes between levels 1 and 2?
  (b') Why is there a difference in the time it takes for ϱ to become perceivable?

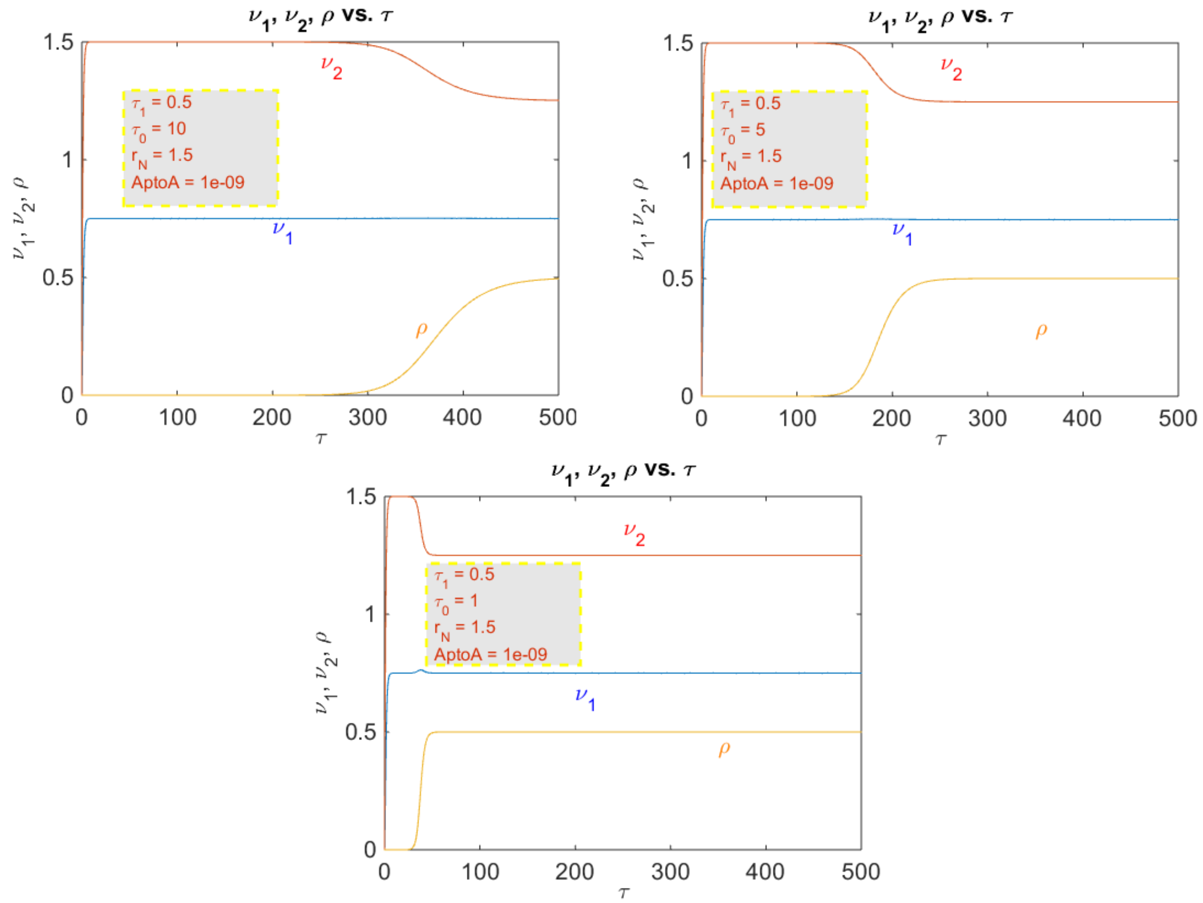

Figure A.1: The solution of Eqs. 11.73, 11.74, 11.75, for $\tau_0 = 10$ or 5.0 or 1.0, and $\tau_1 = 0.5$, $r_N = 1.5$, $A'/A = 10^{-9}$ constant. Note that the notation ρ in the panel is in fact the dimensionless ϱ of Eq. 11.75.

- **Exercise 4.** Create graphical representations of ν_1, ν_2, ϱ versus τ, changing $A'/A = 10^{-9}$ or 10^{-4} or 10^{-1} and keeping $\tau_1 = 0.5, \tau_0 = 10, r_N = 1.5$ constant, and explain them using Eqs. 11.73, 11.74, 11.75.

- **Exercise 5.** Think of the LASER rate differential equations in the dimensionless form

$$\frac{d\nu_1}{d\tau} = \nu_2 + \varrho(\nu_2 - \nu_1) - \frac{\nu_1}{\tau_1}, \tag{A.48}$$

$$\frac{d\nu_2}{d\tau} = r_N + \varrho(\nu_1 - \nu_2) - \nu_2, \tag{A.49}$$

$$\frac{d\varrho}{d\tau} = -\frac{\varrho}{\tau_0} + \left\{\frac{A'}{A}\nu_2 + \varrho(\nu_2 - \nu_1)\right\}\frac{1}{\tau_0(1-\tau_1)}. \tag{A.50}$$

At the steady state, ignoring $\frac{A'}{A} \ll 1$, the following equations hold

$$\nu_1 = \tau_1 r_N, \quad \forall\ r_N \tag{A.51}$$

$$\nu_2 = \begin{cases} r_N, & \forall\ r_N \le 1 \\ \tau_1 r_N + (1-\tau_1), & \forall\ r_N \ge 1 \end{cases} \tag{A.52}$$

$$\varrho = \begin{cases} 0, & \forall\ r_N \le 1 \\ r_N - 1, & \forall\ r_N \ge 1 \end{cases} \tag{A.53}$$

The numerical solution of Eqs. (A.48), (A.49), (A.50) is shown in Figure A.2, where we modify only one of the parameters r_N, τ_1, τ_0, $\frac{A'}{A}$.

(**a**) What is the fraction of the levels' lifetime, $\frac{t_1}{t_2}$;

(**b**) Which parameter is modified and what is the value of the modified parameter at each subfigure?

(**c**) Why is there a difference in the time required to appreciate (i.e. clearly see) the modification of ϱ in the lower subfigures?

(**d**) Why before ϱ becomes appreciatable, i.e. clearly seen, in all subfigures it holds $\frac{\nu_2}{\nu_1} = 2$?

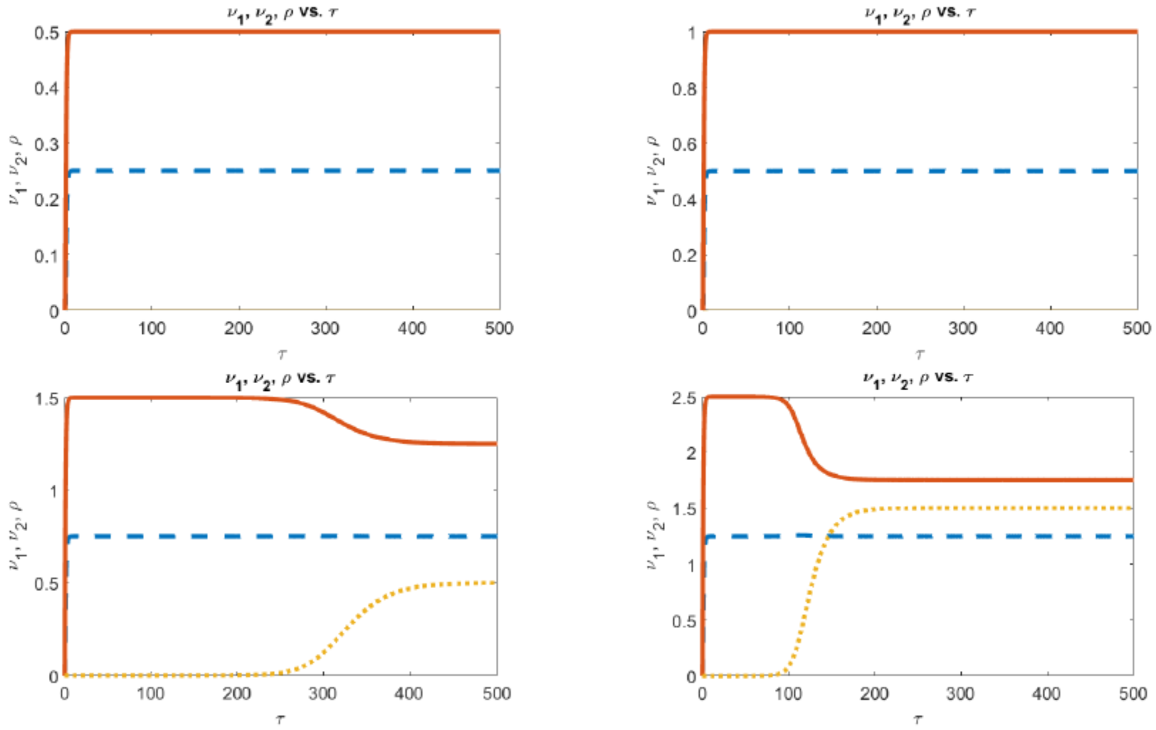

Figure A.2: We modify only one parameter and observe the time evolution of Eqs. (A.48), (A.49), (A.50).

A.12 Exercises for Chapter 12: Various.

There are no exercises in this chapter.

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APPENDIX B

AUXILIARY MATHEMATICS AND CALCULATION DETAILS

B.1 Arithmetic Progression.

We recall the definition of the geometric progression (a_n) and some relevant relationships.

$$\begin{array}{ll} a_{n+1} - a_n = \varpi, \quad n = (0), 1, 2, 3, \ldots & \varpi: \quad \text{difference} \\ a_n = a_1 + (n-1)\varpi & \text{recursive formula} \\ \beta = \dfrac{\alpha + \gamma}{2} & \beta: \quad \text{arithmetic mean} \\ S_n = \dfrac{n}{2}(a_1 + a_n) & \text{sum of the first } n \text{ terms} \end{array} \tag{B.1}$$

B.2 Geometric Progression.

We recall the definition of the geometric progression (a_n) and some relevant relationships.

$$\begin{array}{ll} \dfrac{a_{n+1}}{a_n} = \gimel \neq 0, \quad n = (0), 1, 2, 3, \ldots & \gimel: \quad \text{ratio} \\ a_n = a_1 \gimel^{n-1} & \text{recursive formula} \\ \dfrac{\alpha}{\beta} = \dfrac{\beta}{\gamma} \Leftrightarrow \beta^2 = \alpha\gamma & \beta: \quad \text{geometric mean} \\ S_n = \begin{cases} a_1 \dfrac{\gimel^n - 1}{\gimel - 1}, & \gimel \neq 1 \\ a_1 n, & \gimel = 1 \end{cases} & \text{sum of the first } n \text{ terms} \\ S_\infty = \dfrac{a_1}{1 - \gimel} & \text{sum of infinite terms } (|\gimel| < 1) \end{array} \tag{B.2}$$

B.3 A representation of the delta function.

We will show that the function $\delta_a(x) = \dfrac{1}{\pi|a|}\dfrac{\sin^2(ax)}{x^2}$, where $a \neq 0$, is an approximation to $\delta(x)$. For example:

$$\star \quad \lim_{x\to 0}\delta_a(x) = \lim_{x\to 0}\frac{1}{\pi|a|}\frac{\sin^2(ax)}{a^2x^2}a^2 = \frac{|a|}{\pi}\lim_{x\to 0}\frac{\sin^2(ax)}{a^2x^2} = \frac{|a|}{\pi}\left(\lim_{x\to 0}\frac{\sin ax}{ax}\right)^2$$

$$= \frac{|a|}{\pi}\left(\lim_{ax\to 0}\frac{\sin ax}{ax}\right)^2 = \frac{|a|}{\pi}1^2 = \frac{|a|}{\pi} \Rightarrow$$

$$\boxed{\lim_{x\to 0}\delta_a(x) = \frac{|a|}{\pi}} \Rightarrow \boxed{\lim_{a\to\infty}\left(\lim_{x\to 0}\delta_a(x)\right) = \infty}$$

$$\star \quad \int_{-\infty}^{+\infty}\delta_a(x)dx = \int_{-\infty}^{+\infty}\frac{1}{\pi|a|}\frac{\sin^2 ax}{x^2}dx = \frac{1}{\pi|a|}\pi|a| = 1 \Rightarrow$$

$$\boxed{\int_{-\infty}^{+\infty}\delta_a(x)dx = 1}$$

We just used the definite integral [1]

$$\int_0^{\infty}\frac{\sin^2 ax}{x^2}dx = \frac{\pi}{2}|a|,$$

for $a \neq 0$. In other words, in the limit $a \to \infty$, the function $\delta_a(x)$ represents $\delta(x)$, i.e.

$$\boxed{\lim_{a\to\infty}\delta_a(x) = \delta(x)}.$$

In Figure B.1, $\delta_a(x)$ is depicted for $a = 3, 6$.

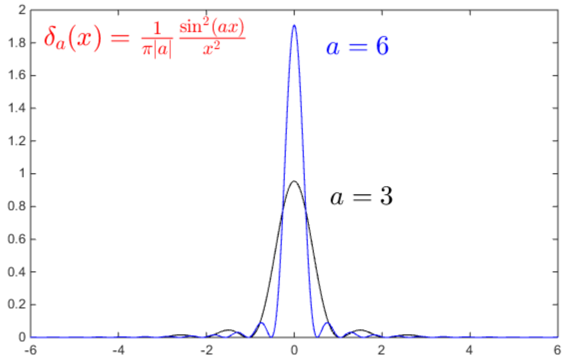


Figure B.1: $\delta_a(x)$ for $a = 3, 6$.

Therefore, in a completely approximate manner, we could write

$$\boxed{\delta(x) \sim \frac{1}{\pi|a|}\frac{\sin^2(ax)}{x^2}}. \tag{B.3}$$

Let us play a little bit more with the function

$$f(x) \equiv \frac{\sin^2 x}{x^2}. \tag{B.4}$$

$$\lim_{x\to 0}\frac{\sin^2 x}{x^2}=\left(\lim_{x\to 0}\frac{\sin x}{x}\right)^2=\left(\lim_{x\to 0}\frac{\cos x}{1}\right)^2=1, \tag{B.5}$$

i.e., for $x = 0$, there is a global maximum with value 1.

$$\left.\begin{aligned} f(x)=0\\ x\neq 0\end{aligned}\right\}\Rightarrow \sin x=0\Rightarrow \text{for } x=n\pi, n\in\mathbb{Z}^*, \text{ there are global minima with value } 0. \tag{B.6}$$

Let us search for local maxima end minima:

$$f'(x)=\frac{2\sin x\cos x\, x^2-\sin^2 x\, 2x}{x^4}\Rightarrow f'(x)=0\Rightarrow 2\ x\ \ \sin x(x\cos x-\sin x)=0\Rightarrow$$

$$\underbrace{x=0}_{\text{global maximum}}\quad \text{or}\quad \underbrace{\sin x=0}_{\substack{x=n\pi,\, n\in\mathbb{Z}^*\\ \text{global minima}}}\quad\text{or}\quad \underbrace{x=\tan x}_{\substack{x\simeq\pm 4.49,\pm 7.72,\ldots\\ \text{inspection leads to local maxima}}}$$

A graphical representation of $f(x)$ is presented in Figure B.2.

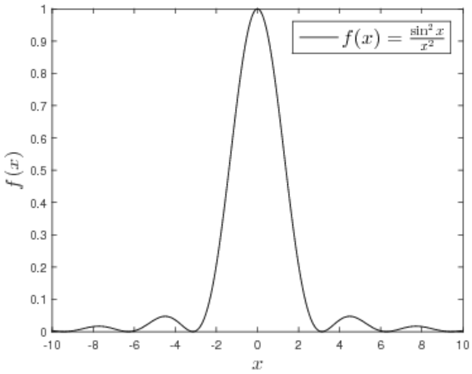


Figure B.2: $f(x) = \frac{\sin^2 x}{x^2}$.

B.4 Some trigonometric relations.

We will show the relation marked by ★ in Section 5.5, i.e.

$$e^{ix}-1=2i\sin\left(\frac{x}{2}\right)e^{i\frac{x}{2}}.$$

$$\begin{aligned}
&\cos x+i\sin x-1=2i\sin\left(\frac{x}{2}\right)\cos\left(\frac{x}{2}\right)+2i\sin\left(\frac{x}{2}\right)i\sin\left(\frac{x}{2}\right)\Leftrightarrow\\
&\cos x+\cancel{i\sin x}-1=\cancel{i\sin x}-2\sin^2\left(\frac{x}{2}\right)\Leftrightarrow\\
&\cos x-\cos^2\left(\frac{x}{2}\right)-\sin^2\left(\frac{x}{2}\right)=-2\sin^2\left(\frac{x}{2}\right)\Leftrightarrow\\
&\cos x-\cos^2\left(\frac{x}{2}\right)=-\sin^2\left(\frac{x}{2}\right)\Leftrightarrow\\
&\cos x=\cos^2\left(\frac{x}{2}\right)-\sin^2\left(\frac{x}{2}\right),
\end{aligned}$$

which holds, since

$$\cos\big(a \pm \beta\big) = \cos a \cos \beta \mp \sin a \sin \beta.$$

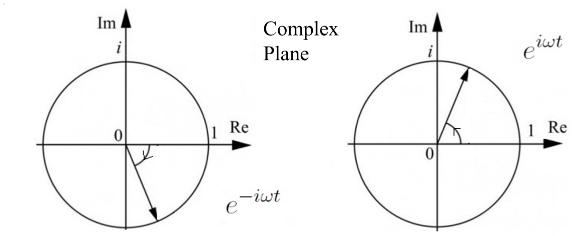
Accordingly, we also mention the relation

$$\sin\big(a \pm \beta\big) = \sin a \cos \beta \pm \sin \beta \cos a.$$

B.5 Rotating waves.

Consider an electric field of the form $\vec{\mathscr{E}}(t) = \mathscr{E}_0 \, \hat{z} \, \cos \omega t$. It is sometimes convenient to decompose it into its positively and negatively rotating components, $\vec{\mathscr{E}}(t)^{(+)}$ and $\vec{\mathscr{E}}(t)^{(-)}$, respectively. That is,

$$\vec{\mathscr{E}}(t) = \frac{\mathscr{E}_0}{2} \hat{z}\Big(e^{-i\omega t} + e^{i\omega t}\Big) = \frac{\mathscr{E}_0}{2} \hat{z} \, e^{-i\omega t} + \frac{\mathscr{E}_0}{2} \hat{z} \, e^{i\omega t} := \vec{\mathscr{E}}(t)^{(+)} + \vec{\mathscr{E}}(t)^{(-)}$$



“positive direction” (clockwise) “negative direction”

Figure B.3: Rotating Waves.

B.6 Matrix elements of operators.

$$\langle \psi | \hat{M} | \phi \rangle = \int dx'' \int dx' \langle \psi | x'' \rangle \langle x'' | \hat{M} | x' \rangle \langle x' | \phi \rangle = \int dx'' \int dx' \psi^*(x'') \langle x'' | \hat{M} | x' \rangle \, \phi(x')$$

$$\left.\begin{array}{l} \langle x'' | \hat{x} | x' \rangle = \langle x'' | x' | x' \rangle = x' \langle x'' | x' \rangle = x' \delta(x'' - x') = x'' \delta(x'' - x') \\ \langle x'' | \hat{p} | x' \rangle \quad \underbrace{=}_{\text{it is shown below} \blacktriangledown} \quad -i\hbar \dfrac{\partial}{\partial x''} \delta(x'' - x') \end{array}\right\} \Rightarrow$$

$\Rightarrow$ expanding in powers of $\hat{x}$ and $\hat{p}$

$$\langle x'' | \hat{M}(\hat{x}, \hat{p}) | x' \rangle = M\Big(x'', -i\hbar \frac{\partial}{\partial x''}\Big) \delta(x'' - x') \qquad \text{1D}$$

$$\langle \vec{r}'' | \hat{M}(\hat{\vec{r}}, \hat{\vec{p}}) | \vec{r}' \rangle = M(\vec{r}'', -i\hbar \vec{\nabla}'') \delta(\vec{r}'' - \vec{r}') \qquad \text{3D}$$

thus, e.g.,

$$\begin{aligned} \langle \Phi_\ell | \hat{M} | \Phi_k \rangle &= \int d^3 r' \int d^3 r \langle \Phi_\ell | \vec{r}' \rangle \langle \vec{r}' | \hat{M} | \vec{r} \rangle \langle \vec{r} | \Phi_k \rangle \\ &= \int d^3 r' \int d^3 r \, \Phi_\ell^*(\vec{r}') \hat{M}(\vec{r}, -i\hbar \vec{\nabla}) \delta(\vec{r}' - \vec{r}) \Phi_k(\vec{r}) \end{aligned}$$

$$= \int d^3r \Phi^*_\ell(\vec{r})\hat{M}(\vec{r}, -i\hbar\vec{\nabla})\Phi_k(\vec{r})$$

which is Eq. 5.29.

$$\begin{aligned}
[\hat{x}, \hat{p}] = i\hbar \Leftrightarrow \hat{x}\hat{p} - \hat{p}\hat{x} &= i\hbar \Rightarrow \\
\langle x''|\, \hat{x}\hat{p}\, |x'\rangle - \langle x''|\, \hat{p}\hat{x}\, |x'\rangle &= i\hbar\langle x''|x'\rangle \Rightarrow \\
\langle x''|\, x''\hat{p}\, |x'\rangle - \langle x''|\, \hat{p}x'\, |x'\rangle &= i\hbar\delta(x'' - x') \Rightarrow \\
(x'' - x')\, \langle x''|\, \hat{p}\, |x'\rangle &= i\hbar\delta(x'' - x') \Rightarrow \\
\underbrace{\delta(x'' - x')}_{\text{it is shown below ▾}} &= -(x'' - x')\frac{\partial}{\partial x''}\delta(x'' - x') \Rightarrow \\
\cancel{(x'' - x')}\, \langle x''|\, \hat{p}\, |x'\rangle &= -i\hbar\cancel{(x'' - x')}\frac{\partial}{\partial x''}\delta(x'' - x') \Rightarrow \\
\langle x''|\, \hat{p}\, |x'\rangle &= -i\hbar\frac{\partial}{\partial x''}\delta(x'' - x')
\end{aligned}$$

Similarly, for Eq. 10.2, we have

$$\begin{aligned}
\langle \hat{A} \rangle = \langle \Psi(t)|\, \hat{A}\, |\Psi(t)\rangle &= \int d^3r' \int d^3r \langle \Psi(t)|\vec{r}\rangle\langle\vec{r}|\hat{A}|\vec{r}'\rangle\langle\vec{r}'|\Psi(t)\rangle \\
&= \int d^3r' \int d^3r\, \Psi^*(\vec{r}, t)\hat{A}(\vec{r}, -i\hbar\vec{\nabla})\delta(\vec{r} - \vec{r}')\Psi(\vec{r}', t) \\
&= \int d^3r \Psi^*(\vec{r}, t)\hat{A}(\vec{r}, -i\hbar\vec{\nabla})\Psi(\vec{r}, t) \\
&= \int d^3r \sum_{k'} c^*_{k'}(t)\Phi^*_{k'}(\vec{r})\hat{A}(\vec{r}, -i\hbar\vec{\nabla}) \sum_k c_k(t)\Phi_k(\vec{r}) \\
&= \sum_{k'} c^*_{k'}(t) \sum_k c_k(t) \int d^3r \Phi^*_{k'}(\vec{r})\hat{A}(\vec{r}, -i\hbar\vec{\nabla})\Phi_k(\vec{r}) \\
&= \sum_{k,k'} c_k(t)c^*_{k'}(t)A_{k'k}
\end{aligned}$$

where we have used Eq. 10.1.

Similarly, for Eq. 10.7, we have

$$\begin{aligned}
\langle \hat{A} \rangle_i = \langle \Psi_i(t)|\hat{A}|\Psi_i(t)\rangle &= \int d^3r \int d^3r' \langle \Psi_i(t)|\vec{r}\rangle\langle\vec{r}|\hat{A}|\vec{r}'\rangle\langle\vec{r}'|\Psi_i(t)\rangle \\
&= \int d^3r \int d^3r' \langle \Psi_i(t)|\vec{r}\rangle\hat{A}(\vec{r}, -i\hbar\vec{\nabla})\delta(\vec{r} - \vec{r}')\langle\vec{r}'|\Psi_i(t)\rangle \\
&= \int d^3r \langle \Psi_i(t)|\vec{r}\rangle\hat{A}(\vec{r}, -i\hbar\vec{\nabla})\langle\vec{r}|\Psi_i(t)\rangle \\
&= \int d^3r \Psi^*_i(\vec{r}, t)\hat{A}(\vec{r}, -i\hbar\vec{\nabla})\Psi_i(\vec{r}, t))\rangle
\end{aligned}$$

or, simpler,

$$= \int d^3r \Psi^*_i(\vec{r}, t)\hat{A}\Psi_i(\vec{r}, t).$$

▾ Let us prove the relation we mentioned above. We will first show that

$$\boxed{x\delta'(x) = -\delta(x)} \tag{B.7}$$

To this end, we will integrate both hand-sides after we multiply them by a function $f(x)$.

Left hand-side:

$$\int_{-\infty}^{+\infty} x\delta'(x)f(x)dx = \Big[x\delta(x)f(x)\Big]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \delta(x)\Big(f(x) - xf'(x)\Big)dx =$$

$$-\int_{-\infty}^{+\infty} \delta(x)f(x)dx + \int_{-\infty}^{+\infty} \delta(x)xf'(x)dx = -f(0) + 0\cdot f'(0) = -f(0)$$

Right hand-side:

$$-\int_{-\infty}^{+\infty} \delta(x)f(x)dx = -f(0)$$

Combining the two sides, the desired property B.7 occurs. Hence,

$$x\delta'(x) = -\delta(x) \quad \text{ή} \quad x\frac{\partial}{\partial x}\delta(x) = -\delta(x) \quad \text{ή} \quad x''\frac{\partial}{\partial x''}\delta(x'') = -\delta(x'')$$

$$(x'' - x')\frac{\partial}{\partial x''}\delta(x'' - x') = -\delta(x'' - x')$$

B.7 Solution of differential equations with the eigenvalue method.

In Chapters 5 and 8 we arrive at some systems of differential equations. For example, the System of Differential Equations 8.189 can be written as (if we omit, for simplicity, the index m that denotes the EM mode)

$$\begin{pmatrix}\dot{c}_1\\ \dot{c}_2\end{pmatrix} = (-i)\begin{pmatrix} n\omega & g\sqrt{n}\\ g\sqrt{n} & \Omega + (n-1)\omega\end{pmatrix}\begin{pmatrix}c_1\\ c_2\end{pmatrix} \tag{B.8}$$

i.e. it is of the form

$$\dot{\vec{x}}(t) = \overleftrightarrow{A}\vec{x}(t) \tag{B.9}$$

with

$$\dot{\vec{x}}(t) = \begin{pmatrix}\dot{c}_1(t)\\ \dot{c}_2(t)\end{pmatrix}, \quad \vec{x}(t) = \begin{pmatrix}c_1(t)\\ c_2(t)\end{pmatrix}, \quad \overleftrightarrow{A} = (-i)\begin{pmatrix} n\omega & g\sqrt{n}\\ g\sqrt{n} & \Omega + (n-1)\omega\end{pmatrix} \tag{B.10}$$

Similarly, the System of Differential Equations 8.207 can be written as (if we omit, for simplicity, the index m that denotes the EM mode)

$$\begin{pmatrix}\dot{c}_1\\ \dot{c}_2\end{pmatrix} = (-i)\begin{pmatrix} (n+1)\omega & g\sqrt{n+1}\\ g\sqrt{n+1} & \Omega + n\omega\end{pmatrix}\begin{pmatrix}c_1\\ c_2\end{pmatrix} \tag{B.11}$$

i.e. it is of the form

$$\dot{\vec{x}}(t) = \overleftrightarrow{A}\vec{x}(t) \tag{B.12}$$

with

$$\dot{\vec{x}}(t) = \begin{pmatrix}\dot{c}_1(t)\\ \dot{c}_2(t)\end{pmatrix}, \quad \vec{x}(t) = \begin{pmatrix}c_1(t)\\ c_2(t)\end{pmatrix}, \quad \overleftrightarrow{A} = (-i)\begin{pmatrix} (n+1)\omega & g\sqrt{n+1}\\ g\sqrt{n+1} & \Omega + n\omega\end{pmatrix} \tag{B.13}$$

Therefore, these problems can be solved using the eigenvalue method, as it was done in Chapter 5.

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APPENDIX C

MATLAB PROGRAMS

C.1 fornu0ofT.m

Code C.1: The matlab code that produces Fig. 2.14, fornu0ofT.m.

```
tic
xl=-5;
xr=+5;
step=(xr-xl)/100;
for i=1:101
x(i)=xl+step*(i-1);
f(i)=3*(exp(x(i))-1) - x(i)*exp(x(i));
end
createfigurefornu0ofT(x,f);
toc
```

Code C.2: The function createfigurefornu0ofT.m called by Code C.1.

```
function createfigurefornu0ofT(X1, Y1)
%CREATEFIGURE2(X1, Y1)
%  X1:  vector of x data
%  Y1:  vector of y data

% Create figure
figure1 = figure;

% Create axes
axes1 = axes('Parent',figure1,'YGrid','on','XGrid','on');
```

```
%% Uncomment the following line to preserve the Y-limits of the
   axes
% ylim(axes1,[-5 5]);
box(axes1,'on');
hold(axes1,'on');

% Create plot
plot(X1,Y1,'DisplayName','f(x)')
axis([-5,5,-5,5])
title('$$f(x)=3(e^x-1)-xe^x$$','interpreter','latex')
xlabel('$$x$$','interpreter','latex')
ylabel('$$f(x)$$','interpreter','latex')

% Create legend
legend1 = legend(axes1,'show');
set(legend1,'FontSize',9);
```

C.2 forlambda0ofT.m

Code C.3: The matlab code that produces Fig. 2.15, forlambda0ofT.m.

```
tic
xl=-10;
xr=+10;
step=(xr-xl)/100;
for i=1:101
x(i)=xl+step*(i-1);
f(i)=5*(exp(x(i))-1) - x(i)*exp(x(i));
end
createfigureforlambda0ofT(x,f);
toc
```

Code C.4: The function createfigureforlambda0ofT.m called by Code C.3.

```
function createfigurefornu0ofT(X1, Y1)
%CREATEFIGURE2(X1, Y1)
%  X1:  vector of x data
%  Y1:  vector of y data

% Create figure
figure1 = figure;

% Create axes
axes1 = axes('Parent',figure1,'YGrid','on','XGrid','on');
%% Uncomment the following line to preserve the Y-limits of the
   axes
% ylim(axes1,[-5 5]);
```

```
box(axes1,'on');
hold(axes1,'on');

% Create plot
plot(X1,Y1,'DisplayName','f(\psi)')
axis([-10,10,-10,50])
title('$$f(\psi)=5(e^\psi-1)-\psi e^\psi$$', 'interpreter','latex')
xlabel('$$\psi$$','interpreter','latex')
ylabel('$$f(\psi)$$','interpreter','latex')


% Create legend
legend1 = legend(axes1,'show');
set(legend1,'FontSize',9);
```

C.3 WienDisplacementANDPlanckofLambda.m

Code C.5: The matlab code that produces Fig. 2.16, WienDisplacementANDPlanckofLambda.m.

```
clear all
clc
tic
xl=0;     % nm
xr=8000; % nm
T = 1595 % K black body temperature
nop=2001;
step=(xr-xl)/(nop-1); % nm
for i=1:nop;
x(i)=xl+step*(i-1);    % nm
x(i)=x(i)*1e-9;
c1 = 499.24825e-26; %8\pi hc = 499.24825322511997970335670474955 x 10^{-26} J m
c2 = 14.38777e-3;    %hc/k_B = 14.387769599838156234952726573188 x 10^{-3} m K
rho(i) = c1/(x(i)^5);
rho(i)=rho(i)/(exp(c2/(x(i)*T))-1);
x(i)=x(i)*1e9;
end
%plot(x,rho); figure(gcf);

lambda0= 2897772/T % nm (Wien Displacement Law)
createfigureforPlanckLambdaofT(x,rho,T,lambda0);
toc
```

Code C.6: The function createfigureforPlanckLambdaofT.m called by Code C.5.

```
function createfigureforPlanckLambdaofT(X1, Y1, T, lambda0)
%CREATEFIGURE2(X1, Y1)
%  X1:  vector of x data
%  Y1:  vector of y data


% Create figure
figure1 = figure;

% Create axes
axes1 = axes('Parent',figure1,'YGrid','on','XGrid','on');
%% Uncomment to preserve the Y-limits of the axes
% ylim(axes1,[-5 5]);
box(axes1,'on');
hold(axes1,'on');

% Create plot
plot(X1,Y1,'DisplayName','\rho(\lambda,T)');
axis([0,8000,0,2000])
%title('Planck`s Law in terms of Wavelength and Temperature')
title(['\rho(\lambda,T)   for T = ', num2str(T),' K','   \lambda_0=',num2str(lambda0),' nm'])
xlabel('\lambda(nm)')
ylabel('\rho(J/m^4)')

% Create legend
legend1 = legend(axes1,'show');
set(legend1,'FontSize',9);
```

C.4 WienDisplacementANDPlanckofLambdaMultipleT.m

Code C.7: The matlab code that produces Fig. 2.17, WienDisplacementANDPlanckofLambdaMultipleT.m.

```
clear all
clc
tic
xl=0;    % nm
xr=5000; % nm
nop=2001;
step=(xr-xl)/(nop-1); % nm
for j=1:5
T(j)=3000+j*500 % K black body temperature
lambda0(j)= 2897772/T(j) % nm (Wien Displacement Law)
for i=1:nop;
x(i)=xl+step*(i-1);   % nm
```

```
x(i)=x(i)*1e-9;
c1 = 499.24825e-26; %8\pi hc = 499.24825322511997970335670474955 x 10^{-26} J m
c2 = 14.38777e-3;   %hc/k_B = 14.387769599838156234952726573188 x 10^{-3} m K
rho(i,j) = c1/(x(i)^5);
rho(i,j)=rho(i,j)/(exp(c2/(x(i)*T(j)))-1);
x(i)=x(i)*1e9;
end
end

colorspec = {[1 0 0]; [1 0.5 0]; [0 1 0]; [0 0 1]; [0.4 0 1]};
figure(1);
title({'\rho(\lambda,T)',[' \lambda_0=',num2str(lambda0,4),' nm']})
xlabel('\lambda(nm)')
ylabel('\rho(J/m^4)')
hold on
for i = 1:5
plot(x,rho(:, i), 'Color', colorspec{i})
end
%legend(num2str(T(:)))
legend([num2str(T(1)),' K'], [num2str(T(2)),' K'], [num2str(T(3)), ' K'], [num2str(T(4)),' K'], [num2str(T(5)),' K'])
hold off

toc
```

C.5 Oscillations.m

Code C.8: The matlab code Oscillations.m that produces Fig. 5.8, which discribes oscillations of a 2LS both in-resonance ($\Delta = 0$) and out-of-resonance ($\Delta \neq 0$).

```
clear all
clc
tic
OmegaR=1
Delta=3*OmegaR
lambda = (sqrt(OmegaR^2+Delta^2))/2
TRonR =(2*pi)/(OmegaR)
TRoffR=(2*pi)/sqrt(OmegaR^2+Delta^2)
pi/lambda-TRoffR
nop=501;
tl= 0;
tr= TRonR;
step=(tr-tl)/(nop-1); % nm
```

```
for i=1:nop;
t(i)=tl+step*(i-1);
P1onR(i)=cos((OmegaR/2)*t(i))^2;
P2onR(i)=sin((OmegaR/2)*t(i))^2;
P1offR(i)= 1 + (OmegaR^2*(cos(2*lambda*t(i))-1))/(2*(OmegaR^2+
   Delta^2));
P2offR(i)=(OmegaR^2)/(OmegaR^2+Delta^2)*sin(lambda*t(i))^2;
end
%plot(x,c,'k',x,y1,'b',x,y2,'r'); figure(gcf);
plot(t,P1onR,'k',t,P2onR,'b','LineWidth',2,'LineStyle','-'); hold
    on;
%legend('P_1(t)','P2(t)')
plot(t,P1offR,'r',t,P2offR,'g','LineWidth',2,'LineStyle','--')
h = legend('$P_1(t)$ on Resonance','$P_2(t)$ on Resonance','$P_1(
   t)$ off Resonance','$P_2(t)$ off Resonance');
set(h,'Interpreter','latex','FontSize',10)
title({'Oscillations in a two-level system';'(On Resonance and
   Off Resonance)'})
xlabel('$t$(s)','Interpreter','latex','FontSize',16)
ylabel('probabilities','FontSize',16)
annotation('textbox',...
[0.7 0.45 0.17 0.15],...
'String',{'plotting with',['\Omega_R = ' num2str(OmegaR),' s^{-1}
   '],['\Delta = ' num2str(Delta),' s^{-1}']]},...
'FontSize',10,...
'FontName','Arial',...
'LineStyle','--',...
'EdgeColor',[1 1 0],...
'LineWidth',2,...
'BackgroundColor',[0.9 0.9 0.9],...
'Color',[0.84 0.16 0]);

hold off;
toc
```

C.6 N1N2DNrho.m

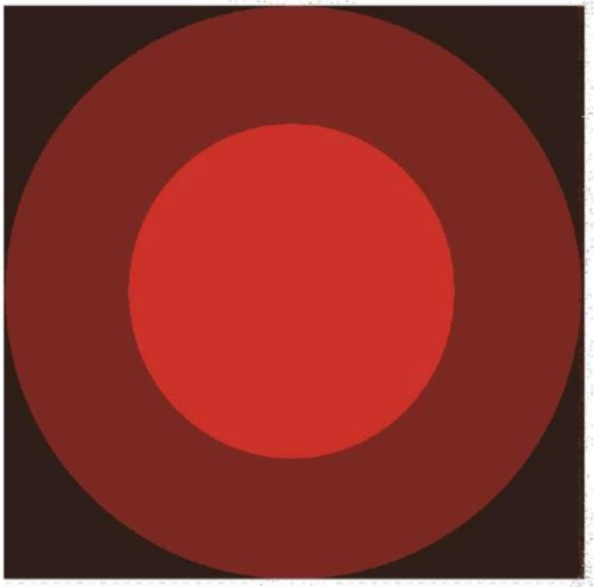
Code C.9: The matlab code N1N2DNrho.m creates a representation of Eqs. 11.47, 11.48, 11.49, 11.51, which describe the level populations, the EM radiation density, and the population inversion in the stationary state.

```
clear all
clc
tic
OmegaR=1
Delta=3*OmegaR
```

```
lambda = (sqrt(OmegaR^2+Delta^2))/2
TRonR =(2*pi)/(OmegaR)
TRoffR=(2*pi)/sqrt(OmegaR^2+Delta^2)
pi/lambda-TRoffR
nop=501;
tl= 0;
tr= TRonR;
step=(tr-tl)/(nop-1); % nm
for i=1:nop;
t(i)=tl+step*(i-1);
P1onR(i)=cos((OmegaR/2)*t(i))^2;
P2onR(i)=sin((OmegaR/2)*t(i))^2;
P1offR(i)= 1 + (OmegaR^2*(cos(2*lambda*t(i))-1))/(2*(OmegaR^2+Delta^2));
P2offR(i)=(OmegaR^2)/(OmegaR^2+Delta^2)*sin(lambda*t(i))^2;
end
%plot(x,c,'k',x,y1,'b',x,y2,'r'); figure(gcf);
plot(t,P1onR,'k',t,P2onR,'b','LineWidth',2,'LineStyle','-'); hold on;
%legend('P_1(t)','P2(t)')
plot(t,P1offR,'r',t,P2offR,'g','LineWidth',2,'LineStyle','--')
h = legend('$P_1(t)$ on Resonance','$P_2(t)$ on Resonance','$P_1(t)$ off Resonance','$P_2(t)$ off Resonance');
set(h,'Interpreter','latex','FontSize',10)
title({'Oscillations in a two-level system';'(On Resonance and Off Resonance)'})
xlabel('$t$(s)','Interpreter','latex','FontSize',16)
ylabel('probabilities','FontSize',16)
annotation('textbox',...
[0.7 0.45 0.17 0.15],...
'String',{'plotting with',['\Omega_R = ' num2str(OmegaR),' s^{-1}'],['\Delta = ' num2str(Delta),' s^{-1}']},...
'FontSize',10,...
'FontName','Arial',...
'LineStyle','--',...
'EdgeColor',[1 1 0],...
'LineWidth',2,...
'BackgroundColor',[0.9 0.9 0.9],...
'Color',[0.84 0.16 0]);

hold off;
toc
```

The book is an introduction and overview, at the undergraduate level, to quantum optics. We analyze the quantum nature of light. We focus on the interaction processes between a photon and a two-level system. We explain what is continuous and what is discrete energy spectrum, as well as intermediate cases such as low-dimensional structures. The interaction of electromagnetic field with matter is tackled, in the first stage, semi-classically, where the electromagnetic field is treated classically and the matter quantum-mechanically. We explain in detail to which extent optical transitions between energy levels are allowed. Then, the interaction between electromagnetic field and matter is treated quantum-mechanically, i.e., the electromagnetic field consists of photons. We explain ladder operators and the differences between bosons and fermions, commutation and anticommutation. Then, we introduce the concept of density matrix and density operator. We explain the operating principles of LASERs. Finally, we develop several related topics. The book contains exercises, auxiliary mathematics and illustrative matlab programs.



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