

2 Light-matter interaction

2.1 Introduction

In this section: What this part of the course is about.

Understanding how light interacts with atoms and molecules, or more generally how electromagnetic fields interact with matter, is of fundamental importance in Physics. A short lecture course such as this one can only offer a brief survey of a small part of this extremely vast topic. The main issue we will focus on is how to describe the interaction of light with matter quantum mechanically. We will look at how an incident beam of light can induce transitions in atoms, molecules, solids, etc., how one can make sense of the fact that some of these transitions occur readily and others not, and how one can calculate the lifetime of excited states decaying by emitting photons. We will address these issues with the help of time-dependent perturbation theory, and in fact the whole of this part of the course can be taken as an example of the use of this method.

The approach we will follow is sometimes described as semiclassical: we will consider systems formed by quantized matter (atoms, molecules, etc., whose state is represented by a wave function satisfying the Schrödinger equation) interacting with a classical electromagnetic field satisfying Maxwell's equations. We will not dwell into the quantum mechanical aspects of light, e.g., its quantum mechanical description in terms of photons. Many of the physical processes visible around us can be described within this approach, albeit with some notable exceptions (e.g., the emission of photons by atoms de-exciting spontaneously). Treating the electromagnetic field as a quantum object is possible and bypasses the limitations of the semiclassical theory, but is outside of the scope of this course.

2.2 Revision: Electromagnetic fields

In this section: The E - and B -fields in terms of vector and scalar potentials; gauge transformations; plane waves; polarization vector; the intensity.

A beam of light, like any electromagnetic field, has an electric field component and a magnetic field component. As is explained in Section 2.4, in ordinary conditions the latter does not need to be considered and one can write the interaction term appearing in the Hamiltonian in terms of the electric field component only. However, this description is not always valid (e.g., as we will see, it fails for X-rays or gamma rays). Writing the Hamiltonian in its most general form, as done in Section 2.3, makes it necessary to describe the electromagnetic field by way of a vector potential and a scalar potential. All the necessary concepts have been covered in the level 2 Electromagnetism course. We will need to remember only the following:

1. An electromagnetic field has an electric field component, $\mathcal{E}(\mathbf{r}, t)$, and a magnetic field component, $\mathcal{B}(\mathbf{r}, t)$.
2. Both $\mathcal{E}(\mathbf{r}, t)$ and $\mathcal{B}(\mathbf{r}, t)$ can be written in terms of a vector potential $\mathbf{A}(\mathbf{r}, t)$ and a scalar potential $\phi(\mathbf{r}, t)$: In SI units,¹

$$\mathcal{E}(\mathbf{r}, t) = -\nabla\phi - \frac{\partial\mathbf{A}}{\partial t}, \quad (2.1)$$

$$\mathcal{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}. \quad (2.2)$$

3. The vector and scalar potentials can be chosen in infinitely many different ways, all equivalent and all giving the same physical fields $\mathcal{E}(\mathbf{r}, t)$ and $\mathcal{B}(\mathbf{r}, t)$. Indeed, for any given function $\chi(\mathbf{r}, t)$ and for any pair of electromagnetic potentials $\phi(\mathbf{r}, t)$ and $\mathbf{A}(\mathbf{r}, t)$, one can define a new pair of potentials $\phi'(\mathbf{r}, t)$ and $\mathbf{A}'(\mathbf{r}, t)$ by the equations

$$\phi'(\mathbf{r}, t) = \phi(\mathbf{r}, t) + \frac{\partial\chi}{\partial t} \quad (2.3)$$

$$\mathbf{A}'(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}, t) - \nabla\chi, \quad (2.4)$$

and the \mathcal{E} and \mathcal{B} fields corresponding to this new pair of potentials are exactly the same as the fields corresponding to $\phi(\mathbf{r}, t)$ and $\mathbf{A}(\mathbf{r}, t)$: If Eqs. (2.1)-(2.4) hold, then one also has

$$\mathcal{E}(\mathbf{r}, t) = -\nabla\phi' - \frac{\partial\mathbf{A}'}{\partial t}, \quad (2.5)$$

$$\mathcal{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}'. \quad (2.6)$$

The transformation defined by Eqs. (2.3) and (2.4) is called a gauge transformation.

4. Using this freedom in the choice of the vector and scalar potentials, one can always arrange that, in empty space (i.e., in the absence of electric charges and electric currents),

$$\phi(\mathbf{r}, t) \equiv 0 \quad (2.7)$$

and

$$\nabla \cdot \mathbf{A} \equiv 0. \quad (2.8)$$

One says that one works in the Coulomb gauge when the vector potential satisfies Eq. (2.8).

¹Gaussian units are used in some Quantum Mechanics textbooks, particularly older ones, with the consequence that some of the equations quoted in these textbooks differ from those mentioned in this course by factors of c , $1/c$ or $4\pi\epsilon_0$. We do not use Gaussian units in this course.

5. Working in the Coulomb gauge, one finds that in empty space the vector potential satisfies the wave equation

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = 0, \quad (2.9)$$

where c is the speed of light. Solutions of this equation are the plane waves

$$\mathbf{A}_{\mathbf{k},\hat{\epsilon}}(\mathbf{r}, t) = A_0 \hat{\epsilon} \cos(\mathbf{k} \cdot \mathbf{r} - \omega t + \varphi), \quad (2.10)$$

where φ is an arbitrary constant phase angle, as well as any linear combinations of these plane waves. Since we assume that $\phi(\mathbf{r}, t) \equiv 0$, the electric field component of the electromagnetic wave described by the vector potential $\mathbf{A}_{\mathbf{k},\hat{\epsilon}}(\mathbf{r}, t)$ is given by Eq. (2.1) as

$$\mathbf{E}_{\mathbf{k},\hat{\epsilon}}(\mathbf{r}, t) = -\frac{\partial \mathbf{A}_{\mathbf{k},\hat{\epsilon}}}{\partial t} = -\mathcal{E}_0 \hat{\epsilon} \sin(\mathbf{k} \cdot \mathbf{r} - \omega t + \varphi), \quad (2.11)$$

with

$$\mathcal{E}_0 = \omega A_0. \quad (2.12)$$

6. The vectors \mathbf{k} and $\hat{\epsilon}$ appearing in Eqs. (2.10) and (2.11) are necessarily orthogonal to each other:

$$\mathbf{k} \cdot \hat{\epsilon} = 0. \quad (2.13)$$

They are both constant. The vector \mathbf{k} is the wave vector. Its direction is also the direction of propagation of the wave represented by Eq. (2.10). In empty space, its norm, the wave number k , is related to the angular frequency ω by the dispersion relation

$$\omega = ck. \quad (2.14)$$

(Recall that $\omega = 2\pi\nu$, where ν is the frequency, and that $k = 2\pi/\lambda$, where λ is the wavelength.) The vector $\hat{\epsilon}$ is a unit vector which defines the direction $\mathbf{A}_{\mathbf{k},\hat{\epsilon}}(\mathbf{r}, t)$ “points” to, i.e., the polarization of this wave: As shown by Eq. (2.11), the direction of $\hat{\epsilon}$ is the direction in which the electric field $E_{\mathbf{k},\hat{\epsilon}}(\mathbf{r}, t)$ oscillates. Eq. (2.13) thus means that this wave is transverse: the electric field $E_{\mathbf{k},\hat{\epsilon}}(\mathbf{r}, t)$ is normal to its direction of propagation, which is the direction of the wave vector \mathbf{k} .

7. The plane wave described by Eq. (2.10) carries energy. Averaged over one period of oscillation, the flow of energy passing per unit time through a unit area perpendicular to \mathbf{k} is the intensity (or irradiance), I . In terms of the electric field amplitude \mathcal{E}_0 ,

$$I = \frac{1}{2} \epsilon_0 c \mathcal{E}_0^2. \quad (2.15)$$

- Note 1: It should be understood that in normal conditions the strength of the electric field component of a beam of light is very weak compared to the electric field of the nucleus “inside” an atom. For example, for a laser beam of an intensity of 1 W cm^{-2} , which is dangerously high and could easily blind someone without adequate eye protection, the electric field amplitude \mathcal{E}_0 is about $3 \times 10^3 \text{ V m}^{-1}$; by contrast, the electric field of a proton at a distance of 1 Bohr radius is about $5 \times 10^{11} \text{ V m}^{-1}$.
- Note 2: As defined here, the polarization vector $\hat{\epsilon}$ is real, not complex. One says that the wave described by Eq. (2.10) is linearly polarized, in the sense that the electric field vector remains aligned in a constant direction as t increases. One can also work in terms of complex polarization vectors representing states of circular or elliptical polarization, in which the electric field vector rotates. For example, take the electric field

$$\mathbf{E}(\mathbf{r}, t) = \mathcal{E}_0 [\hat{\mathbf{x}} \cos(kz - \omega t) + \hat{\mathbf{y}} \sin(kz - \omega t)] / \sqrt{2}, \quad (2.16)$$

where $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ are units vectors in the x - and y -directions, respectively. This field is a linear combination of two waves propagating in the z -direction, one linearly polarized in the x -direction and one linearly polarized in the y -direction, out of phase by $\pi/2$ with each other. It is easy to see that $\mathbf{E}(\mathbf{r}, t)$ rotates in the $x - y$ plane when t increases, with a constant norm. This field is thus circularly polarized, not linearly polarized. Its direction is not described by a single *real* polarization vector. However, one can introduce a *complex* polarization vector, namely

$$\hat{\epsilon} = (\hat{\mathbf{x}} - i\hat{\mathbf{y}}) / \sqrt{2}, \quad (2.17)$$

in terms of which Eq. (2.16) reads

$$\mathbf{E}(\mathbf{r}, t) = \mathcal{E}_0 \text{Re}(\hat{\epsilon} \exp[i(kz - \omega t)]). \quad (2.18)$$

[More precisely, Eqs. (2.16)-(2.18) describe a right-handed circularly polarized field: when followed in the positive z -direction from the origin *for a fixed time* t , the electric field vector describes a right-hand helix similar to that described by the thumb of your right-hand when you rotate your hand clockwise while moving it forward. The complex polarization vector for a left-handed circularly polarized field propagating in the positive z -direction is $(\hat{\mathbf{x}} + i\hat{\mathbf{y}}) / \sqrt{2}$.]

- Note 3: Whereas the Coulomb gauge is the usual choice for non-relativistic quantum mechanical calculations, the Lorenz gauge, defined by the condition

$$\nabla \cdot \mathbf{A} + \frac{1}{c^2} \frac{\partial \phi}{\partial t} = 0, \quad (2.19)$$

is more commonly used in Relativistic Electrodynamics and in Particle Physics.

2.3 The Hamiltonian of a charged particle in an EM field

In this section: The Hamiltonian in terms of vector and scalar potentials.

The Hamiltonian for a particle of mass m and electric charge q in an electromagnetic field is

$$H = \frac{1}{2m} [-i\hbar\nabla - q\mathbf{A}(\mathbf{r}, t)]^2 + q\phi(\mathbf{r}, t), \quad (2.20)$$

if the particle has no spin and is not submitted to any other force than that imparted by the field. In this equation, the functions $\mathbf{A}(\mathbf{r}, t)$ and $\phi(\mathbf{r}, t)$ are the vector potential and the scalar potential describing the field.

- It may seem strange that the Hamiltonian is written in terms of the electromagnetic potentials $\mathbf{A}(\mathbf{r}, t)$ and $\phi(\mathbf{r}, t)$ rather than in terms of the electric and magnetic field components of the field. Eq. (2.20) is the quantum mechanical equivalent of the classical Hamiltonian, which for a charged particle also needs, in general, to be written in terms of the electromagnetic potentials (more information about the classical Hamiltonian is provided in Appendix F, for interest). However, the real justification for Eq. (2.20) is that the theoretical results derived from this Hamiltonian are in agreement with experiment. As we will see in Section 2.4, it is often possible to pass to a formulation in which the Hamiltonian depends only on the electric field, but this involves an approximation which is not always justified.
- Sanity check: If there is no field, one can set $\mathbf{A}(\mathbf{r}, t) \equiv 0$ and $\phi(\mathbf{r}, t) \equiv 0$. Eq. (2.20) then reduces to

$$H = \frac{1}{2m} [-i\hbar\nabla]^2 = -\frac{\hbar^2}{2m} \nabla^2, \quad (2.21)$$

which is indeed the Hamiltonian of a free particle.

- The reason for the assumption that the particle has no spin is that a particle of non-zero spin has a magnetic dipole moment contributing an additional potential energy term to the Hamiltonian. See Part 5 of these course notes for more details about this point.

Note 1: The fact that the Hamiltonian depends on the electromagnetic potentials rather than on the physical fields $\mathcal{E}(\mathbf{r}, t)$ and $\mathcal{B}(\mathbf{r}, t)$ has interesting consequences. For example, the way the wave function of an electron evolves in time is affected by a non-zero vector potential *even if the corresponding \mathcal{E} - and \mathcal{B} -fields are zero*. A consequence of this dependence on $\mathbf{A}(\mathbf{r}, t)$ is the famous Aharonov-Bohm effect, about which much information can be found online.

2.4 The dipole approximation

In this section: The dipole (or long wavelength) approximation; the length form of the Hamiltonian; the dipole operator; validity of the dipole approximation.

We now concentrate on the interaction of a light beam with an atomic system, specifically an atom of hydrogen to keep the problem as simple as possible. We start by representing this light beam by a monochromatic, linearly polarized plane wave, before considering more general cases.² As is explained in Section 2.2, we can describe this wave by the vector potential $\mathbf{A}_{\mathbf{k},\hat{\epsilon}}(\mathbf{r},t)$ defined by Eq. (2.10), with a scalar potential $\phi(\mathbf{r},t) \equiv 0$. We assume here that the field propagates as in empty space (the atom is very far from other atoms, say). Taking the origin of the system of coordinates on the nucleus, the Hamiltonian reads

$$H = \frac{1}{2m} [-i\hbar\nabla + e\mathbf{A}_{\mathbf{k},\hat{\epsilon}}(\mathbf{r},t)]^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}, \quad (2.22)$$

where m is the mass of the electron (in the approximation where the nucleus is considered to have an infinite mass). Note that the charge q appearing in Eq. (2.20) is $-e$ here, the charge of the electron.

Note 1: As mentioned above, in our choice of gauge the scalar potential for the incident electromagnetic wave, $\phi(\mathbf{r},t)$, is zero everywhere, and therefore Eq. (2.22) does not include a term in $-e\phi(\mathbf{r},t)$. However, the Coulomb potential figuring in this equation is nothing else than $-e\phi_p(\mathbf{r})$, where $\phi_p(\mathbf{r})$ is the scalar potential describing the electrostatic field of the proton, $\phi_p(\mathbf{r}) = (1/4\pi\epsilon_0)(e/r)$.

It is important to understand that in many cases the electromagnetic field varies in space on a very different scale than the relevant wave functions. Quantum systems such as atoms or small molecules have a typical size of about 0.1 nm (the Bohr radius, a_0 , is about 0.05 nm, half an angstrom). By contrast, light in the visible part of the electromagnetic spectrum has a wavelength of about 500 nm, which is ten thousand times larger.³ In many applications of this theory, the vector potential is therefore almost constant over the region of space occupied by the system of interest. The dipole approximation consists in taking the field to be exactly constant over this region.

Making this long wavelength approximation in Eq. (2.22) amounts to replacing the position vector \mathbf{r} by a constant in $\mathbf{A}_{\mathbf{k},\hat{\epsilon}}(\mathbf{r},t)$. Without loss of generality,

²The word monochromatic means that the wave contains only one frequency component (literally, a “single colour”).

³The visible extends from approximately 400 nm to approximately 700 nm.

we can simply take \mathbf{r} to be zero (the position of the nucleus in our system of coordinates). This yields

$$H = \frac{1}{2m} [-i\hbar\nabla + e\mathbf{A}(t)]^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \quad (2.23)$$

with

$$\mathbf{A}(t) = A_0 \hat{\mathbf{e}} \cos(\omega t - \varphi). \quad (2.24)$$

This vector potential, being constant in \mathbf{r} , satisfies Eq. (2.8) and has a zero curl ($\nabla \times \mathbf{A}(t) = 0$). The corresponding electric field, $\mathcal{E}(t)$, is also homogeneous [see Eq. (2.11)]:

$$\mathcal{E}(t) = \mathcal{E}_0 \hat{\mathbf{e}} \sin(\omega t - \varphi). \quad (2.25)$$

However, the corresponding magnetic field, $\nabla \times \mathbf{A}(t)$, is zero everywhere.

Note 2: Taking the field to be that at a point \mathbf{r}_0 other than the nucleus would simply introduce a constant phase $\mathbf{k} \cdot \mathbf{r}_0$ in the argument of the cosine function, which can be merged with φ to form a new phase angle φ' . We will see later that the probability of the transitions induced by this field does not depend on the value of this phase angle.

Given that $\nabla \cdot \mathbf{A}(t) = 0$, expanding the square in Eq. (2.23) results in

$$H = -\frac{\hbar^2}{2m} \nabla^2 - i\frac{e\hbar}{m} \mathbf{A}(t) \cdot \nabla + \frac{e^2}{2m} \mathbf{A}^2(t) - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}. \quad (2.26)$$

This Hamiltonian can be simplified by making a judicious gauge transformation. [Remember that a gauge transformation transforms the pair of electromagnetic potentials (\mathbf{A}, ϕ) into another pair, (\mathbf{A}', ϕ') , corresponding to the same E-field and B-field. See Section 2.2.] In particular, it is possible to pass to a formulation in which the vector potential is zero everywhere and the scalar potential is given by $-\mathcal{E}(t) \cdot \mathbf{r}$, so that the Hamiltonian takes on the form

$$H = -\frac{\hbar^2}{2m} \nabla^2 + e\mathcal{E}(t) \cdot \mathbf{r} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}. \quad (2.27)$$

Note 3: Alternatively, it is also possible to remove the term in \mathbf{A}^2 from Eq. (2.26) through another gauge transformation and work with the Hamiltonian

$$H = -\frac{\hbar^2}{2m} \nabla^2 - i\frac{e\hbar}{m} \mathbf{A}(t) \cdot \nabla - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}. \quad (2.28)$$

One often refers to the $\mathbf{A}(t) \cdot \nabla$ term as the “velocity form” of the interaction, since $-i\hbar\nabla$ is the momentum operator and the momentum of a particle divided by its mass is its velocity. By contrast, the interaction is said to be in the “length form” in the formulation of Eq. (2.27). These two forms of the interaction are completely equivalent, as long as one does not make further approximations. However, simplifying the Hamiltonian to the forms of Eqs. (2.27) or (2.28) is possible only within the dipole approximation.

Note 4: The transformations leading to Eqs. (2.27) and (2.28) are the topic of one of the exercises proposed in Worksheet 4. Briefly, the Hamiltonian of Eq. (2.27) is obtained by setting $\chi(\mathbf{r}, t) = \mathbf{A}(t) \cdot \mathbf{r}$ in Eqs. (2.3) and (2.4), while the Hamiltonian of Eq. (2.28) is obtained by setting

$$\chi(\mathbf{r}, t) = \frac{e}{2m} \int^t \mathbf{A}^2(t') dt'.$$

These transformations also transform the wave function: multiplying a solution of the time-dependent Schrödinger equation for the Hamiltonian of Eq. (2.23) by an appropriate phase factor transforms it into a solution of this equation for the Hamiltonian of either Eq. (2.27) or Eq. (2.28). As phase factors do not affect probabilities, it does not matter whether one works with Eq. (2.27) or Eq. (2.28) (at least, as long as no further approximation is made).

Eq. (2.27) is particularly noteworthy: in this formulation, the interaction between the atomic electron and the light beam represented by Eq. (2.10) merely contributes a term $e\mathcal{E}(t) \cdot \mathbf{r}$ to the field-free Hamiltonian. This term is easily recognized to be the potential energy of the electron due to its interaction with the electric field component of the electromagnetic field. It can also be recognized as being the potential energy of an electric dipole moment $-e\mathbf{r}$ in the electric field $\mathcal{E}(t)$:

$$e\mathcal{E}(t) \cdot \mathbf{r} \equiv -\mathbf{D} \cdot \mathcal{E}(t), \quad (2.29)$$

where \mathbf{D} is the dipole operator,

$$\mathbf{D} = -e\mathbf{r}. \quad (2.30)$$

(The charge of the nucleus, in hydrogen, is e . An electron of charge $-e$ at a position \mathbf{r} relative to the nucleus thus forms an electric dipole moment $-e\mathbf{r}$ with the latter. See, e.g., Chapter 21 of Young and Freedman.) Hence, within the dipole approximation, the atom interacts with the field as if it was a dipole moment.

The dipole approximation is widely used in quantum physics, as treating the field as spatially homogeneous simplifies calculations considerably. It has limitations, though:

- This approximation fails if the wavelength is not long enough. For instance, it cannot be used to accurately model the interaction of atoms with hard X-rays of a wavelength of about 0.1 nm or less.
- As we will see later, calculations done within the dipole approximation predict that certain transitions are impossible, although they are in fact possible and can be observed. (These “forbidden” transitions usually have a much smaller probability than the transitions “allowed” under the dipole approximation.)

Note 5: A plane electromagnetic wave such as that described by Eq. (2.10) can be understood as consisting of a flux of photons of energy $\hbar\omega$ and momentum $\hbar\omega/c = \hbar k$. An atom absorbing energy from this wave, e.g., in a transition from the ground state to an excited state, would also absorb momentum, and recoil as a consequence. This effect is absent in a description of the interaction of light with matter based on the dipole approximation. Indeed, taking $\exp(i\mathbf{k}\cdot\mathbf{r})$ to be constant effectively amounts to taking $\mathbf{k} = 0$, which means a zero momentum. Recoil effects must be taken into account in the absorption or emission of gamma rays by nuclei, and even, in some circumstances, in the absorption and emission of visible light by atoms (e.g., in respect to laser cooling).

Note 6: That the electron is primarily interacting with the electric field component of the wave is not surprising if one considers the problem classically: in the presence of both an E-field and B-field, an electron of velocity \mathbf{v} is submitted to the Lorentz force $-e(\mathcal{E} + \mathbf{v} \times \mathcal{B})$. However, for a monochromatic plane wave, the term in $\mathbf{v} \times \mathcal{B}$ is a factor $|v/c|$ smaller than the term in \mathcal{E} . Therefore the dynamics is dominated by the E-field unless the speed of the electron is close to the speed of light — in which case a non-relativistic description such as one based on Eq. (2.22) would not be meaningful.

Note 7: The electron has a non-zero spin, hence a non-zero magnetic dipole moment coupling with the magnetic field component of the incident wave (see Part 5 of these course notes). In principle, this coupling should contribute an additional term to the Hamiltonian. We have not written this contribution in Eq. (2.22) because it is a very small correction compared to the term in $\mathbf{A}_{\mathbf{k},\epsilon}(\mathbf{r}, t)$, and in any case the magnetic field component of the wave is considered to be zero if one makes the dipole approximation. In our non-relativistic description, its effect for an atom of hydrogen would simply be to change the spin state of the electron (which without spin-orbit coupling has no impact on the probability of transitions between electronic states). For consistency, taking it account would also require to take into account the magnetic dipole moment arising from the orbital angular momentum of the electron and other small effects neglected in the dipole approximation.

2.5 Absorption and stimulated emission

In this section: Obtaining the probability of a transition induced by a propagating polarized EM field described by a plane wave.

We continue with the example of an atom of hydrogen exposed to an electromagnetic wave, in the formulation where the Hamiltonian is taken to be

$$H = -\frac{\hbar^2}{2m}\nabla^2 + e\mathcal{E}(t) \cdot \mathbf{r} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}. \quad (2.31)$$

We suppose that the field is abruptly turned on at a time $t = 0$ and given by Eq. (2.25) at later times, so that

$$H = H_0 + H'(t) \quad (2.32)$$

with

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \quad (2.33)$$

and

$$H'(t) = \begin{cases} 0 & t < 0 \\ e\mathcal{E}_0 \hat{\mathbf{e}} \cdot \mathbf{r} \sin(\omega t - \varphi). & t \geq 0. \end{cases} \quad (2.34)$$

Clearly, $H'(t)$ describes a harmonic perturbation. What we have seen in Section 1.6 therefore applies. Proceeding as in this section, we express $H'(t)$ as the sum of a term oscillating like $\exp(i\omega t)$ and a term oscillating like $\exp(-i\omega t)$:

$$H'(t) = \begin{cases} 0 & t < 0 \\ A \exp(i\omega t) + A^\dagger \exp(-i\omega t) & t \geq 0, \end{cases} \quad (2.35)$$

where here ω is the angular frequency of the field (2π times the frequency), and

$$A = \frac{1}{2i} \exp(-i\varphi) e\mathcal{E}_0 \hat{\mathbf{e}} \cdot \mathbf{r} \quad (2.36)$$

$$A^\dagger = -\frac{1}{2i} \exp(i\varphi) e\mathcal{E}_0 \hat{\mathbf{e}} \cdot \mathbf{r}. \quad (2.37)$$

(Don't be confused by the similarity in the notation: the operators A and A^\dagger defined here are not the vector potential of the field!)

Note 1: Recall that the polarization vector $\hat{\mathbf{e}}$ is real — see Note 2 of Section 2.2. Hence, $\hat{\mathbf{e}}$ is not complex conjugated in Eq. (2.37).

Let us suppose, as before, that the atom is initially in a certain bound state a (e.g., the ground state of the field-free Hamiltonian H_0). Under the action of the field, this initial state evolves into a complicated superposition of eigenstates of H_0 (typically an infinite number of eigenstates). If the atom is found to be in

an eigenstate b of H_0 other than state a , one says that it has made a transition to that state. In the case where state b is higher in energy than state a , the atom will have absorbed energy from the field to make this transition. In the opposite case, where state b is lower in energy, the atom will have transferred energy to the field, i.e., effectively, emitted light. The latter process is called stimulated emission, in view of the fact that in the time evolution described by the Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi(\mathbf{r}, t), \quad (2.38)$$

it is the presence of the field which makes it possible that the atom is found in state b .⁴ Stimulated emission is related to spontaneous emission, which is the process in which the atom makes a transition to a state lower in energy independently from the presence of an external electromagnetic field. (Spontaneous emission is not described by the Schrödinger equation. More about this topic in Section refsection:spont.

Note 2: Physically, the field would change if the atom absorbs or emits energy (the emission of energy being here the emission of light). However, in the approach we are following, the back action of the atom on the field is not taken into account: it is simply assumed that the field itself is unperturbed by its interaction with the atom. How the field is actually modified by the absorption and emission of photons by an atom or an ensemble of atoms is outside the scope of this course.

We will assume that the electric field of the incident wave is much weaker than the electric field the electron is submitted to due to its proximity to the nucleus (which is almost always the case unless the atom would be initially in a very highly excited state or the incident field would be a super-intense laser pulse, see Note 1 of Section 2.2). We thus use first order time-dependent perturbation theory. Accordingly, the probability for a transition to a bound state b is given by Eq. (1.61) or (1.63) of Section 1.6, the former if state b is higher in energy than state a and the latter if it is lower. These two equations give the transition probability in terms of the matrix elements A_{ba} or A_{ba}^\dagger defined, respectively, by Eqs. (1.54) and (1.55).

From the definition of these matrix elements and Eqs. (2.36) and (2.37), we have here

$$A_{ba} = \frac{1}{2i} \exp(-i\varphi) e\mathcal{E}_0 \int \psi_b^{(0)*}(\mathbf{r}) \hat{\mathbf{e}} \cdot \mathbf{r} \psi_a^{(0)}(\mathbf{r}) d^3r, \quad (2.39)$$

$$A_{ba}^\dagger = -\frac{1}{2i} \exp(i\varphi) e\mathcal{E}_0 \int \psi_b^{(0)*}(\mathbf{r}) \hat{\mathbf{e}} \cdot \mathbf{r} \psi_a^{(0)}(\mathbf{r}) d^3r. \quad (2.40)$$

⁴Explanation: If $\mathcal{E}_0 = 0$ and therefore $H \equiv H_0$, the atom remains in state a at all times since $\psi_a^{(0)}(\mathbf{r}) \exp(-iE_a^{(0)}t/\hbar)$ is then a solution of Eq. (2.38) even for $t > 0$.

Let us express $\hat{\mathbf{e}}$ and \mathbf{r} in terms of unit vectors in the x -, y - and z -directions, $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$, respectively:

$$\hat{\mathbf{e}} = \epsilon_x \hat{\mathbf{x}} + \epsilon_y \hat{\mathbf{y}} + \epsilon_z \hat{\mathbf{z}}, \quad \mathbf{r} = x \hat{\mathbf{x}} + y \hat{\mathbf{y}} + z \hat{\mathbf{z}}. \quad (2.41)$$

Thus $\hat{\mathbf{e}} \cdot \mathbf{r} = \epsilon_x x + \epsilon_y y + \epsilon_z z$ and therefore

$$\int \psi_b^{(0)*}(\mathbf{r}) \hat{\mathbf{e}} \cdot \mathbf{r} \psi_a^{(0)}(\mathbf{r}) d^3r = \epsilon_x x_{ba} + \epsilon_y y_{ba} + \epsilon_z z_{ba} \quad (2.42)$$

with

$$x_{ba} = \int \psi_b^{(0)*}(\mathbf{r}) x \psi_a^{(0)}(\mathbf{r}) d^3r, \quad (2.43)$$

$$y_{ba} = \int \psi_b^{(0)*}(\mathbf{r}) y \psi_a^{(0)}(\mathbf{r}) d^3r, \quad (2.44)$$

$$z_{ba} = \int \psi_b^{(0)*}(\mathbf{r}) z \psi_a^{(0)}(\mathbf{r}) d^3r. \quad (2.45)$$

These three matrix elements can be taken as being the x -, y - and z -components of a vector, which we will denote by the symbol \mathbf{r}_{ba} :

$$\mathbf{r}_{ba} = x_{ba} \hat{\mathbf{x}} + y_{ba} \hat{\mathbf{y}} + z_{ba} \hat{\mathbf{z}}. \quad (2.46)$$

Introducing this vector makes it possible to write Eq. (2.42) in the more compact form

$$\int \psi_b^{(0)*}(\mathbf{r}) \hat{\mathbf{e}} \cdot \mathbf{r} \psi_a^{(0)}(\mathbf{r}) d^3r = \hat{\mathbf{e}} \cdot \mathbf{r}_{ba}. \quad (2.47)$$

Hence

$$A_{ba} = \frac{1}{2i} \exp(-i\varphi) e\mathcal{E}_0 \hat{\mathbf{e}} \cdot \mathbf{r}_{ba}, \quad (2.48)$$

$$A_{ba}^\dagger = -\frac{1}{2i} \exp(i\varphi) e\mathcal{E}_0 \hat{\mathbf{e}} \cdot \mathbf{r}_{ba}. \quad (2.49)$$

Using Eqs. (1.60) and (1.63) and remembering that $|\exp(\pm i\varphi)| = 1$, we thus find that

$$P_{ba}^{(1)}(t) \approx \frac{e^2 \mathcal{E}_0^2}{2\hbar^2} |\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2 F(t, \omega_{ba} - \omega) \quad (2.50)$$

for absorption (when state b is higher in energy than state a), and

$$P_{ba}^{(1)}(t) \approx \frac{e^2 \mathcal{E}_0^2}{2\hbar^2} |\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2 F(t, |\omega_{ba}| - \omega) \quad (2.51)$$

for stimulated emission (when state b is lower in energy than state a). We see that these transition probabilities do not depend on the value of the phase angle φ , which is good since the value of φ is to some extent arbitrary (see Note 2 of Section 2.4).

Note 3: While here the equation giving the transition probability is the same for absorption and for stimulated emission, this might not be the case for other choices of polarization, or more generally for other types of transitions for which $|A_{ba}|^2 \neq |A_{ba}^\dagger|^2$. However, one always have that the probability for a transition from state a to state b is the same as the probability for the inverse process, i.e., a transition from state b to state a . Mathematically, this equality stems from the identity $A_{ba}^\dagger = A_{ab}^*$ mentioned in Note 2 of Section 1.7.

2.6 Broad band fields and unpolarized fields

In this section: Extending the results of the previous section to the case of an incoherent, broad band, unpolarized and multidirectional field.

It is useful for the following to express the transition probabilities in terms of the intensity of the beam, I . Recalling the relation between the intensity and the electric field amplitude [Eq. (2.15)], we simply replace \mathcal{E}_0^2 by $2I/(\epsilon_0 c)$ in Eqs. (2.50) and (2.51). For example, when written in terms of the intensity, Eq. (2.50) takes on the form

$$P_{ba}^{(1)}(t) \approx \frac{e^2}{\hbar^2 \epsilon_0 c} I |\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2 F(t, \omega_{ba} - \omega). \quad (2.52)$$

This simple change makes it possible to generalize these results to the case of an *incoherent* incident field containing a number of frequency components. The concept of coherence in Optics is not easy and would require many pages to explain fully — which I won't attempt to do as this concept is outside the scope of the course. Roughly speaking, a field is incoherent if it is a superposition of different components (e.g., of waves of different frequencies) which are not locked in phase with each other. The absence of a well defined relative phase between the components has the effect that they do not interfere constructively or destructively, as is illustrated by an example in Appendix G. As the components act independently from each other, the total probability for a transition is obtained by summing the probability for each of these components. For a discrete superposition, this gives

$$P_{ba}^{(1)}(t) \approx \sum_j \frac{e^2}{\hbar^2 \epsilon_0 c} I_j |\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2 F(t, \omega_{ba} - \omega_j), \quad (2.53)$$

where ω_j is the angular frequency of the j -th component and I_j is its intensity.

A more common case, however, is that the incident light is both incoherent and distributed continuously in frequency (think, e.g., to sun light or to light

emitted by a lighting bulb). One can then define an “intensity distribution per unit angular frequency range”, namely a function $I(\omega)$ such that the product $I(\omega) d\omega$ is the intensity of the field in the angular frequency range $[\omega, \omega + d\omega]$. Replacing the sum over discrete frequency components by an integral in Eq. (2.53) gives

$$P_{ba}^{(1)}(t) \approx \frac{e^2}{\hbar^2 \epsilon_0 c} |\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2 \int_0^\infty I(\omega) F(t, \omega_{ba} - \omega) d\omega. \quad (2.54)$$

In many applications of this theory, the intensity distribution varies with ω much more slowly than the function $F(t, \omega_{ba} - \omega)$, and differs significantly from zero over a wide range of angular frequencies encompassing ω_{ba} . (To re-take the same example as above, the intensity distribution of the light produced by a lighting bulb extends over a frequency range of the order of 10^{14} Hz in width, which is typically seven orders of magnitude wider than the frequency ranges over which light can be considered to be resonant with specific atomic transitions.) It turns out that when the intensity has this broad frequency distribution the integration over ω can be performed regardless of the details of how $I(\omega)$ varies. One finds

$$P_{ba}^{(1)}(t) \approx \frac{\pi e^2}{\hbar^2 \epsilon_0 c} |\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2 I(\omega_{ba}) t. \quad (2.55)$$

Note 1: The calculation leading to Eq. (2.55) has similarities with the calculation outlined in Note 5 of Section 1.8 in relation to Fermi’s Golden Rule. Briefly: If $I(\omega) \neq 0$ at $\omega = \omega_{ba}$, then for t large enough the integral is dominated by the range of values of ω spanning the sharp peak the function $F(t, \omega_{ba} - \omega)$ has at $\omega = \omega_{ba}$. If $I(\omega)$ varies little in this range, then this function can be treated as a constant equal to $I(\omega_{ba})$ in regards to this integral, and we simply have

$$P_{ba}^{(1)}(t) \approx \frac{e^2}{\hbar^2 \epsilon_0 c} |\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2 I(\omega_{ba}) \int_0^\infty F(t, \omega_{ba} - \omega) d\omega. \quad (2.56)$$

As $F(t, \omega_{ba} - \omega) \approx 0$ for $\omega \ll \omega_{ba}$, one can extend the range of integration to negative values of ω (these values are unphysical, but this does not matter since their contribution is practically zero) and make use of the identity

$$\int_{-\infty}^\infty F(t, \omega_{ba} - \omega) dt = \pi t. \quad (2.57)$$

(As was mentioned below Eq. (1.85), this integral cannot be worked out by elementary methods.) Eq. (2.55) follows.

Remarkably, Eq. (2.55) predicts that the transition probability for a field with a broad, continuous distribution of frequencies depends linearly on t . This equation is not valid for very short times (there might be a transient behaviour before the probability settles to a linear law). It is not valid either for very long

times (the probability should remain much smaller than 1 for the perturbative approach to make sense). However, in between these two limits, the transition *probability* increases proportionally to t , and therefore the transition *rate*, $W_{ba}(\hat{\epsilon})$, is constant in time:

$$W_{ba}(\hat{\epsilon}) \equiv \frac{d}{dt} P_{ba}^{(1)}(t) \approx \frac{\pi e^2}{\hbar^2 \epsilon_0 c} |\hat{\epsilon} \cdot \mathbf{r}_{ba}|^2 I(\omega_{ba}). \quad (2.58)$$

(The transition rate is the transition probability per unit time.)

Clearly, the same calculations can be done for the case where state b is lower in energy than state a . We will denote the corresponding transition rate by $\bar{W}_{ba}(\hat{\epsilon})$ (or $\bar{W}_{ab}(\hat{\epsilon})$ if we would go from a state b to a state a lower in energy). Proceeding as above, one finds

$$\bar{W}_{ba}(\hat{\epsilon}) \approx \frac{\pi e^2}{\hbar^2 \epsilon_0 c} |\hat{\epsilon} \cdot \mathbf{r}_{ba}|^2 I(|\omega_{ba}|). \quad (2.59)$$

This equation is practically identical to the equation for the case where state b is higher in energy than state a , Eq. (2.58).

Also worth noting is that these transition rates are a product of a factor depending on the properties of the atom (through the vector \mathbf{r}_{ba}) and a factor depending only on the intensity of the field. In fact, these rates are proportional to the intensity: increasing the intensity by, say, a factor of two increases the transition rates by the same factor (within the limits of applicability of perturbation theory, that is). This dependence in the intensity is not related to properties of the atom. It is often advantageous to remove it and work instead with transition rates per unit photon flux, which do not depend on how strong the field is. The concept of photon flux is easy to grasp: an electromagnetic field propagating in a certain direction can be thought of as being a stream of photons. The number of photons crossing a surface of unit area normal to their trajectory is the photon flux. Since a photon of angular frequency ω carries an energy $\hbar\omega$, a flux $F(\omega)$ of photons of that angular frequency corresponds to a flux of energy, i.e., an intensity, $I(\omega) = \hbar\omega F(\omega)$. Hence, one defines the transition rates per unit photon flux

$$\sigma_{ba} = W_{ba}(\hat{\epsilon})/F(\omega_{ba}) \quad \text{and} \quad \bar{\sigma}_{ba} = \bar{W}_{ba}(\hat{\epsilon})/F(|\omega_{ba}|), \quad (2.60)$$

where $F(\omega)$ is the flux of photons at the angular frequency ω ,

$$F(\omega) = \frac{I(\omega)}{\hbar\omega}. \quad (2.61)$$

The normalized transition probabilities σ_{ba} and $\bar{\sigma}_{ba}$ are called, respectively, the absorption cross section and the cross section for stimulated emission. These cross sections have the physical dimensions of an area.

Note 2: Rates of transitions induced by an incident beam of particles are often described in terms of cross sections — i.e., rates of transitions per unit projectile flux. Although cross sections generally have the physical dimensions of an area, they do not represent the area of a real surface; in particular, they do not represent the area of an obstacle an atom or other target would oppose to the incident beam.

In preparation for next section, we close by generalizing the transition rates obtained above to the case of an incoherent superposition of infinitely many plane waves uniformly distributed in direction of propagation and in direction of polarization. First, we note Eqs. (2.58) and (2.59) do not explicitly depend on the direction of propagation of the field (there is a hidden dependence, though, in that this direction is meant to be normal to the polarization vector $\hat{\mathbf{e}}$). However, the fact that these equations are written in terms of an intensity distribution implies that the field is directional (an intensity refers to a flux of energy, thus to a propagation in a well defined direction). We can generalize them to the case of a field which may or may not be directional simply by re-writing them in terms of the “energy density distribution per unit angular frequency range”, $\rho(\omega)$. That is, a function such that the integral

$$\int_{\omega_1}^{\omega_2} \rho(\omega) d\omega$$

is the energy per unit volume carried by the field in the angular frequency interval (ω_1, ω_2) . (We mean, here, the energy density averaged over time, not the instantaneous energy density; please refer to Note 6 below or to your level 2 Electromagnetism course for details.) For a directional field,

$$\rho(\omega) = I(\omega)/c. \quad (2.62)$$

Note 3: Explanation: A general result of Electromagnetism is that in vacuo an electromagnetic field has an instantaneous energy density

$$u(\mathbf{r}, t) = \frac{1}{2} \epsilon_0 [|\mathcal{E}(\mathbf{r}, t)|^2 + c^2 |\mathcal{B}(\mathbf{r}, t)|^2]. \quad (2.63)$$

(Instantaneous means that $u(\mathbf{r}, t)$ is the energy density at a particular instant: $u(\mathbf{r}, t)$ normally varies in time.) For the plane wave described by Eq. (2.10), one finds

$$u(\mathbf{r}, t) = \epsilon_0 \mathcal{E}_0^2 \sin^2(\mathbf{k} \cdot \mathbf{r} - \omega t + \varphi). \quad (2.64)$$

The corresponding energy density ρ is the time-average of $u(\mathbf{r}, t)$ over one period of oscillation of the wave:

$$\rho = \frac{1}{T} \int_0^T u(\mathbf{r}, t) dt = \frac{1}{2} \epsilon_0 \mathcal{E}_0^2, \quad (2.65)$$

where $T = 2\pi/\omega$. (Recall that the average of a \sin^2 function over one period of oscillation is $1/2$.) For the plane wave of Eq. (2.10), $\epsilon_0 \mathcal{E}_0^2/2 = I/c$.

The same conclusion can also be reached through the following reasoning: By definition of the intensity, in a time δt a field of intensity I carries an average energy $\delta E = I \delta t \delta A$ across an area δA normal to its direction of propagation (δE is the energy averaged over the oscillation of the field). As this energy is carried at the speed of light, δE is also the average energy contained in a volume $c \delta t \delta A$. The energy density of the field, ρ , is thus $\delta E/(c \delta t \delta A)$, which is I/c .

Further, we also want to have rates for absorption or stimulated emission for the case where the field is unpolarized.⁵ These can be obtained simply by averaging the rates $W_{ba}(\hat{\mathbf{e}})$ and $\bar{W}_{ba}(\hat{\mathbf{e}})$ over the direction of the vector $\hat{\mathbf{e}}$. The calculation is explained in Note 4, at the end of this section. It results in the following equations for the corresponding transition rates:

$$W_{ba} \approx \frac{\pi e^2}{3\hbar^2 \epsilon_0} |\mathbf{r}_{ba}|^2 \rho(\omega_{ba}), \quad (2.66)$$

$$\bar{W}_{ba} \approx \frac{\pi e^2}{3\hbar^2 \epsilon_0} |\mathbf{r}_{ba}|^2 \rho(|\omega_{ba}|), \quad (2.67)$$

where

$$|\mathbf{r}_{ba}|^2 = |x_{ba}|^2 + |y_{ba}|^2 + |z_{ba}|^2. \quad (2.68)$$

Note 4: Averaging $W_{ba}(\hat{\mathbf{e}})$ and $\bar{W}_{ba}(\hat{\mathbf{e}})$ over the direction of the vector $\hat{\mathbf{e}}$ only involves averaging $|\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2$. We should remember that whilst the x -, y - and z -components of the vector $\hat{\mathbf{e}}$ are real numbers here, those of the vector \mathbf{r}_{ba} may be complex. Thus

$$|\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2 = (\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}^{\text{R}})^2 + (\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}^{\text{I}})^2, \quad (2.69)$$

where the real vectors $\mathbf{r}_{ba}^{\text{R}}$ and $\mathbf{r}_{ba}^{\text{I}}$ are, respectively, the real and the imaginary parts of the complex vector \mathbf{r}_{ba} . We begin by averaging $(\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}^{\text{R}})^2$. To make the calculation easier, we take the z -direction to coincide with the direction of the vector $\mathbf{r}_{ba}^{\text{R}}$ (this vector points in a certain direction, and we have the freedom to choose the system of coordinates in such a way that the positive z -axis points in the same direction as this vector). The angle between $\hat{\mathbf{e}}$ and $\mathbf{r}_{ba}^{\text{R}}$ is therefore the polar angle θ for this system of coordinates, and

⁵A field is said to be unpolarized if it has no specific direction of polarization and can be considered to be an incoherent superposition of states of well defined polarization.

$$(\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}^R)^2 = |\hat{\mathbf{e}}|^2 |\mathbf{r}_{ba}^R|^2 \cos^2 \theta, \quad (2.70)$$

where $|\mathbf{r}_{ba}^R|$ is the norm of the vector \mathbf{r}_{ba}^R and $\hat{\mathbf{e}}$ is the norm of the vector $\hat{\mathbf{e}}$. ($|\hat{\mathbf{e}}| = 1$, recall that $\hat{\mathbf{e}}$ is a unit vector). Thus

$$\langle (\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}^R)^2 \rangle = |\mathbf{r}_{ba}^R|^2 \langle \cos^2 \theta \rangle, \quad (2.71)$$

where the $\langle \rangle$ brackets indicate an average over the direction of $\hat{\mathbf{e}}$. Now,

$$\langle \cos^2 \theta \rangle = \frac{\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi \cos^2 \theta}{\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi}. \quad (2.72)$$

The result is that $\langle \cos^2 \theta \rangle = 1/3$, since

$$\int_0^{2\pi} d\phi = 2\pi, \quad \int_0^\pi d\theta \sin \theta = 2, \quad \int_0^\pi d\theta \sin \theta \cos^2 \theta = 2/3. \quad (2.73)$$

Hence $\langle (\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}^R)^2 \rangle = |\mathbf{r}_{ba}^R|^2 / 3$. Similarly, $\langle (\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}^I)^2 \rangle = |\mathbf{r}_{ba}^I|^2 / 3$, and thus

$$\begin{aligned} \langle |\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2 \rangle &= (|\mathbf{r}_{ba}^R|^2 + |\mathbf{r}_{ba}^I|^2) / 3 \\ &= (|x_{ba}|^2 + |y_{ba}|^2 + |z_{ba}|^2) / 3. \end{aligned} \quad (2.74)$$

Eqs. (2.66) and (2.67) follow.

2.7 Spontaneous emission and the Einstein coefficients

In this section: Spontaneous emission; the Einstein A and B coefficients; their relation with the quantum mechanical rates of absorption and stimulated emission; the radiative lifetime of excited states.

In this course, as in the Quantum Mechanics courses you have taken previously, quantum states are described by a wave function or a state vector satisfying the time-dependent Schrödinger equation. However, this formulation does not account for the fact that excited states or atoms, nuclei or molecules have a finite lifetime and may spontaneously decay to a state of lower energy by emitting light. Suppose, for example, that an atom of hydrogen is prepared at time $t = 0$ in an excited eigenstate of the field-free Hamiltonian H_0 , state b say, and is then left completely undisturbed. The wave function representing the state of this atom, $\Psi(\mathbf{r}, t)$, is such that

$$i\hbar \frac{\partial \Psi}{\partial t} = H_0 \Psi(\mathbf{r}, t) \quad (2.75)$$

for $t \geq 0$. The Hamiltonian remains H_0 at all times since the atom is left completely undisturbed after having been prepared in state b . Our assumption that the atom is initially in state b means that

$$\Psi(\mathbf{r}, t = 0) = \psi_b^{(0)}(\mathbf{r}) \quad (2.76)$$

where the wave function $\psi_b^{(0)}(\mathbf{r})$ is such that

$$H_0 \psi_b^{(0)}(\mathbf{r}) = E_b^{(0)} \psi_b^{(0)}(\mathbf{r}). \quad (2.77)$$

Hence

$$\Psi(\mathbf{r}, t) \equiv \psi_b^{(0)}(\mathbf{r}) \exp(-iE_b^{(0)}t/\hbar) \quad (2.78)$$

at later times, since there is no other solution of Eq. (2.75) that satisfies the initial condition set by Eq. (2.76). Therefore, according to Eq. (2.75), the atom remains in state b at all times. However, it is an experimental fact that even if left undisturbed, an atom initially in an excited state will sooner or later end up in the ground state, the transition being accompanied by the emission of one or several photons.

A rigorous theoretical description of these processes of spontaneous decay would require that the electromagnetic field itself be treated as a quantum object. This is a problem of Quantum Electrodynamics outside the scope of this course. Nonetheless, we can obtain a quantum mechanical equation predicting the lifetime of these excited states by following an approach based on a theory of absorption and emission of light proposed by Einstein in 1917. Einstein formulated the problem in terms of Statistical Mechanics, but he made use of two of the very few quantum mechanical concepts which were already known at the time, namely that atoms have discrete energy levels and that the energy density distribution of black body radiation is given by Planck's law. He reasoned as follows.

Suppose that a population of identical atoms is confined inside a cavity kept at temperature T , and that these atoms have just two energy levels, E_a and E_b (with $E_b > E_a$). The numbers of atoms in these energy levels are $N_a(t)$ and $N_b(t)$, respectively. The total number of atoms in the cavity is constant and equal to $N_a(t) + N_b(t)$. Einstein postulated that over an infinitesimal interval of time dt , the number $N_b(t)$ changes by an infinitesimal amount dN_b given by the equation

$$\frac{dN_b}{dt} = B_{ba} \rho(\omega_{ba}) N_a(t) - [A_{ab} + B_{ab} \rho(\omega_{ba})] N_b(t), \quad (2.79)$$

or equivalently

$$dN_b = B_{ba} \rho(\omega_{ba}, t) N_a(t) dt - [A_{ab} + B_{ab} \rho(\omega_{ba}, t)] N_b(t) dt, \quad (2.80)$$

where $\omega_{ba} = (E_b - E_a)/\hbar$ and $\rho(\omega, t)$ is the energy density distribution of the field at time t . In Eq. (2.80), the term

$$B_{ba} \rho(\omega_{ba}, t) N_a(t) dt$$

is the number of atoms which, in the interval of time dt , make a transition from the energy level E_a to the energy level E_b . For an individual atom in E_a , the probability of making a transition is $B_{ba} \rho(\omega_{ba}, t) dt$. Thus the rate of transition (the transition probability per unit time) is $B_{ba} \rho(\omega_{ba}, t)$. Einstein made the reasonable assumption that this rate is proportional to the energy density of the field at the frequency of the transition, $\rho(\omega_{ba}, t)$ (Eq. (2.66) was not known at the time). The factor B_{ba} is now called the Einstein coefficient for absorption.

The second term in the right-hand side of Eq. (2.80),

$$[A_{ab} + B_{ab} \rho(\omega_{ba}, t)] N_b(t) dt,$$

is the number of atoms leaving the energy level E_b during the interval of time dt . The total rate of transition from E_b to E_a is thus the sum of a rate $B_{ab} \rho(\omega_{ba}, t)$ proportional to the energy density of the field and a rate A_{ab} which does not depend on the field. The former corresponds to emission induced by the field, and for this reason B_{ab} is called the Einstein coefficient for stimulated emission. The latter represents the rate at which an atom in E_b would emit a photon of energy $\hbar\omega_{ba}$ and decay to E_a even if there were no other photons in the cavity, which corresponds to spontaneous emission.

Note 1: The Einstein A- and B-coefficients are still often used. Eq. (2.79) exemplifies an approach, followed in countless investigations, in which the interaction of light with matter is modelled entirely in terms of populations and transition rates. Many phenomena can be understood within this approach. However, the picture it gives is not complete and may be wrong in certain cases. For instance, Eq. (2.79) does not explain the Rabi oscillations observed when atoms are exposed to coherent monochromatic light (see Section 1.7).

As time increases, such a system evolves towards a state of thermodynamic equilibrium in which $N_a(t)$ and $N_b(t)$ are constant. Setting $dN_b/dt = 0$ in Eq. (2.79) gives an equation relating the equilibrium values of N_a and N_b to the equilibrium energy density distribution, namely

$$B_{ba} \rho(\omega_{ba}) N_a = [A_{ab} + B_{ab} \rho(\omega_{ba})] N_b, \quad (2.81)$$

or, rearranging this equation,

$$\frac{N_b}{N_a} = \frac{B_{ba} \rho(\omega_{ba})}{A_{ab} + B_{ab} \rho(\omega_{ba})}. \quad (2.82)$$

However, at equilibrium, the atom numbers N_a and N_b follow a Boltzmann distribution, so that

$$\frac{N_b}{N_a} = \frac{g_b \exp(-E_b/k_B T)}{g_a \exp(-E_a/k_B T)} = \frac{g_b}{g_a} \exp(-\hbar\omega_{ba}/k_B T), \quad (2.83)$$

where k_B is Boltzmann constant. The constants g_a and g_b appearing in this equation are the degrees of degeneracy of the respective energy levels.⁶ Moreover, at equilibrium, the energy density distribution is given by Planck's law,

$$\rho(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{\exp(\hbar\omega/k_B T) - 1}. \quad (2.84)$$

As explained in Note 2 below, one can show that Eqs. (2.82), (2.83) and (2.84) are compatible at any temperature T only if

$$A_{ab} = \frac{\hbar \omega_{ba}^3}{\pi^2 c^3} B_{ab} \quad (2.85)$$

and

$$g_a B_{ba} = g_b B_{ab}. \quad (2.86)$$

(You will probably encounter these two relations in other courses, too.)

Note 2: Eqs. (2.85) and (2.86) can be obtained by making use of Eq. (2.84) to recast Eq. (2.82) in the form

$$\frac{N_b}{N_a} = \frac{B_{ba}}{C[\exp(\hbar\omega_{ba}/k_B T) - 1]A_{ab} + B_{ab}},$$

where $C = \pi^2 c^3 / \hbar \omega_{ba}^3$. Multiplying numerator and denominator by $\exp(-\hbar\omega_{ba}/k_B T)$ gives

$$\frac{N_b}{N_a} = \frac{B_{ba} \exp(-\hbar\omega_{ba}/k_B T)}{C[1 - \exp(-\hbar\omega_{ba}/k_B T)]A_{ab} + \exp(-\hbar\omega_{ba}/k_B T)B_{ab}}.$$

Equating the left-hand side of this equation to the right-hand side of Eq. (2.83) then gives a relation between A_{ab} , B_{ab} and B_{ba} which is possible for any value of T only if Eqs. (2.85) and (2.86) are fulfilled.

⁶The degree of degeneracy of an energy level is the number of distinct (linearly independent) states it corresponds to. For example, for an atom, states of same principal and angular momentum quantum numbers but different magnetic quantum numbers all have the same energy in the absence of a magnetic field. In this case, a state for which there would be, say, three possible values of the magnetic quantum number would have a degree of degeneracy g equal to 3.

How the coefficients B_{ba} and B_{ab} are related to the rates for absorption and stimulated emission found in the previous section is particularly simple if the energies E_a and E_b are not degenerate (i.e., if $g_a = g_b = 1$). Indeed, in this case, only one state (state a) has the energy E_a and only one state (state b) has the energy E_b . Hence, a transition between the energy levels E_a and E_b is necessarily a transition between state a and state b . The corresponding quantum mechanical transition rate is given by Eq. (2.66). Equating $B_{ba} \rho(\omega_{ba})$ to W_{ba} gives

$$B_{ba} = \frac{\pi e^2}{3\hbar^2 \epsilon_0} |\mathbf{r}_{ba}|^2. \quad (2.87)$$

Likewise, $B_{ab} \rho(\omega_{ba})$ can be equated to the quantum mechanical rate \bar{W}_{ab} for a transition from state b to state a by stimulated emission. The rate \bar{W}_{ab} is given by Eq. (2.67) but with states b and a interverted (recall that the rate \bar{W}_{ba} defined by Eq. (2.67) is the rate for a downward transition from state a to state b , whereas here the atom also goes down in energy but starts from state b and ends in state a):

$$\bar{W}_{ab} \approx \frac{\pi e^2}{3\hbar^2 \epsilon_0} |\mathbf{r}_{ab}|^2 \rho(\omega_{ba}). \quad (2.88)$$

Therefore

$$B_{ab} = \frac{\pi e^2}{3\hbar^2 \epsilon_0} |\mathbf{r}_{ab}|^2. \quad (2.89)$$

As $|\mathbf{r}_{ab}|^2 = |\mathbf{r}_{ba}|^2$ (see Problem 1 of Worksheet 4), $B_{ab} = B_{ba}$ here, in agreement with Eq. (2.86) (recall that we assume that $g_a = g_b = 1$). Furthermore, combining Eqs. (2.85) and (2.89) yields a quantum mechanical expression for the rate of spontaneous emission,

$$A_{ab} = \frac{e^2 \omega_{ba}^3}{3\pi \hbar \epsilon_0 c^3} |\mathbf{r}_{ab}|^2. \quad (2.90)$$

This rate is closely related to the radiative lifetime of state b (i.e., its lifetime if one ignores any decay process other than the spontaneous emission of light, such as collisions with other atoms). To see this, suppose that N_0 atoms are initially ($t = 0$) in state b . Suppose also that the atoms are not exposed to an electromagnetic field, so that no stimulated emission is possible, and that the light emitted in the decays leaves the medium without interacting with the atoms. The rate equation (2.79) then becomes

$$\frac{dN_b}{dt} = -A_{ab} N_b(t). \quad (2.91)$$

Solving this equation subject to the initial condition $N_b(t = 0) = N_0$ gives

$$N_b(t) = N_0 \exp(-t/\tau_b) \quad (2.92)$$

with

$$\tau_b = 1/A_{ab}. \quad (2.93)$$

The population of atoms in the upper state b thus decreases exponentially. The time τ_b is called the radiative lifetime of state b . As defined by Eq. (2.92), τ_b is the time at which the number of atoms in state b is a factor $1/e$ smaller than what it was initially. (It is important to understand that τ_b is merely a characteristic time for the decrease of the population in the excited state. The word “lifetime” should not suggest that atoms would have a particularly high probability to decay at times $t \approx \tau_b$, or that the process leading to the emission of a photon would take a time of about τ_b to complete.)

As shown by Eq. (2.93), τ_b is simply the inverse of the A-coefficient A_{ab} . The state is thus short-lived or long-lived depending on whether A_{ab} is large or small, which, as seen from Eq. (2.90), depends both on the magnitude of ω_{ba} and on the magnitude of $|\mathbf{r}_{ba}|$. If $A_{ab} = 0$, which happens if $|\mathbf{r}_{ba}| = 0$, then the radiative lifetime predicted by this theory is infinite (we will come back to this point in Section 2.9).

More generally, if state b can decay to several different final states — states a_1, a_2, \dots, a_N say — then one can assign an A-coefficient to each of these transitions and the lifetime τ_b is the inverse of the total A-coefficient:

$$\tau_b = 1/A_{\text{tot}} \quad (2.94)$$

with

$$A_{\text{tot}} = A_{a_1b} + A_{a_2b} + \dots + A_{a_Nb}. \quad (2.95)$$

Each of these final states defines a particular decay route. The “branching ratios”, namely the ratios

$$\frac{A_{a_1b}}{A_{\text{tot}}}, \frac{A_{a_2b}}{A_{\text{tot}}}, \dots, \frac{A_{a_Nb}}{A_{\text{tot}}},$$

are the probabilities that the decay occurs through the respective routes.

The relation between the Einstein coefficients and the microscopic theory is less straightforward if E_a or E_b are degenerate, as then there is no one-to-one correspondence between number of atoms in a certain energy level and number of atoms in a certain quantum state. However, radiative lifetimes can also be calculated from first principles, using the theory of Quantum Electrodynamics. The result is in agreement with the above and shows that Eqs. (2.90), (2.94) and (2.95) apply even if state b belongs to a degenerate energy level.

These considerations can be illustrated by the example of the $3p_{m=0}$ state of atomic hydrogen, neglecting spin-orbit coupling and other relativistic effects. This state can decay only to the 2p and 1s states. Indeed, the Bohr angular frequency ω_{ba} would be zero for a transition to a 3s or 3d state since they have the same energy as the $3p_{m=0}$ state; the corresponding A-coefficients would therefore be zero, which means a zero probability of transition. Moreover, only the 1s, 2s and 2p states are lower in energy than the $3p_{m=0}$ state. (A decay to

a state higher in energy would of course be impossible, by conservation of the energy.) As we will see in Section 2.9, the A-coefficient is also zero for a transition from a 3p state to a 2p state within the dipole approximation. Eq. (2.90) gives $A_{ab} = 0.22 \times 10^8 \text{ s}^{-1}$ for a transition to the 2s state and $1.67 \times 10^8 \text{ s}^{-1}$ for a transition to the 1s state. The total A-coefficient for this state is $1.90 \times 10^8 \text{ s}^{-1}$, which corresponds to a lifetime $\tau_b = 1/(1.90 \times 10^8 \text{ s}^{-1}) = 5.27 \text{ ns}$. Moreover, there is a 12% probability that the atom decays to the 2s state and an 88% probability that it decays to the ground state (12% and 88% are the branching ratios):

$$\frac{0.22 \times 10^8 \text{ s}^{-1}}{1.90 \times 10^8 \text{ s}^{-1}} = 0.12, \quad \frac{1.67 \times 10^8 \text{ s}^{-1}}{1.90 \times 10^8 \text{ s}^{-1}} = 0.88.$$

Other examples of the application of this formalism are given by the third homework of the course, in which Eq. (2.90) is used to calculate the lifetime of the $2p_{m=0}$ state of atomic hydrogen, and by one of the problems of Worksheet 5, in which you are invited to show that the rate of spontaneous decay from the $2p_{m=0}$ state is the same whether it is calculated using the “length” form of the Hamiltonian [(Eq. (2.27))] or its “velocity” form [(Eq. 2.28)].

2.8 The width of spectral lines

In this section: A brief introduction to line broadening; the natural width of a spectral line.

In the theory developed in the previous section, atoms initially in a state of energy $E_b^{(0)}$ emit photons of energy $\hbar\omega_{ba} = E_b^{(0)} - E_a^{(0)}$ when de-exciting spontaneously to a state of energy $E_a^{(0)}$. However, we should not ignore the fact that state b has a finite lifetime since it decays. Its energy is therefore not perfectly well defined but has a certain uncertainty δE_b . Hence, if state a is stable and well defined in energy, the photons emitted will have a range of energies extending from about $\hbar\omega_{ba} - \delta E_b/2$ to about $\hbar\omega_{ba} + \delta E_b/2$. If recorded with a spectrometer of sufficient resolution, and if there is no other line broadening mechanism, the spectral line would thus have a width $\delta\omega = \delta E_b/\hbar$ in angular frequency. Taking $\delta E_b = \hbar/\tau_b$, where τ_b is the lifetime of state b ,

$$\delta\omega = 1/\tau_b. \quad (2.96)$$

The width of a spectral line arising from the finite lifetime of the initial (or final) state is called the natural width of the line. As many other broadening mechanisms may also play a role, the observed width of a spectral line is often much larger than its natural width; however, in the right experimental conditions, the width is essentially the natural width.

Note 1: The choice of taking δE_b exactly equal to \hbar/τ_b may seem arbitrary, although one would indeed expect that $\delta E_b \approx \hbar/\tau_b$ since the atom has a high probability to decay within an interval of time τ_b after it has been excited to state b . However, there is a good reason for making this choice: an in depth analysis of the process shows that the full width at half maximum of the angular frequency distribution of the emitted photons is $1/\tau_b$. If both state a and state b are unstable, then one finds that the full width at half maximum of this distribution is $1/\tau_a + 1/\tau_b$.

Note 2: The above ignores the recoil shift, which is absent when the interaction is described within the dipole approximation. The difference $E_b^{(0)} - E_a^{(0)}$ is the change in the internal energy of the atom. However, because photons carry momentum, an atom recoils upon emitting a photon. This changes the kinetic energy of the atom as a whole. Hence, by energy conservation, the energy of the emitted photon differs from the value $\hbar\omega_{ba}$ it would have if the atom did not recoil. The difference between the emitted energy and $\hbar\omega_{ba}$ is called the recoil shift. This shift is often negligible for photons emitted by atoms, although there are cases where it needs to be taken into account (e.g., for transitions involving the very long-lived states used in some atomic clocks). It can be significant for photons emitted by excited nuclei.

Amongst the other line broadening mechanisms, the two most important ones are often collisional broadening and Doppler broadening.

- Collisional broadening: This refers to the broadening of the spectral lines arising from interactions involving the atoms or molecules emitting the light such as collisions with other atoms. These interactions both shift the energy levels and perturb the wave function, which often results in line widths much larger than the natural width.
- Doppler broadening: The spectral lines will be also broadened by the Doppler effect if the atoms or molecules emitting the light do not all move with the same velocity with respect to the observer. Different relative velocities means different Doppler shift, and therefore a distribution of velocities translates into a distribution of observed frequencies. This effect is often large enough to mask the natural width of the lines completely.

Note 3: A very common origin of Doppler broadening is the thermal motion of the atoms (or molecules) emitting the light. Consider, for instance, atoms or molecules forming a gas cloud. Each of these emitters has a certain velocity

$$\mathbf{v} = v_x \hat{\mathbf{x}} + v_y \hat{\mathbf{y}} + v_z \hat{\mathbf{z}}$$

with respect to an observer recording a spectrum of the light they emit. Let us take the z -axis of the system of coordinates to be in the direction in which the observer sees the cloud. Then, if the angular frequency of an emitted photon is ω_0 in the reference frame of the atom or molecule which emitted it, and this atom or molecule has a velocity v_z in the z -direction, the angular frequency recorded by the observer is ω with

$$\omega = \omega_0(1 - v_z/c). \quad (2.97)$$

(We assume that the emitters move at non-relativistic speeds, so that we don't need to go beyond the first order in v_z/c . Here $v_z < 0$ when the emitter moves towards the observer and $v_z > 0$ when it moves away.) Assuming that the atoms cloud is in thermal equilibrium at a temperature T , the velocities v_z follow a Maxwell-Boltzmann distribution. (See Young and Freedman. However, note that the distribution in question is a distribution of velocities in a given direction, not a distribution of speeds.) Accordingly, the number of emitters with a velocity between v_z and $v_z + dv_z$ in the z -direction is a certain dN given by the equation

$$dN = N_0 \sqrt{\frac{M}{2\pi k_B T}} \exp\left(-\frac{M v_z^2}{2k_B T}\right) dv_z, \quad (2.98)$$

where N_0 is the total number of emitters (atoms or molecules) and M is the mass of one of these emitters. Unless other line broadening mechanisms would be significant, this distribution of velocities translates into a distribution of angular frequencies $I(\omega)$ of the recorded light with

$$I(\omega) \propto \exp\left[-\frac{M c^2}{2k_B T} \left(\frac{\omega - \omega_0}{\omega_0}\right)^2\right]. \quad (2.99)$$

$I(\omega)$ is a Gaussian distribution peaking at $\omega = \omega_0$. As can be checked easily, its full width at half maximum is given by the relatively complicated equation

$$\Delta\omega = \frac{2\omega_0}{c} \sqrt{\frac{2 \ln 2 k_B T}{M}}. \quad (2.100)$$

(By definition of the full width at half maximum, $I(\omega_0 \pm \Delta\omega/2) = I(\omega_0)/2$). The main message of this equation is that the thermal Doppler width increases with temperature, which is not surprising.

Spectral lines are often broadened not only by this thermal Doppler effect or other mechanisms imparting a Gaussian profile to the lines, but also by other mechanisms. The resulting line profiles may then be more complex than obtained here.

2.9 Selection rules

In this section: Selection rules for electric dipole transitions in atomic hydrogen; parity.

You may remember that the first homework of the course involved, amongst other things, to calculate the probability for a transition from the 1s to the 2s state for a hydrogen atom exposed to an electric field oriented in the z -direction. The answer was that this probability is zero in first order of time-dependent perturbation theory because

$$\int \psi_{200}^*(\mathbf{r}) z \psi_{100}(\mathbf{r}) d^3r = 0, \quad (2.101)$$

where $\psi_{100}(\mathbf{r})$ and $\psi_{200}(\mathbf{r})$ are the wave functions of, respectively, the 1s state and the 2s state of the field-free Hamiltonian. Recall that the factor z sandwiched between $\psi_{200}^*(\mathbf{r})$ and $\psi_{100}(\mathbf{r})$ originates from the perturbation $e\mathcal{E} \cdot \mathbf{r}$, which for a field \mathcal{E} oriented in the z -direction is simply $e|\mathcal{E}|z$.

There are different ways of showing that this integral vanishes. The approach followed in the model solution was to note that $z = r \cos \theta$ and that the wave functions $\psi_{100}(\mathbf{r})$ and $\psi_{200}(\mathbf{r})$ are both of the form $R(r)Y_{00}(\theta, \phi)$, where $R(r)$ is a function of r only. (The relevant spherical harmonic is $Y_{00}(\theta, \phi)$ since s-states have $l = m = 0$.) The implication is that

$$\int \psi_{200}^*(\mathbf{r}) z \psi_{100}(\mathbf{r}) d^3r \propto \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi Y_{00}^*(\theta, \phi) \cos \theta Y_{00}(\theta, \phi). \quad (2.102)$$

Since $Y_{00}(\theta, \phi) = (4\pi)^{-1/2}$, we see that

$$\int \psi_{200}^*(\mathbf{r}) z \psi_{100}(\mathbf{r}) d^3r \propto \int_0^\pi d\theta \sin \theta \cos \theta, \quad (2.103)$$

which is zero.

Eq (2.101) can also be obtained in the following way: First, we note that $\psi_{100}(\mathbf{r})$ and $\psi_{200}(\mathbf{r})$ do not depend on the direction of the vector \mathbf{r} since the spherical harmonic $Y_{00}(\theta, \phi)$ is a constant. These two wave functions thus depend on the x -, y - and z -coordinates of the electron only through the norm of \mathbf{r} , which is $(x^2 + y^2 + z^2)^{1/2}$. Let us compare the value of the product $\psi_{200}^*(\mathbf{r}) z \psi_{100}(\mathbf{r})$ at a point of position vector \mathbf{r}_0 to its value at the point of position vector $-\mathbf{r}_0$. The first point has the coordinates (x_0, y_0, z_0) , the second the coordinates $(-x_0, -y_0, -z_0)$. As \mathbf{r}_0 and $-\mathbf{r}_0$ have the same norm, $\psi_{100}(-\mathbf{r}_0) = \psi_{100}(\mathbf{r}_0)$ and $\psi_{200}^*(-\mathbf{r}_0) = \psi_{200}^*(\mathbf{r}_0)$. However, since z changes sign, the value of $\psi_{200}^*(\mathbf{r}) z \psi_{100}(\mathbf{r})$ at $\mathbf{r} = -\mathbf{r}_0$ is the negative of its value at $\mathbf{r} = \mathbf{r}_0$. Hence, the contribution to the integral of the point at $\mathbf{r} = -\mathbf{r}_0$ cancels the contribution of the point at $\mathbf{r} = \mathbf{r}_0$. Since this is the case for any position vector \mathbf{r}_0 , the whole integral is necessarily

zero, which is Eq (2.101). In fact, for the same reason, we would also have that

$$\int \psi_{200}^*(\mathbf{r}) x \psi_{100}(\mathbf{r}) d^3r = 0, \quad (2.104)$$

$$\int \psi_{200}^*(\mathbf{r}) y \psi_{100}(\mathbf{r}) d^3r = 0. \quad (2.105)$$

As a consequence, the transition probability is zero for *any* orientation of the electric field: Indeed, if

$$\boldsymbol{\mathcal{E}} = \mathcal{E}_x \hat{\mathbf{x}} + \mathcal{E}_y \hat{\mathbf{y}} + \mathcal{E}_z \hat{\mathbf{z}}, \quad (2.106)$$

then the interaction Hamiltonian reads

$$e\boldsymbol{\mathcal{E}} \cdot \mathbf{r} = e\mathcal{E}_x x + e\mathcal{E}_y y + e\mathcal{E}_z z \quad (2.107)$$

and the transition probability is proportional to

$$e^2 \left| \int \psi_{200}^*(\mathbf{r}) (\mathcal{E}_x x + \mathcal{E}_y y + \mathcal{E}_z z) \psi_{100}(\mathbf{r}) d^3r \right|^2,$$

which is zero in view of Eqs. (2.101), (2.104) and (2.105).

Note 1: In fact, one can immediately see that the transition probability must be zero for any direction of the electric field if it is zero for the z -direction: since the initial and final states are spherically symmetric (they do not depend on the angles), the transition probability cannot depend on the direction of the electric field...

Now, in the above we have not made any use of the fact that $\psi_{100}(\mathbf{r})$ and $\psi_{200}(\mathbf{r})$ are wave functions of states with principal quantum number $n = 1$ or 2 . Hence,

$$x_{ba} = y_{ba} = z_{ba} = 0 \quad (2.108)$$

and

$$\mathbf{r}_{ba} = x_{ba} \hat{\mathbf{x}} + y_{ba} \hat{\mathbf{y}} + z_{ba} \hat{\mathbf{z}} = 0 \quad (2.109)$$

for transitions between *any* s-states. Therefore, within the theory developed in Section 2.5 an electromagnetic field cannot induced a transition (absorption or stimulated emission of a photon) between two s-states, and an s-state cannot spontaneously decay to another s-state.

This impossibility is a particular case of a more general rule: Within the dipole approximation, absorption or emission of a photon by a hydrogen atom is possible only if the initial and final states have orbital angular momentum quantum numbers differing by exactly 1. In other words, within the dipole

approximation, and to first order of perturbation theory, a radiative transition can take place between a state a with quantum numbers n_a, l_a, m_a , and a state b with quantum numbers n_b, l_b, m_b only if

$$l_b = l_a \pm 1. \quad (2.110)$$

Note 2: This result cannot be proved by a short calculation without a specialist knowledge of the properties of associated Legendre functions. A rather lengthy proof based on the commutation relations between the angular momentum operators and the vector \mathbf{r} can be found in Griffiths.

The first homework also involved showing that the probability of a transition to the $2p_{m=1}$ state is zero, too, if the atom is initially in the $1s$ state and the electric field is oriented in the z -direction. This is a particular case of a more general rule, which is that an electric field oriented in the z -direction cannot induce a transition between states of different magnetic quantum numbers. The proof is relatively simple:

Proof

For a field oriented in the z -direction, the probability of a transition between a state a with quantum numbers n_a, l_a, m_a , and a state b with quantum numbers n_b, l_b, m_b is proportional to

$$\left| \int \psi_{n_b l_b m_b}^*(\mathbf{r}) z \psi_{n_a l_a m_a}(\mathbf{r}) d^3 r \right|^2.$$

The factor z is simply $r \cos \theta$ in spherical polar coordinates, and therefore does not depend on the angle ϕ . The wave functions $\psi_{n_a l_a m_a}(\mathbf{r})$ and $\psi_{n_b l_b m_b}(\mathbf{r})$ depend on the angle ϕ only through the spherical harmonics $Y_{l_a m_a}(\theta, \phi)$ and $Y_{l_b m_b}(\theta, \phi)$. However, a spherical harmonic $Y_{lm}(\theta, \phi)$ is a product of a normalization constant, a function of θ , and the complex exponential $\exp(im\phi)$ (see your notes from last year, or Section 4.1 of the QM Primer). Hence,

$$\int \psi_{n_b l_b m_b}^*(\mathbf{r}) z \psi_{n_a l_a m_a}(\mathbf{r}) d^3 r \propto \int_0^{2\pi} \exp(-im_b \phi) \exp(im_a \phi) d\phi. \quad (2.111)$$

It is not difficult to show that⁷

$$\int_0^{2\pi} \exp[i(m_a - m_b)\phi] d\phi = \begin{cases} 2\pi & m_a = m_b, \\ 0 & m_a \neq m_b. \end{cases} \quad (2.112)$$

⁷The calculation uses the fact that $\exp(2\pi mi) = 1$ when m is an integer.

Therefore, when $m_a \neq m_b$

$$\left| \int \psi_{n_b l_b m_b}^*(\mathbf{r}) z \psi_{n_a l_a m_a}(\mathbf{r}) d^3r \right|^2 = 0 \quad (2.113)$$

and the transition probability is zero. Q.E.D.

In short, when the electric field is oriented in the z -direction, the perturbation Hamiltonian is independent of ϕ and therefore cannot change how the wave function varies with ϕ .

One can show, through similar arguments, that for an electric field oriented in the x - or y -direction the transition probability is zero if $m_a \neq m_b \pm 1$. Likewise, one can also show that within the dipole approximation a hydrogen atom initially in a state with a magnetic quantum number m_b can emit a photon and spontaneously decay to a state with a magnetic quantum number m_a only if

$$m_b = m_a \quad \text{or} \quad m_b = m_a \pm 1. \quad (2.114)$$

(Be careful not to be confused: If one exposes an atom in a state a to a field *polarized* in the z -direction, then the probability of a transition to a state b higher in energy can be non-zero only if $m_a = m_b$, and similarly for the probability of a transition from b to a by stimulated emission. However, for absorption or stimulated emission in an *unpolarized* field and for spontaneous decay, the transition probability can also be non-zero when $m_a = m_b + 1$ or $m_b - 1$.)

The conditions expressed by Eqs. (2.110) and (2.114) are selection rules, i.e., rules which say which transitions would be impossible for a certain interaction. Transitions violating these rules are said to be forbidden. Forbidden transitions may still occur, as selection rules are generally based on approximations and are rarely absolute, but usually are much less probable than allowed transitions. For example:

- An hydrogen atom in the $3d_{m=0}$ state cannot spontaneously decay to the $1s$ state according to this rule: since $l = 2$ for a d-state and 0 for an s-state, $|l_a - l_b|$ would be 2 for this transition, not 1 as required by Eq. (2.110) and therefore the transition is forbidden.
- By contrast, the $3d_{m=0}$ state may decay to a $2p$ state, as in this case $|l_a - l_b| = 2 - 1 = 1$ and the transition is allowed.
- An hydrogen atom in the $3d_{m=0}$ state may still decay directly to the $1s$ state, but the probability that this happens is about 20,000 times smaller than the probability of a decay to the $2p$ state. A $3d$ state decays directly to the $1s$ state primarily through an “electric quadrupole transition”, a type of radiative transition not amenable to calculations based on the dipole approximation.

- An hydrogen atom in the 2s state or in a 2p state can only decay to the 1s state, since amongst the other eigenstates of the field-free Hamiltonian only the 1s state is lower in energy. However, a transition from the 2s state to the 1s state is forbidden by the above selection rule, whereas a transition from the 2p state to the 1s state is allowed. The 2s state has therefore a much longer lifetime than the 2p state.
- In fact, the 2s state has a negligibly small probability to decay by emission of one photon. An atom prepared in the 2s state and left completely by itself would decay primarily through the emission of two photons. The rate for this process is very small indeed, which gives the 2s state an extraordinarily long radiative lifetime compared to the 2p states: the lifetime of the 2s state is about 0.13 s, almost 100 million times longer than the lifetime of a 2p state (1.6 ns). States with very long lifetimes are said to be metastable. (In practice, an atom in the 2s state is likely to decay to the ground state on a much shorter time scale, due to collisions or to some other interaction with its surrounding.)

The selection rules mentioned here apply to “electric dipole transitions” between non-relativistic states of atomic hydrogen. Similar selection rules also exist for atoms more complex than hydrogen, for molecules, for nuclei, etc., and also for other types of transition.

Note 3: Two proofs of Eq. (2.101) were given at the beginning of this section. The second one was based on the fact that the product $\psi_{200}^*(\mathbf{r})z\psi_{100}(\mathbf{r})$ changes sign when z is changed into $-z$. As mentioned, the same reasoning also leads to Eqs. (2.104) and (2.105). In fact, it also applies for any initial and final states. Changing x into $-x$, y into $-y$ and z into $-z$ is called a reversal of space, or a reflection through the origin. As it is easy to visualize, this transformation changes right into left and left into right. (E.g., draw a right-handed system of three axes pointing in the *positive* x -, y - and z -directions, and compare with a system of three axes pointing in the *negative* x -, y - and z -directions. A transformation which swap left and right is called a parity transformation.)

The wave functions $\psi_{nlm}(\mathbf{r})$ (the field-free eigenfunctions of atomic hydrogen) are either even or odd under this transformation. Namely, for given quantum numbers n , l and m , one has either that $\psi_{nlm}(-\mathbf{r}) = \psi_{nlm}(\mathbf{r})$, in which case the wave function $\psi_{nlm}(\mathbf{r})$ is said to be of even parity, or that $\psi_{nlm}(-\mathbf{r}) = -\psi_{nlm}(\mathbf{r})$, in which case $\psi_{nlm}(\mathbf{r})$ is said to be of odd parity. Therefore, if $\psi_{n_a l_a m_a}(\mathbf{r})$ and $\psi_{n_b l_b m_b}(\mathbf{r})$ are both of even parity or both of odd parity, the product $\psi_{n_b l_b m_b}^*(\mathbf{r})\psi_{n_a l_a m_a}(\mathbf{r})$ does not change sign when \mathbf{r} is changed by $-\mathbf{r}$. Repeating the reasoning above, one easily sees that in that case

$$\begin{aligned}
\int \psi_{n_b l_b m_b}^*(\mathbf{r}) x \psi_{n_a l_a m_a}(\mathbf{r}) &= \\
\int \psi_{n_b l_b m_b}^*(\mathbf{r}) y \psi_{n_a l_a m_a}(\mathbf{r}) &= \int \psi_{n_b l_b m_b}^*(\mathbf{r}) z \psi_{n_a l_a m_a}(\mathbf{r}) = 0.
\end{aligned}
\tag{2.115}$$

Hence, for a transition to be possible within the dipole approximation, the initial and final states must have opposite parity.

For atomic hydrogen, there is a simple correspondence between the parity of the wave function and the value of the orbital angular momentum quantum number l . Indeed, in spherical polar coordinates, a reflection through the origin amounts to replacing θ by $\pi - \theta$ and ϕ by $\phi + \pi$, without changing r , and it turns out that

$$Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi). \tag{2.116}$$

(A proof of this equation is given in Appendix H for interest.) Since the wave functions $\psi_{nlm}(\mathbf{r})$ are proportional to $Y_{lm}(\theta, \phi)$ and have no other dependence in θ or ϕ , these wave functions are of even parity for even values of l (0, 2, ...), and of odd parity for odd values of l (1, 3, ...). Hence, for atomic hydrogen, the parity selection rule amounts to saying that a transition is not possible if $|l_b - l_a|$ is an even number. However, we were already aware of this impossibility since we have seen that the transition is forbidden if $|l_b - l_a|$ is not equal to 1. Hence, the parity selection rule does not anything new here. (It is relevant for complex atoms and various other systems, though.)

Note 4: Selection rules are related to the question of how quantum states and interactions vary under certain transformations such as rotations or reflections — i.e., to questions of symmetry, in the sense this word has in Physics. The derivation of selection rules for complicated systems such as non-linear molecules or complex atoms is often based on concepts of Group Theory, the mathematical theory of symmetry.