TILLEGG 15

15 Semi-classical Radiation Theory

We would really like to study processes involving emission or absorption of single photons. However, this requires quantization of the electromagnetic field, which is treated in a more advanced course. In the present course we therefore have to rely on the so-called semi-classical radiation theory, in which the radiation field is treated as a classical field. The interactions between the particles and the radiation field then correspond to certain interaction terms in the Hamiltonian, which are treated by time-dependent perturbation theory. The particles, including the Coulomb interactions between them, are treated quantum-mechanically. That is why this is called a semi-classical radiation theory. The presentation given here follows chapter 12 in Hemmer’s book quite closely. References will be given also to relevant sections in Bransden & Joachain (B&J) and in Griffiths (G).

15.1 Charged particle in external field

(H 12.1, B&J 11.1)

15.1.a The Schrödinger equation

If the Hamiltonian for a single particle without the electromagnetic field present is

\[ \tilde{H}_0 = \frac{\hat{p}^2}{2m} + U(r, t), \]

then according to the so-called minimal-coupling recipe, the Hamiltonian in the presence of the electromagnetic field is obtained by the substitutions

\[ \tilde{H}_0 \rightarrow \tilde{H} - q\Phi(r, t) \]

\[ \hat{p} \rightarrow \hat{p} - qA(r, t). \]

Here, \( q \) is the charge of the particle and \( A(r, t) \) and \( \Phi(r, t) \) are the vector and scalar potentials of the field, defined by

\[ B = \nabla \times A \quad \text{and} \quad E = -\nabla \Phi - \frac{\partial A}{\partial t}. \]

\( ^1 \)The potential \( U(r, t) \) represents possible non-electromagnetic forces.
This substitution gives
\[ \vec{H} - q\Phi = \frac{1}{2m}(\vec{p} - qA)^2 + U(r, t). \]

This recipe is the same as the one used in classical mechanics. (See, e.g., Appendix A in Hemmer.) In the absence of non-electromagnetic forces \((U(r, t) = 0)\) we then arrive at the following one-particle Schrödinger equation:

\[ i\hbar \frac{\partial \Psi}{\partial t} = \left[ \frac{1}{2m}(\vec{p} - qA)^2 + q\Phi \right] \Psi, \quad \left( \vec{p} \equiv \frac{\hbar}{i} \nabla \right). \tag{T15.2} \]

### 15.1.b Gauge transformations of the potentials

The physical fields
\[ \mathbf{B} = \nabla \times \mathbf{A} \quad \text{and} \quad \mathbf{E} = -\nabla \Phi - \frac{\partial \mathbf{A}}{\partial t} \]
do not define the potentials \( \mathbf{A} \) and \( \Phi \) uniquely. Thus, if \( \mathbf{A} \) and \( \Phi \) are a suitable choice, we may just as well replace them by a new set of potentials:

\[ \begin{align*}
A(r, t) &\rightarrow A'(r, t) = A(r, t) + \nabla \chi(r, t), \\
\Phi(r, t) &\rightarrow \Phi'(r, t) = \Phi(r, t) - \frac{\partial \chi(r, t)}{\partial t},
\end{align*} \tag{T15.3} \]

where \( \chi(r, t) \) is an arbitrary differentiable function. This so-called **gauge transformation**\(^2\) does not alter the fields, because

\[ \nabla \times \mathbf{A}' = \nabla \mathbf{A} + \nabla \times \nabla \chi = \nabla \times \mathbf{A} \]

and

\[ -\nabla \Phi' - \frac{\partial A'}{\partial t} = -\nabla \Phi - \frac{\partial \mathbf{A}}{\partial t} + \left( \nabla \frac{\partial}{\partial t} - \frac{\partial}{\partial t} \nabla \right) \chi = -\nabla \Phi - \frac{\partial \mathbf{A}}{\partial t} \]

for an arbitrary function \( \chi(r, t) \).

The freedom to make gauge transformations is in general an advantage, because it allows us to "choose the gauge" that is most suitable for each problem. In the present context we shall use the so-called **Coulomb gauge**, where we choose the vector potential in such a way that it is divergence-free:

\[ \nabla \cdot \mathbf{A}(r, t) = 0. \quad \text{(Coulomb gauge)} \tag{T15.4} \]

Maxwell’s equation \( \nabla \cdot \mathbf{E} = \rho/\epsilon_0 \) then gives

\[ \nabla \cdot \left( \frac{\partial \mathbf{A}}{\partial t} - \nabla \Phi \right) = -\nabla^2 \Phi(r, t) = \rho(r, t)/\epsilon_0, \]

\(^2\)The pronunciation of **gauge** is similar to that of cage and rage. A commonly used Norwegian term is "juster-transformasjon".
which we recognize as Poisson’s equation, with the solution

$$\Phi(r, t) = \int \frac{\rho(r', t)d^3r'}{4\pi\varepsilon_0|\mathbf{r} - \mathbf{r}'|} \left( \text{Instantaneous Coulomb potential} \right).$$  \hspace{1cm} (T15.5)

Here we note that the scalar potential $\Phi$ at $\mathbf{r}, t$ is given by the charge distribution $\rho(\mathbf{r}', t)$ at the same instant $t$. It is therefore called the instantaneous Coulomb potential. The gauge corresponding to the choice $\nabla \cdot \mathbf{A} = 0$ is therefore called the Coulomb gauge.

The fact that the Schrödinger equation involves the gauge-dependent potentials (rather than the unique physical fields) may perhaps cause you to worry — it means in fact that the wave function will depend on our choice of gauge. However, we shall see that this gauge dependence enters the wave function only in terms of a phase factor. Thus, measurable quantities like the probability density and expectation values turn out to be gauge independent. To see how this comes about, let $\Psi'$ be the solution of the Schrödinger equation with the transformed potentials,

$$i\hbar \frac{\partial \Psi'}{\partial t} = \left[ \frac{1}{2m} (\mathbf{\hat{p}} - q\mathbf{A'})^2 + q\Phi' \right] \Psi'.$$  \hspace{1cm} (T15.6)

We want to find out how the solution $\Psi'$ of this equation is related to the solution $\Psi$ for the original potentials, which satisfies (T15.2),

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[ \frac{1}{2m} (\mathbf{\hat{p}} - q\mathbf{A})^2 + q\Phi \right] \Psi.$$

Inserting

$$\mathbf{A} = \mathbf{A'} - \nabla \chi \quad \text{and} \quad \Phi = \Phi' + \frac{\partial \chi}{\partial t}$$

into the latter equation, moving the term $\frac{q\partial \chi}{\partial t}$ to the left side, and multiplying on both sides by $\exp(\frac{iq\chi}{\hbar})$, we have

$$e^{\frac{iq\chi}{\hbar}} \left| i\hbar \frac{\partial \Psi}{\partial t} - q\Psi \frac{\partial \chi}{\partial t} = \left[ \frac{1}{2m} \left( \frac{\hbar}{i}\nabla - q\mathbf{A'} + q\nabla \chi \right)^2 + q\Phi' \right] \Psi; \quad \Downarrow \quad \frac{\hbar}{i}\nabla f(r, t)e^{\frac{iq\chi}{\hbar}} = e^{\frac{iq\chi}{\hbar}} \left( \frac{\hbar}{i}\nabla - q\mathbf{A'} + q\nabla \chi \right) f(r, t),$$

we have the identity

$$e^{\frac{iq\chi}{\hbar}} \left( \frac{\hbar}{i}\nabla - q\mathbf{A'} + q\nabla \chi \right) f = \left( \frac{\hbar}{i}\nabla - q\mathbf{A'} \right) e^{\frac{iq\chi}{\hbar}} f,$$

which may be used twice to move the exponential function in (T15.7) to the right. The result is

$$i\hbar \frac{\partial}{\partial t} \left[ \Psi e^{\frac{iq\chi}{\hbar}} \right] = \left[ \frac{1}{2m} \left( \frac{\hbar}{i}\nabla - q\mathbf{A'} \right)^2 + q\Phi' \right] \Psi e^{\frac{iq\chi}{\hbar}}.$$  \hspace{1cm} (T15.8)
We can conclude that (T15.6), with the transformed potentials, is satisfied by
\[ \Psi' = \Psi e^{iq\chi/\hbar}. \]

Thus, as announced, the two wave functions differ only by a phase factor. The freedom to multiply the wave function by a \textbf{global phase factor} (independent of \( r \) and \( t \)) is something we learnt about a long time ago. What we see here, is that we may even multiply the wave function by a \textbf{local phase factor} \( \exp\left[iq\chi(r, t)/\hbar\right] \) if we compensate by adjusting the potentials accordingly; we are allowed to make the gauge transformation
\[
\Psi(r, t) \rightarrow \Psi'(r, t) = \Psi(r, t) \exp\left[iq\chi(r, t)/\hbar\right],
\]
\[
A(r, t) \rightarrow A'(r, t) = A(r, t) + \nabla\chi(r, t),
\]
\[
\Phi(r, t) \rightarrow \Phi'(r, t) = \Phi(r, t) - \frac{\partial\chi(r, t)}{\partial t}.
\] (T15.9)

15.2 The field as a perturbation

(H 12.2, B&J 11.1)

15.2.a Interaction terms

Here we consider a charged particle together with a pure radiation field. This means that there is no “external” charge distribution \( \rho(r, t) \). Thus, \( \Phi(r, t) \) equals zero in the Coulomb gauge (\( \nabla \cdot A = 0 \)). Then we may write the Hamiltonian as
\[
\widehat{H} = \frac{1}{2m} (\hat{p} - qA)^2 = \widehat{H}_0 + \widehat{H}',
\]
where \( \widehat{H}_0 = \hat{p}^2/2m \) and
\[
\widehat{H}' = \widehat{H} - \widehat{H}_0 = \frac{1}{2m} \left[ (\hat{p} - qA)^2 - \hat{p}^2 \right]
\]
\[
= -\frac{q}{2m} (\hat{p} \cdot A - A \cdot \hat{p}) + \frac{q^2A^2}{2m}.
\]
In the Coulomb gauge, the momentum operator commutes with the vector potential; for an arbitrary function \( f(r, t) \) we have
\[
\hat{p} \cdot A f(r, t) = \frac{\hbar}{i} \nabla (A f) = \frac{\hbar}{i} (\nabla \cdot A) f + A \cdot \frac{\hbar}{i} \nabla f = A \cdot \hat{p} f(r, t).
\] (T15.10)

Thus, the interaction between the charged particle and the radiation field is represented by the interaction terms
\[
\widehat{H}' = -\frac{q}{m} A \cdot \hat{p} + \frac{q^2A^2}{2m} \equiv \widehat{H}'_1 + \widehat{H}'_2.
\] (T15.11)
For a system of particles (like e.g. the hydrogen atom), we may similarly write
\[ \hat{H} = \hat{H}_p + \hat{H}', \]  
(T15.12)
where
\[ \hat{H}_p = \sum_i \frac{\hat{p}_i^2}{2m_i} + V_C(r_1, r_2, \cdots) \]  
(T15.13)
is the Hamiltonian in the absence of the radiation field (but including the Coulomb interaction terms between the charged particles), and
\[ \hat{H}' = \sum_i \left\{ -\frac{q_i}{m_i} \mathbf{A}(r_i, t) \cdot \hat{p}_i + \frac{q_i^2}{2m_i} [\mathbf{A}(r_i, t)]^2 \right\} \]  
(T15.14)
represents the interaction between the charged particles and the radiation field.

In what follows we shall treat \( \hat{H}' \) as a perturbation. Thus the initial and final states will be eigenstates of \( \hat{H}_p \). We shall limit ourselves to considering processes for which the transition probability is given dominantly by the first-order contribution due to the term

\[ \hat{H}' = -\frac{q}{m} \mathbf{A} \cdot \hat{p}, \]  
(T15.15)
and for which the \( \mathbf{A}^2 \) term gives negligible contributions.

### 15.2.b The radiation field

Applying the Coulomb gauge (\( \nabla \cdot \mathbf{A} = 0 \)) for the radiation field, we see from (T15.5) that far away from the sources we may set the scalar field \( \Phi(r, t) \) equal to zero. Thus the physical fields

\[ \mathbf{E} = -\frac{\partial \mathbf{A}(r, t)}{\partial t} \quad \text{and} \quad \mathbf{B} = \nabla \times \mathbf{A}(r, t) \]

may both be expressed in terms of the vector potential \( \mathbf{A}(r, t) \). This potential can be written as a superposition of plane harmonic waves of the type

\[ \mathbf{A}(r, t) \propto e^{i(k \cdot r - \omega t)} \mathbf{e}_k \quad (\omega = ck). \]

Here, the unit vector \( \mathbf{e}_k \) is a polarization vector (giving the direction of \( \mathbf{E} \)). We shall consider a simple monochromatic wave

\[ \mathbf{A}(r, t) = 2A_0 \mathbf{e}_k \cos(k \cdot r - \omega t) = A_0 \left( \mathbf{e}_k e^{i(k \cdot r - \omega t)} + \text{complex conj.} \right), \]  
(T15.16)
corresponding to the fields

\[ \mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t} = -2\omega A_0 \mathbf{e}_k \sin(k \cdot r - \omega t) \]  
(T15.17)
\[ \mathbf{B} = \nabla \times \mathbf{A} = -2A_0(k \times \mathbf{e}_k) \sin(k \cdot r - \omega t). \]

Here, we note that due to the condition

\[ \nabla \cdot \mathbf{A} = A_0 \mathbf{e}_k \cdot \nabla \cos(k \cdot r - \omega t) = -A_0 \sin(k \cdot r - \omega t) \mathbf{e}_k \cdot \mathbf{k} = 0, \]  
(T15.18)
the polarization vector \( \mathbf{e}_k \) is perpendicular to the propagation vector \( \mathbf{k} \). Thus, \( \mathbf{E} \) is transverse to \( \mathbf{k} \), and \( \mathbf{B} \) is transverse to \( \mathbf{k} \) and \( \mathbf{E} \), as shown in the figure on the left.
As shown in the figure on the right, we may choose to work with two real orthogonal polarization vectors $\vec{e}_1$ and $\vec{e}_2$.  

We shall later need the relation between the amplitude $A_0$ and the energy density of the plane wave, which is

$$\frac{1}{2} \varepsilon_0 E^2 + \frac{1}{2} \mu_0 B^2 = \frac{1}{2} \varepsilon_0 (E^2 + c^2 B^2) \quad \left(\mu_0 \varepsilon_0 = 1/c^2\right)$$

$$= \frac{1}{2} \varepsilon_0 (2A_0)^2 \sin^2 (\mathbf{k} \cdot \mathbf{r} - \omega t) (\omega^2 + c^2 k^2).$$

Averaged over time the energy density of the harmonic wave (T15.15) then is

$$u = 2 \varepsilon_0 A_0^2 \omega^2,$$

(T15.19)
corresponding to an energy flux $I = uc = 2 \varepsilon_0 A_0^2 \omega^2 c$.

15.3 Transitions between atomic states

(H 12.3, B&J 11.2, G 9.2)

In sections 14.5 and 14.6 we considered respectively the cases of discrete $\rightarrow$ continuous transitions (e.g. ionization) and continuous $\rightarrow$ continuous transitions (e.g. scattering on a static potential) and established Fermi’s golden rule. We shall now consider the case of discrete $\rightarrow$ discrete transitions, where an electromagnetic wave induces either excitation of an atom (via absorption) or de-excitation (via stimulated emission):

**absorption**

\[ \omega_{fi} = \frac{E_2 - E_1}{\hbar} > 0 \]

**stimulated emission**

\[ \omega_{fi} = \frac{E_1 - E_2}{\hbar} < 0 \]

We assume (to begin with) that the incident beam of radiation is a mixture of harmonic waves with a quasi-continuous frequency distribution, so that the number of waves (i.e. frequencies) in the interval $\Delta \omega$ is $\rho(\omega) \Delta \omega$. Each of these waves is of the type (T15.16),


3If we want to describe a wave with e.g. circular polarization, we have to use a complex polarization vector.
with an amplitude $A_0(\omega)$. We assume that they all have the same direction of propagation $\hat{k} = k/k$ and polarization $\mathbf{e}_k$.

With $q = -e$ (the electron charge), the perturbation term corresponding to one harmonic wave is given by (T15.15) and (T15.16) and may be written on the standard form (T14.24) for a harmonic perturbation,

$$\widetilde{H}_1' = -\frac{q}{m} \mathbf{A} \cdot \mathbf{\hat{p}} = \frac{e}{m} A_0(\omega) \mathbf{\hat{p}} \cdot (\mathbf{e}_k e^{i(kr - \omega t)} + \text{c.c.})$$

$$\equiv \hat{\mathcal{V}}(\mathbf{r}, \omega) e^{-i\omega t} + \hat{\mathcal{V}}(\mathbf{r}, \omega) e^{+i\omega t},$$

where

$$\hat{\mathcal{V}}(\mathbf{r}, \omega) = \frac{e}{m} A_0(\omega) \mathbf{e}_k \mathbf{\hat{p}} e^{i\mathbf{k} \cdot \mathbf{r}}. \tag{T15.20}$$

### 15.3.a Stimulated emission as probable as absorption

According to (T14.35–37), the transition rates for stimulated emission and absorption due to one harmonic wave are equal, given by

$$w_{2\rightarrow1} = w_{1\rightarrow2} = \frac{2\pi}{\hbar} |\mathcal{V}_{21}|^2 \delta(E_2 - E_1 - \hbar \omega)$$

$$= \frac{2\pi}{\hbar^2} |\mathcal{V}_{21}|^2 \delta(\omega_{21} - \omega) \quad \left(\omega_{21} = \frac{E_2 - E_1}{\hbar}\right).$$

But what happens when we have a whole bunch of harmonic waves in the beam? The answer is that, provided that the radiation is incoherent, we can add the transition rates for all the waves; there is no interference between the different harmonic waves. The same holds for the energy density in the beam. Thus with $\rho(\omega)d\omega$ frequencies in the interval $d\omega$, we have from (T15.19) that

$$u(\omega)d\omega = 2\epsilon_0 A_0^2(\omega) \omega^2 \cdot \rho(\omega)d\omega, \tag{T15.21}$$

where $u(\omega)$ is the energy density per unit angular frequency (the spectral energy density). For the total transition rate we get

$$w_{2\rightarrow1} = w_{1\rightarrow2} = \frac{2\pi}{\hbar^2} \int |\mathcal{V}_{21}|^2 \delta(\omega_{21} - \omega) \cdot \rho(\omega)d\omega$$

$$= \frac{2\pi}{\hbar^2} \frac{e^2}{m^2} A_0^2(\omega_{21}) \rho(\omega_{21}) \left|\mathbf{e}_k \cdot \langle \psi_2 | \mathbf{\hat{p}} e^{i\mathbf{k} \cdot \mathbf{r}} | \psi_1 \rangle\right|^2.$$  

Using (T15.21), we have

$$A_0^2(\omega_{21}) \rho(\omega_{21}) = \frac{u(\omega_{21})}{2\epsilon_0 \omega_{21}^2},$$

which allows us to express this result in terms of the spectral energy density $u(\omega)$:

$$w_{2\rightarrow1} = w_{1\rightarrow2} = \frac{2\pi}{\hbar^2} \frac{e^2}{m^2} \frac{u(\omega_{21})}{\epsilon_0 \omega_{21}^2} \left|\mathbf{e}_k \cdot \langle \psi_2 | \mathbf{\hat{p}} e^{i\mathbf{k} \cdot \mathbf{r}} | \psi_1 \rangle\right|^2. \tag{T15.22}$$
15.3.b The dipole approximation

The Bohr frequency $\omega_{21}$ corresponding to a transition between atomic states typically is of the order of

$$\omega_{21} = \frac{E_2 - E_1}{\hbar} \sim \frac{10 \text{ eV}}{\hbar} \sim 10^{16} \text{s}^{-1}.$$ 

The transitions $1 \to 2$ and $2 \to 1$ thus are induced by radiation with a wavelength of the order of

$$\lambda = \frac{2\pi c}{\omega} \sim 10^{-7} \text{m},$$

which is a factor $10^3$ larger than the radii of the orbitals $\psi_1$ and $\psi_2$. In the matrix element

$$\langle \psi_2 | \hat{\mathbf{p}} e^{i\mathbf{k} \cdot \mathbf{r}} | \psi_1 \rangle$$

we may therefore expand the exponential $\exp(i\mathbf{k} \cdot \mathbf{r})$ in a rapidly converging series:

$$e^{i\mathbf{k} \cdot \mathbf{r}} = 1 + i\mathbf{k} \cdot \mathbf{r} - \frac{1}{2} (i\mathbf{k} \cdot \mathbf{r})^2 + \cdots.$$ 

Since $\mathbf{k} \cdot \mathbf{r} \sim 2\pi r/\lambda << 1$, the first non-vanishing term in the resulting matrix element will be a very good approximation. The first term, i.e. $\exp(i\mathbf{k} \cdot \mathbf{r}) \approx 1$, gives the so-called electric-dipole approximation. If this term does not contribute, the next term, $i\mathbf{k} \cdot \mathbf{r}$, corresponding to magnetic-dipole and electric-quadrupole radiation, will of course give a much smaller transition rate.

The electric-dipole approximation

For the case that the first term ($e^{i\mathbf{k} \cdot \mathbf{r}} \approx 1$) does contribute, we may simplify the matrix element as follows: Firstly, we remember (cf section 15.2.a) that the states $\psi_1$ and $\psi_2$ are eigenstates of the unperturbed part of the Hamiltonian (the “particle part” $\hat{H}_p$):

$$\hat{H}_p \psi_n = \left[ \frac{\hat{\mathbf{p}}^2}{2m} + V_C(\mathbf{r}) \right] \psi_n = E_n \psi_n; \quad n = 1, 2.$$  \hspace{1cm} (T15.23)

Secondly, we note that

$$[\hat{\mathbf{H}}_p, x] = \frac{1}{2m} [\hat{p}_x^2, x] = \frac{1}{2m} \{ \hat{p}_x [\hat{p}_x, x] + [\hat{p}_x, x] \hat{p}_x \} = \frac{\hbar}{im} \hat{p}_x,$$  \hspace{1cm} (T15.24)

which can be generalized to

$$\hat{\mathbf{p}} = \frac{im}{\hbar} [\hat{\mathbf{H}}_p, \mathbf{r}].$$  \hspace{1cm} (T15.25)

In the electric-dipole approximation (often simply called the dipole approximation), we then have from (T15.23)

$$\langle \psi_2 | \hat{\mathbf{p}} e^{i\mathbf{k} \cdot \mathbf{r}} | \psi_1 \rangle \approx \frac{im}{\hbar} \langle \psi_2 | \hat{H}_p \mathbf{r} - r \hat{H}_p | \psi_1 \rangle$$

$$= \frac{im}{\hbar} \langle \psi_2 | E_2 \mathbf{r} - r E_1 | \psi_1 \rangle = im \frac{E_2 - E_1}{\hbar} \langle \psi_2 | \mathbf{r} | \psi_1 \rangle$$

$$\equiv im \omega_{21} d_{21},$$  \hspace{1cm} (T15.26)
where
\[ d_{21} \equiv \langle \psi_2 | r | \psi_1 \rangle = \int \psi_2^* r \psi_1 \, d^3r \] (T15.27)
is called the dipole moment of the transition. Thus, in the dipole approximation, the transition rates for absorption and stimulated emission are given by
\[ w_{1\rightarrow 2} = w_{2\rightarrow 1} = \frac{\pi e^2}{\hbar^2 \epsilon_0} u(\omega_{21}) |e_k \cdot d_{21}|^2, \] (electric-dipole approximation) (T15.28)

where \( u(\omega_{21}) \) is the spectral energy density (energy density per unit angular frequency) in the beam.

### 15.4 Spontaneous emission via Einstein’s equilibrium argument

(H 12.4, B&J 11.3, G 9.3)
The equality of the transition rates for absorption and stimulated emission was proved already in 1917 by Einstein, eight years before the advent of quantum mechanics.

#### 15.4.a Einsteins equilibrium argument

As discussed in section 8.3.d in Tillegg 8, Einstein considered an ensemble of atoms in equilibrium with thermal radiation at a temperature \( T \). Let us briefly review his argument. At equilibrium the radiation energy density per unit angular frequency is given by Planck’s law (T8.53) as
\[ u(\nu) = \frac{u(\nu) d\nu}{d\omega} = \frac{\hbar \nu^3}{\pi^2 c^3} e^{\hbar \nu / kT} \left( e^{\hbar \nu / kT} - 1 \right). \] (T15.29)
Furthermore, the ratio between the number of atoms in the states \( \psi_1 \) and \( \psi_2 \) is given by the Boltzmann factor
\[ \frac{N_1}{N_2} = e^{-i(E_1 - E_2)/kT} = e^{\hbar \omega/kT}, \] (T15.30)
where \( \omega = \omega_{21} \). For each atom in the state \( \psi_2 \), there is a certain transition rate \( w_{2\rightarrow 1}^{\text{sp}} = A \) of spontaneous emission and de-excitation to the state \( \psi_1 \). This rate is independent of the temperature and thus occurs even in the absence of radiation. The rate of absorption, \( B_{1\rightarrow 2} u(\omega) \), on the other hand, is proportional to \( u(\omega) \). The same turns out to be the case for the rate of stimulated emission, \( B_{2\rightarrow 1} u(\omega) \). This is how the three Einstein coefficients, \( A, B_{1\rightarrow 2} \) and \( B_{2\rightarrow 1} \), come into play.
induced by $u(\omega)$ independent of $u(\omega)$

Rates per atom: $B_{1\to 2} u(\omega)$ $B_{2\to 1} u(\omega)$ $A$

Total rates: $N_1 B_{1\to 2} u(\omega)$ $N_2 B_{2\to 1} u(\omega)$ $N_2 A$

At equilibrium, the total rates of emission and absorption must balance each other. Using (T15.30), we get

$$
\frac{dN_1}{dt} = N_2 (A + B_{2\to 1}) u(\omega) - N_1 B_{1\to 2} u(\omega) = N_2 \left[ A + B_{2\to 1} u(\omega) - e^{\hbar \omega / kT} B_{1\to 2} u(\omega) \right] = 0,
$$

or, solving for $u(\omega)$,

$$u(\omega) = \frac{A}{B_{1\to 2}} \frac{1}{e^{\hbar \omega / kT} - B_{2\to 1} / B_{1\to 2}}.
$$

Comparing with (T15.29), we see that

$$B_{1\to 2} = B_{2\to 1} \equiv B \quad \text{and} \quad A = \frac{\hbar \omega^3}{\pi^2 c^3} B_{1\to 2}.
$$

(T15.31)

Thus, Einstein’s results may be summarized as follows:

The transition rate $B_{2\to 1} u(\omega)$ of stimulated emission is exactly equal to the rate of absorption, $B_{1\to 2} u(\omega)$, that is, $B_{2\to 1} = B_{1\to 2}$.

(T15.32)

and

The ratio between the rates of spontaneous emission and absorption (or stimulated emission) is given by

$$
\frac{A}{B_{1\to 2} u(\omega)} = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{u(\omega)} = e^{\hbar \omega / kT} - 1.
$$

(T15.33)
15.4.b Approximate result for $B_{1\rightarrow 2} = B_{2\rightarrow 1}$

In 1917, before quantum mechanics, Einstein was only able to find the ratios between his coefficients. We are now in a position to find the size of the rates for absorption and stimulated emission, using the quantum-mechanical results calculated for the radiation beam in section 15.3.b.

Contrary to the beam, the thermal radiation is isotropically distributed over all angles, and it is of course also unpolarized.

Let us therefore change the scene and consider the case on the right, where the energy density $u(\omega)$ per unit angular frequency is distributed isotropically. We must then take the average of the result for the beam,

$$w_{1\rightarrow 2} = w_{2\rightarrow 1} = \frac{\pi e^2}{\hbar^2 \epsilon_0} u(\omega_{21}) |\mathbf{e}_k \cdot \mathbf{d}_{21}|^2,$$

over all directions of $\mathbf{k}$ and over polarizations.

This corresponds to averaging $|\mathbf{e}_k \cdot \mathbf{d}_{21}|^2 = |\mathbf{d}_{21}|^2 \cos^2 \theta$ over all directions of $\mathbf{d}_{21}$. With $^4$

$$\frac{1}{\cos^2 \theta} = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_{-1}^1 d(cos \theta) \cos^2 \theta = \frac{1}{3}$$

$^4$The factor 1/3 holds also for the case where $\mathbf{d}_{21}$ is complex, and where $\Re(\mathbf{d}_{21})$ and $\Im(\mathbf{d}_{21})$ point at different angles ($\theta_R$ and $\theta_I$) with respect to $\mathbf{e}_k$. Then

$$|\mathbf{e}_k \cdot (\Re(\mathbf{d}_{21}) + i \Im(\mathbf{d}_{21}))|^2 = |\mathbf{e}_k \cdot \Re(\mathbf{d}_{21})|^2 + |\mathbf{e}_k \cdot \Im(\mathbf{d}_{21})|^2 = |\Re(\mathbf{d}_{21})|^2 \cos^2 \theta_R + |\Im(\mathbf{d}_{21})|^2 \cos^2 \theta_I.$$ 

Averaging over $\cos^2 \theta_R$ and $\cos^2 \theta_I$, we get

$$|\Re(\mathbf{d}_{21})|^2 \cdot \frac{1}{3} + |\Im(\mathbf{d}_{21})|^2 \cdot \frac{1}{3} = \frac{1}{3} |\mathbf{d}_{21}|^2, \ \text{q.e.d.}$$
we simply get the result
\[ w_{1\rightarrow 2} = w_{2\rightarrow 1} = \frac{\pi e^2}{3\hbar^2 \epsilon_0} u(\omega_{21}) |d_{21}|^2 \quad \text{(isotropic case)} \] (T15.34)
for the rates of absorption and stimulated emission in the case where \( u(\omega_{21}) \) is isotropically distributed.

So, now we are one step ahead of Einstein: For the **size** of the \( B \)-coefficient our result (to first order in the perturbation, and in the dipole approximation) is
\[ B_{1\rightarrow 2} = \frac{w_{1\rightarrow 2}}{u(\omega_{21})} = \frac{\pi e^2}{3\hbar^2 \epsilon_0} |\langle \psi_2 | r | \psi_1 \rangle|^2 = B_{2\rightarrow 1}. \] (T15.35)

Can we rely on this result, which has been derived using semi-classical radiation theory? The answer is yes: The result agrees with that obtained using non-relativistic **quantum electrodynamics**, where also the electromagnetic field is quantized, leading to the concepts of creation and annihilation of photons.

**15.4.c Approximate result for spontaneous emission**

Can our semiclassical theory also be used to obtain the rate of **spontaneous** emission? The answer is no: In the absence of radiation, there is no perturbation and hence no de-excitation, according to the semi-classical theory.

Here, we are rescued by the second of the Einstein relations above. According to Einstein’s equilibrium argument, de-excitation via spontaneous emission does occur, at a rate
\[ w_{2\rightarrow 1}^{sp} = A = \frac{\hbar \omega_{21}^3}{2 \pi^2 c^3} B_{1\rightarrow 2} = \frac{e^2 \omega_{21}^3}{3 \pi \epsilon_0 \hbar c^3} |d_{21}|^2 \]
or, with \( \alpha = e^2/(4\pi \epsilon_0 \hbar c) \approx 1/137.036 \),
\[ w_{2\rightarrow 1}^{sp} = A = \alpha \frac{4 \omega_{21}^3}{3 e^2} |\langle \psi_2 | r | \psi_1 \rangle|^2, \] (rate of spontaneous emission) (T15.36)
valid to first order in the perturbation and in the electric-dipole approximation (as the other results).

Can this result be obtained directly? Yes, if we quantize the electromagnetic field as just mentioned, and apply first-order perturbation theory, we can calculate the rate of spontaneous de-excitation from \( \psi_2 \) to \( \psi_1 \), where a photon with polarization \( e_k \) is emitted into a solid angle \( d\Omega \), as
\[ dw_{2\rightarrow 1}^{sp} = \frac{\alpha}{2\pi} \frac{\omega_{21}}{m^2 c^2} |e_k^* \cdot \langle \psi_1 | e^{-i k \cdot r} \hat{p} | \psi_2 \rangle|^2 d\Omega \]
\[ = \frac{\alpha}{2\pi} \frac{\omega_{21}}{m^2 c^2} |e_k \cdot \langle \psi_2 | e^{i k \cdot r} \hat{p} | \psi_1 \rangle|^2 d\Omega. \]
Introducing the dipole approximation (cf (T15.26)), \( \langle \psi_2 | e^{i k \cdot r} \hat{p} | \psi_1 \rangle = im \omega_{21} \langle \psi_2 | r | \psi_1 \rangle \), we can simplify this to
\[ \frac{dw_{2\rightarrow 1}^{sp}}{d\Omega} = \frac{\alpha}{2\pi} \frac{\omega_{21}^3}{2 e^2} |e_k \cdot \langle \psi_2 | r | \psi_1 \rangle|^2 \] (dipole approx.). (T15.37)
A small exercise:

\[ \mathbf{e}_{1k} \text{ in the plane through } \hat{k} \text{ and } \mathbf{d}_{21} \implies \mathbf{e}_{2k} \perp \mathbf{d}_{21} \]

Suppose that \( \langle \psi_2 | r | \psi_1 \rangle = \mathbf{d}_{21} \) is real, and consider a photon emitted in the direction \( \hat{k} \).

a) Why is the photon polarized in the plane through \( \hat{k} \) and \( \mathbf{d}_{21} \)? [Hint: Let \( \mathbf{e}_{1k} \) be a polarization vector in this plane, and let \( \mathbf{e}_{2k} \) be orthogonal to \( \mathbf{e}_{1k} \), \( \hat{k} \) and hence to \( \mathbf{d}_{21} \). What is then \( dw_{2-1}^{sp}/d\Omega \) for photons with \( \mathbf{e}_k = \mathbf{e}_{1k} \)?]

b) Express \( dw_{2-1}^{sp}/d\Omega \) in terms of the angle \( \theta_{kd} \) between \( \hat{k} \) and \( \mathbf{d}_{21} \). Show that (T15.36) follows by integrating this expression over angles.

15.5 Selection rules for electric-dipole radiation

(H 12.5, B&J pp 530–541, G 9.3)

15.5.a Selection rules

As we have just seen, the transition rates in the electric-dipole approximation are governed by the matrix elements ("dipole moments")

\[ \mathbf{d}_{fi} = \int \psi_f^*(r) \mathbf{r} \psi_i(r) d^3r. \]

The selection rules (in the electric-dipole approximation) are simple rules telling us when these matrix elements are different from zero.

The simplest case is that of particles moving in a spherically symmetric potential, with an initial state

\[ \psi_i(r) = R_{nl}(r) Y_{lm}(\theta, \phi). \]

It turns out that \( \mathbf{d}_{fi} \) differs from zero only for a selection of final states

\[ \psi_f(r) = R_{n'l'}(r) Y_{l'm'}(\theta, \phi), \]

such that the changes of the quantum numbers are limited to

\[ \Delta m \equiv m' - m = 0, \pm 1 \quad \text{and} \quad \Delta l \equiv l' - l = \pm 1. \]

(T15.38)
For transitions which do not satisfy both these conditions, the matrix elements $d_{fi}$ are equal to zero. Such transitions are “forbidden” in the electric-dipole approximation. Of course they do not have to be absolutely forbidden; the rules above only tell us that the first term in the expansion $\exp(\pm ik \cdot r) = 1 \pm ik \cdot r + \cdots$ does not contribute. This means that for such a transition the rate will be much smaller than for those which are allowed in the electric-dipole approximation.

How the rules are proved

Starting with the identity
\[
\begin{align*}
r &= \hat{e}_x r \sin \theta \cos \phi + \hat{e}_y r \sin \theta \sin \phi + \hat{e}_z r \cos \theta \\
&= r \sqrt{\frac{4\pi}{3}} \left[ \frac{\hat{e}_z Y_{10} - \hat{e}_x - i\hat{e}_y}{\sqrt{2}} Y_{11} + \frac{\hat{e}_x + i\hat{e}_y}{\sqrt{2}} Y_{1,-1} \right],
\end{align*}
\]

we note that the matrix element $d_{fi}$ can be written as a radial integral
\[
I_{\text{rad}} \equiv \int_0^\infty R_{m'l'}(r) r R_{ml}(r)r^2 dr
\]

multiplied by a linear combination of three angular integrals of the type
\[
J_{m''} \equiv \sqrt{\frac{4\pi}{3}} \int Y_{lm}^* Y_{l'm'} Y_{lm} d\Omega,
\]

where $m'' = 0, +1$ or $-1$. Since the parity of $Y_{lm}$ is $(-1)^l$, we note at once that the parity of the angular integrand is
\[
(-1)^{l'+1+l} = (-1)^{2l}(-1)^{l'-1} = (-1)^{\Delta l + 1}.
\]

Thus, the integrand is antisymmetric (and $J_{m''}$ and hence $d_{fi}$ are equal to zero) unless $\Delta l$ is odd.

Next, we note that the angular integral $J_{m''}$ contains the factor
\[
\int_0^{2\pi} e^{i\phi(m-m'+m'')} d\phi = \int_0^{2\pi} e^{i\phi(m''-\Delta m)} d\phi = 2\pi \delta_{m'',\Delta m},
\]

which is zero unless $\Delta m = m'' = 0, \pm 1$. This proves the $\Delta m$ part of the selection rules, and allows us to write the matrix element as
\[
d_{fi} = I_{\text{rad}} \left( \hat{e}_z J_0 \delta_{m',m} - \hat{e}_x - i\hat{e}_y \frac{J_1 \delta_{m',m+1}}{2} + \hat{e}_x + i\hat{e}_y \frac{J_{-1} \delta_{m',m-1}}{2} \right),
\]

where $J_0$, $J_1$ and $J_{-1}$ are given by (T15.41).

It remains to show why $\Delta l$ is restricted to $\pm 1$. A simple argument goes as follows: If the initial state is an $s$-state, with $Y_{lm} = Y_{00} = 1/\sqrt{4\pi}$, we simply have
\[
J_{m''} = \sqrt{1/3} \int Y_{l'm'}^* Y_{lm} d\Omega = \sqrt{1/3} \delta_{l',1}\delta_{m',m''},
\]

showing that the final state is a $p$-wave ($\Delta l = 1$).

For $l \geq 1$, we may use our experience with the addition of angular momenta. The product $Y_{lm'}Y_{lm}$ occurring in (T15.41) may be regarded as a product state resulting from
separate measurements of the $z$-components of two angular momenta (with $l_1 = 1$ and $l_2 = l$). According to the triangular inequality, the “old” product states can be linearly combined to “new” states with a resulting quantum number $l - 1, l$, and $l + 1$. Inverting these linear combinations, we can of course express the product state in terms of the “new” states, as follows

$$Y_{lm'} Y_{lm} = c_1 Y_{l+1,m+m''} + c_2 Y_{l-1,m+m''}. $$

(There is no term $Y_{l,m+m''}$ on the right because it has the wrong parity.) Inserting this expression into (T15.41), we see that the rule $\Delta l = l' - l = \pm 1$ follows from the orthogonality of the spherical harmonics.

**A small exercise:**

a) The product

$$Y_{11} Y_{20} = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi} \cdot \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

may be expressed in terms of two spherical harmonics. Which are these?

b) Check that

$$Y_{10} Y_{20} = \frac{3}{2} \sqrt{\frac{3}{35\pi}} Y_{30} + \sqrt{\frac{1}{5\pi}} Y_{10}.$$

c) What is the direction of $d_f$ for a transition with $\Delta m = 0$?

### 15.5.b Examples, for hydrogen

Atomic spectra (spectral lines) provide the best measurements of atomic energy levels. The figure below illustrates (electric-dipole) transitions to the ground state $1s$ ($n = 1, l = 0$) for hydrogen. The initial state must then be a $p$-state, so that $\Delta l = -1$. The lowest of the photon energies here is approximately 10.2 eV. Therefore the entire series of these spectral lines are in the ultraviolet region. These lines are known as the Lyman series.

Transitions to $2s$ and $2p$
Here the energy differences

\[ \Delta E = -\frac{1}{2} \alpha^2 mc^2 \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \quad (n = 3, 4, \ldots) \]

are of the order of 2 eV, corresponding to spectral lines in the visible part of the spectrum. These lines are known as the Balmer series (Balmer, ca 1885), which was the basis for Balmer’s empirical formula (see Tillegg 1), which in turn formed part of the background for the Bohr model.

Cascade

As illustrated above, there is no restriction on \( \Delta n \), the change of the principal quantum number. However, it happens (e.g. when free electrons and protons recombine) that a hydrogen atom is found in a highly excited state where \( l \) has the maximal value \( n - 1 \).

Then, as illustrated in the figure, electric-dipole transitions are only possible for \( \Delta n = \Delta l = -1 \). This way we get a whole cascade of transitions, with spectral lines corresponding to a whole series of energy differences between neighbouring levels.

15.5.c Lifetime. Line width

It is important to remember that the spontaneous transition rate (T15.36),

\[ w_{i \rightarrow f}^{sp} = \alpha \frac{4 \omega_{if}^2}{3c^2} |d_{fi}|^2, \]

gives the probability per unit time for transition from the state \( \psi_i \) to the state \( \psi_f \). This means that we are not able to predict what happens with a single atom in an excited state \( \psi_i \); we cannot tell when the photon will be emitted, and we don’t know in which direction.

So, in order to compare our theory with experiments, we must consider an ensemble of a large number of atoms. With \( N(t) \) atoms in the state \( \psi_i \) at the time \( t \), the theory predicts that the number that is expected to decay into \( \psi_f \) in the time interval \( (t, t + dt) \) is

\[ dN_f = N(t) w_{i \rightarrow f}^{sp} dt. \]

Summing over the possible final states \( \psi_f \), we then find that the expected change of \( N(t) \) in the interval \( dt \) is

\[ dN = - \sum_f dN_f = -N(t) w_i dt, \]
where

\[ w_i = \sum_f w_{i \to f}^{sp} \tag{T15.43} \]

is the total rate of de-excitation for the state \( \psi_i \). Then,

\[ \frac{dN}{N(t)} = -w_i \, dt, \]

which is readily integrated to

\[ N(t) = N(0) e^{-w_i t} \equiv N(0) e^{-t/\tau_i}; \tag{T15.44} \]

Here, \( \tau_i = 1/w_i \) is called the lifetime for the state \( \psi_i \).

**A small exercise:**

Show that \( \tau_i \) indeed is the average lifetime of the ensemble \( N(0) \). [Hint: The expected number “dying” in the interval \( (t, t + dt) \) is \( |dN| = w_i N(t) dt \).]

As an example we consider the hydrogen atom, with the initial state \( \psi_i = \psi_{210} \). Then there is only one possible transition, to the ground state \( \psi_{100} \). With a dipole moment \( |d_{fi}| \) of the order \( a_0 \), and a frequency \( \omega_{21} \sim 10^{16} \text{s}^{-1} \), we then get a transition rate

\[ w_{i \to f} \sim \alpha \frac{\omega_{21}^3}{c^2} |a_0|^2 \sim 10^{-2} \frac{10^{48}}{10^{17}} 10^{-20} \text{s}^{-1} = 10^9 \text{s}^{-1}. \]

The lifetime of this state then is of the order of

\[ \tau_i = \frac{1}{w_i} \sim 10^{-9} \text{s}. \]

We notice that the lifetime is much longer than the natural atomic period \( T = 2\pi/\omega_{21} \sim 10^{-16} \text{s} \).

As another example, let the initial state be \( \psi_{410} \).

The possible final states (allowed in the dipole approximation) then are the three 3d-states \( \psi_{320}, \psi_{321} \) and \( \psi_{32, -1} \), together with the s-states \( \psi_{300}, \psi_{200} \) and \( \psi_{100} \). Each of these contribute to the total transition rate (T15.43).

Note that the transition from \( \psi_{200} \) to \( \psi_{100} \) is “forbidden” in the electric-dipole approximation. De-excitation here is effected mainly by two-photon emission, with a rate which is much smaller than in the example above. In fact, the lifetime is as long as \( \sim 0.1 \text{s} \). Such long-lived states are often called meta-stable states.
Natural line width

In classical radiation theory, if a charge undergoes a damped oscillation with frequency $\omega_0$ and a damping time $\tau$, then also the amplitude of the radiated wave will be damped. Fourier analyzing this signal, we then get a frequency distribution with a peak at $\omega_0$, but with a finite width $\Delta\omega$ of the order $1/\tau$. This width corresponds to a finite line width $\Delta\lambda = \lambda\Delta\omega/\omega$.

It turns out that quantum mechanics gives a similar result for spontaneous emission. As an example, in the spontaneous de-excitation $2p \rightarrow 1s$ in hydrogen, the spread in the energy of the emitted photons is $\hbar\Delta\omega = \hbar w_i$, where $w_i$ is the transition rate. More precisely, it can be shown that the probability distribution of the photons emitted goes as

$$P(\hbar\omega) \propto \frac{1}{(\hbar\omega - \hbar\omega_{21})^2 + (\frac{1}{2}\hbar w_i)^2},$$

where $w_i = w_{2-1}^{sp} = 1/\tau_i$ is the spontaneous transition rate from (any of) the $2p$ state(s) to the ground state. This is called a Lorentzian probability distribution.

As illustrated in the figure, the “full width at half maximum” of the peak is $\Delta\omega = w_i$. The interpretation of this result (using energy conservation) is that the energy of the initial excited state is not sharp, but has a probability distribution with a width

$$\Delta E_2 = \hbar\Delta\omega = \hbar w_i = \hbar/\tau_i.$$  

(T15.46)

It is fairly common to call the width $\Delta E_2$ the energy uncertainty of the $2p$ level, and to call the relation

$$\Delta E \cdot \tau = \hbar$$

a time-energy uncertainty relation, but that may be somewhat misleading.\footnote{Strictly speaking, $\Delta E$ is not an ordinary uncertainty, because the root-mean-square deviation does not exist for the distribution (T15.45). Also, time is not an observable, just a parameter.}

\footnote{See, e.g., section 11.5 in Bransden & Joachain, or W. Heitler, The Quantum Theory of Radiation (3rd edition), Chap. V, 18 p 181.}

\footnote{Note that the initial state $\psi_2$ is an eigenstate of the “particle part” $\hat{H}_p$ of the Hamiltonian, but not of the total Hamiltonian $\hat{H}$. Therefore the initial energy can not be sharp.}
We note that the smaller the lifetime of an excited state is, the larger its energy width is. This is important in particle physics, where most of the "elementary" particles have lifetimes of the order of $10^{-23}$ s, and hence an energy width of the order of 100 MeV, and a mass width $\sim$100 MeV/$c^2$, which can be up to 10 percent of the particle mass.

For excited atomic levels, the relative widths become small. Thus, for the example above the relative width is given by

$$\frac{\Delta \omega}{\omega} = \frac{w_i}{\omega} \sim \frac{10^9 \text{s}^{-1}}{10^{16} \text{s}^{-1}} \approx 10^{-7}.$$  

The corresponding width $\Delta \lambda$ of the wavelength is called the **natural line width**, and is in principle measurable in atomic spectra. However, observed spectral lines usually have much greater widths than this, due to collisions and Doppler broadening.