Lecture notes 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 [1]

$$\widehat{H}_0 = \frac{\widehat{\mathbf{p}}^2}{2m} + U(\mathbf{r}, t),$$

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

$$\widehat{H}_0 \quad \rightarrow \quad \widehat{H} - q\Phi(\mathbf{r}, t)$$

$$\widehat{\mathbf{p}} \quad \rightarrow \quad \widehat{\mathbf{p}} - q\mathbf{A}(\mathbf{r}, t). \tag{T15.1}$$

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

$$\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A} \qquad \text{and} \qquad \boldsymbol{\mathcal{E}} = -\boldsymbol{\nabla}\Phi - \frac{\partial \mathbf{A}}{\partial t}.$$

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[1]The potential $U(\mathbf{r}, t)$ represents possible non-electromagnetic forces.

This substitution gives

$$\widehat{H} - q\Phi = \frac{1}{2m}(\widehat{\mathbf{p}} - q\mathbf{A})^2 + U(\mathbf{r}, t).$$

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 ($U(\mathbf{r}, t) = 0$) we then arrive at the following one-particle Schrödinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[\frac{1}{2m}(\widehat{\mathbf{p}} - q\mathbf{A})^2 + q\Phi \right] \Psi, \qquad \left(\widehat{\mathbf{p}} \equiv \frac{\hbar}{i} \boldsymbol{\nabla} \right). \qquad \text{(T15.2)}$$

15.1.b Gauge transformations of the potentials

The physical fields

$$\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A} \qquad \text{and} \qquad \boldsymbol{\mathcal{E}} = -\boldsymbol{\nabla}\Phi - \frac{\partial \mathbf{A}}{\partial t}$$

do not define the potentials $\mathbf{A}$ and Φ uniquely. Thus, if $\mathbf{A}$ and Φ are a suitable choice, we may just as well replace them by a new set of potentials:

$$\mathbf{A}(\mathbf{r}, t) \quad \rightarrow \quad \mathbf{A}'(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}, t) + \boldsymbol{\nabla} \chi(\mathbf{r}, t),$$

$$\text{(T15.3)}$$

$$\Phi(\mathbf{r}, t) \quad \rightarrow \quad \Phi'(\mathbf{r}, t) = \Phi(\mathbf{r}, t) - \frac{\partial \chi(\mathbf{r}, t)}{\partial t},$$

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

$$\boldsymbol{\nabla} \times \mathbf{A}' = \boldsymbol{\nabla}\mathbf{A} + \boldsymbol{\nabla} \times \boldsymbol{\nabla} \chi = \boldsymbol{\nabla} \times \mathbf{A}$$

and

$$-\boldsymbol{\nabla} \Phi' - \frac{\partial \mathbf{A}'}{\partial t} = -\boldsymbol{\nabla} \Phi - \frac{\partial \mathbf{A}}{\partial t} + (\boldsymbol{\nabla} \frac{\partial}{\partial t} - \frac{\partial}{\partial t} \boldsymbol{\nabla})\chi = -\boldsymbol{\nabla} \Phi - \frac{\partial \mathbf{A}}{\partial t}$$

for an arbitrary function $\chi(\mathbf{r}, t)$.

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:

$$\boxed{\boldsymbol{\nabla}\cdot\mathbf{A}(\mathbf{r}, t) = 0.} \qquad \text{(Coulomb gauge)} \qquad \text{(T15.4)}$$

Maxwell's equation $\boldsymbol{\nabla}\cdot\boldsymbol{\mathcal{E}} = \rho/\epsilon_0$ then gives

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

---

[2]The pronounciation 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

$$\Phi(\mathbf{r}, t) = \int \frac{\rho(\mathbf{r}', t) d^3 r'}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} \qquad \left(\begin{array}{c} \text{Instantaneous} \\ \text{Coulomb potential} \end{array} \right). \qquad \text{(T15.5)}$$

Here we note that the scalar potential Φ 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 $\boldsymbol{\nabla}\cdot\mathbf{A} = 0$ 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 Ψ' be the solution of the Schrödinger equation with the transformed potentials,

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

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

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

Inserting

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

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

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

$$\Updownarrow$$

$$i\hbar \frac{\partial}{\partial t} \left[\Psi\, e^{iq\chi/\hbar} \right] = e^{iq\chi/\hbar} \left[\frac{1}{2m} \left(\frac{\hbar}{i} \boldsymbol{\nabla} - q\mathbf{A}' + q\boldsymbol{\nabla}\chi \right)^2 + q\Phi' \right] \Psi. \qquad \text{(T15.7)}$$

Since

$$\frac{\hbar}{i} \boldsymbol{\nabla} f(\mathbf{r}, t) e^{iq\chi/\hbar} = e^{iq\chi/\hbar} \left(\frac{\hbar}{i} \boldsymbol{\nabla} + q\boldsymbol{\nabla}\chi \right) f(\mathbf{r}, t),$$

we have the identity

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

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

$$i\hbar \frac{\partial}{\partial t} \left[\Psi\, e^{iq\chi/\hbar} \right] = \left[\frac{1}{2m} (\frac{\hbar}{i} \boldsymbol{\nabla} - q\mathbf{A}')^2 + q\Phi' \right] \Psi\, e^{iq\chi/\hbar}. \qquad \text{(T15.8)}$$

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 **global phase factor** (independent of $\mathbf{r}$ 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 **local phase factor** $\exp[iq\chi(\mathbf{r}, t)/\hbar]$ if we compensate by adjusting the potentials accordingly; we are allowed to make the gauge transformation

$$\Psi(\mathbf{r}, t) \quad \rightarrow \quad \Psi'(\mathbf{r}, t) = \Psi(\mathbf{r}, t) \exp[iq\chi(\mathbf{r}, t)/\hbar],$$

$$\mathbf{A}(\mathbf{r}, t) \quad \rightarrow \quad \mathbf{A}'(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}, t) + \boldsymbol{\nabla}\chi(\mathbf{r}, t), \tag{T15.9}$$

$$\Phi(\mathbf{r}, t) \quad \rightarrow \quad \Phi'(\mathbf{r}, t) = \Phi(\mathbf{r}, t) - \frac{\partial\chi(\mathbf{r}, t)}{\partial t}.$$

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 $\rho(\mathbf{r}, t)$. Thus, $\Phi(\mathbf{r}, t)$ equals zero in the Coulomb gauge ($\boldsymbol{\nabla}\cdot\mathbf{A} = 0$). Then we may write the Hamiltonian as

$$\widehat{H} = \frac{1}{2m}(\widehat{\mathbf{p}} - q\mathbf{A})^2 = \widehat{H}_0 + \widehat{H}',$$

where $\widehat{H}_0 = \widehat{\mathbf{p}}^2/2m$ and

$$\begin{aligned}
\widehat{H}' &= \widehat{H} - \widehat{H}_0 = \frac{1}{2m}\left[(\widehat{\mathbf{p}} - q\mathbf{A})^2 - \widehat{\mathbf{p}}^2\right] \\
&= -\frac{q}{2m}(\widehat{\mathbf{p}}\cdot\mathbf{A} - \mathbf{A}\cdot\widehat{\mathbf{p}}) + \frac{q^2\mathbf{A}^2}{2m}.
\end{aligned}$$

In the Coulomb gage, the momentum operator commutes with the vector potential; for an arbitrary function $f(\mathbf{r}, t)$ we have

$$\widehat{\mathbf{p}}\cdot\mathbf{A}\, f(\mathbf{r}, t) = \frac{\hbar}{i}\boldsymbol{\nabla}(\mathbf{A}f) = \frac{\hbar}{i}(\boldsymbol{\nabla}\cdot\mathbf{A})f + \mathbf{A}\cdot\frac{\hbar}{i}\boldsymbol{\nabla}f = \mathbf{A}\cdot\widehat{\mathbf{p}}\, f(\mathbf{r}, t). \tag{T15.10}$$

Thus, the interaction between the charged particle and the radiation field is represented by the interaction terms

$$\widehat{H}' = -\frac{q}{m}\,\mathbf{A}\cdot\widehat{\mathbf{p}} + \frac{q^2\mathbf{A}^2}{2m} \equiv \widehat{H}_1' + \widehat{H}_2'. \tag{T15.11}$$

For a *system of particles* (like e.g. the hydrogen atom), we may similarly write

$$\widehat{H} = \widehat{H}_p + \widehat{H}', \tag{T15.12}$$

where

$$\widehat{H}_p = \sum_i \frac{\widehat{\mathbf{p}}_i^2}{2m_i} + V_C(\mathbf{r}_1, \mathbf{r}_2, \cdots) \tag{T15.13}$$

is the Hamiltonian in the absence of the radiation field (but including the Coulomb interaction terms between the charged particles), and

$$\widehat{H}' = \sum_i \left\{ -\frac{q_i}{m_i} \, \mathbf{A}(\mathbf{r}_i, t) \cdot \widehat{\mathbf{p}}_i + \frac{q_i^2}{2m_i} \left[\mathbf{A}(\mathbf{r}_i, t) \right]^2 \right\} \tag{T15.14}$$

represents the interaction between the charged particles and the radiation field.

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

$$\widehat{H}' = -\frac{q}{m} \, \mathbf{A} \cdot \widehat{\mathbf{p}}, \tag{T15.15}$$

and for which the $\mathbf{A}^2$ term gives negligible contributions.

15.2.b The radiation field

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

$$\boldsymbol{\mathcal{E}} = -\frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} \qquad \text{and} \qquad \mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}(\mathbf{r}, t)$$

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

$$\mathbf{A}(\mathbf{r}, t) \propto e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \mathbf{e_k} \qquad (\omega = ck).$$

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

$$\mathbf{A}(\mathbf{r}, t) = 2A_0 \, \mathbf{e_k} \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) = A_0 \left(\mathbf{e_k} \, e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + \text{complex conj.} \right), \tag{T15.16}$$

corresponding to the fields
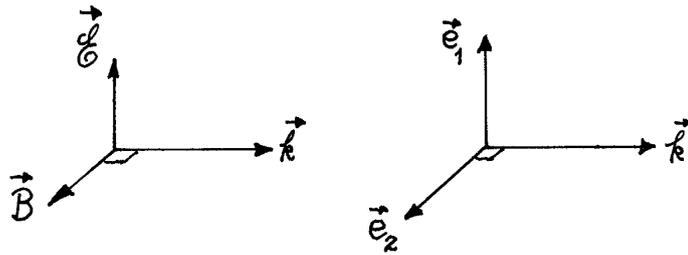
$$\boldsymbol{\mathcal{E}} = -\frac{\partial \mathbf{A}}{\partial t} = -2\omega A_0 \, \mathbf{e_k} \sin(\mathbf{k} \cdot \mathbf{r} - \omega t)$$

$$\tag{T15.17}$$

$$\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A} = -2A_0 (\mathbf{k} \times \mathbf{e_k}) \sin(\mathbf{k} \cdot \mathbf{r} - \omega t).$$

Here, we note that due to the condition

$$\boldsymbol{\nabla} \cdot \mathbf{A} = A_0 \, \mathbf{e_k} \cdot \boldsymbol{\nabla} \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) = -A_0 \sin(\mathbf{k} \cdot \mathbf{r} - \omega t) \, \mathbf{e_k} \cdot \mathbf{k} = 0, \tag{T15.18}$$

the polarization vector $\mathbf{e_k}$ is perpendicular to the propagation vector $\mathbf{k}$. Thus, $\boldsymbol{\mathcal{E}}$ is transverse to $\mathbf{k}$, and $\mathbf{B}$ is transverse to $\mathbf{k}$ and $\boldsymbol{\mathcal{E}}$, 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 $\mathbf{e}_1$ and $\mathbf{e}_2$. [3]

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

$$
\begin{aligned}
\tfrac{1}{2}\epsilon_0 \boldsymbol{\mathcal{E}}^2 + \frac{1}{2\mu_0}\mathbf{B}^2 &= \tfrac{1}{2}\epsilon_0(\boldsymbol{\mathcal{E}}^2 + c^2\mathbf{B}^2) \qquad\qquad (\mu_0\epsilon_0 = 1/c^2) \\
&= \tfrac{1}{2}\epsilon_0(2A_0)^2 \sin^2(\mathbf{k}\cdot\mathbf{r} - \omega t)(\omega^2 + c^2 k^2).
\end{aligned}
$$

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

$$
u = 2\epsilon_0 A_0^2 \omega^2, \tag{T15.19}
$$

corresponding to an energy flux $\quad I = u\,c = 2\epsilon_0 A_0^2 \omega^2 c.$

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 $\to$ continuous transitions (e.g. ionization) and continuous $\to$ continuous transitions (e.g. scattering on a static potential) and established Fermi's golden rule. We shall now consider the case of discrete $\to$ discrete transitions, where an electromagnetic wave induces either excitation of an atom (via absorption) or de-excitation (via stimulated emission):

<div align="center">absorption   stimulated emission</div>

$$
\omega_{fi} = \frac{E_2 - E_1}{\hbar} > 0 \qquad\qquad\qquad \omega_{fi} = \frac{E_1 - E_2}{\hbar} < 0
$$
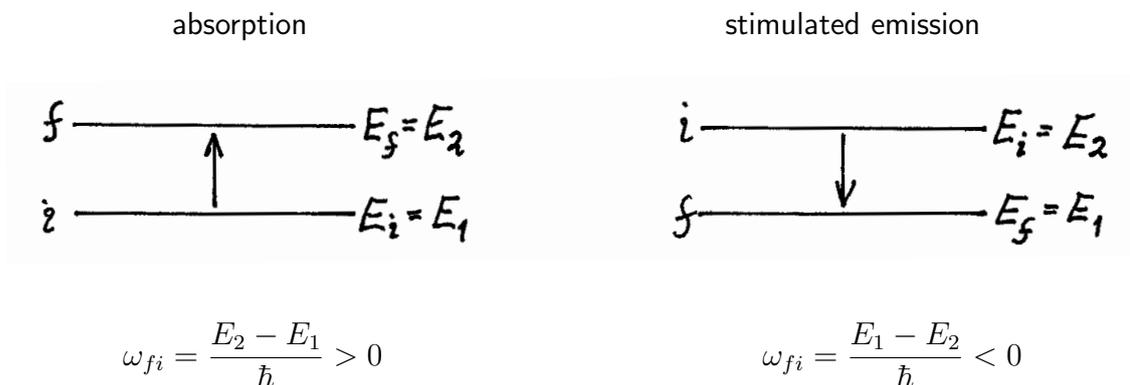
We assume (to begin with) that the the incident beam of radiation is a mixture of harmonic waves with a quasi-continuous frequency distribution, so that the number of waves (i.e. frequencies) in the interval $\Delta\omega$ is $\rho(\omega)\Delta\omega$. Each of these waves is of the type (T15.16),

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[3]If we want to desribe 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 $\hat{k} = \mathbf{k}/k$ 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,

$$
\begin{aligned}
\widehat{H}'_1 &= -\frac{q}{m}\,\mathbf{A}{\cdot}\widehat{\mathbf{p}} = \frac{e}{m}\,A_0(\omega)\,\widehat{\mathbf{p}}{\cdot}\left(\mathbf{e_k}\,e^{i(\mathbf{k}{\cdot}\mathbf{r}-\omega t)} + \text{c.c.}\right) \\
&\equiv \widehat{\mathcal{V}}(\mathbf{r},\omega)e^{-i\omega t} + \widehat{\mathcal{V}}^\dagger(\mathbf{r},\omega)e^{+i\omega t},
\end{aligned}
$$

where

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

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

$$
\begin{aligned}
w_{2\to1} = w_{1\to2} &= \frac{2\pi}{\hbar}|\mathcal{V}_{21}\omega)|^2\delta(E_2 - E_1 - \hbar\omega) \\
&= \frac{2\pi}{\hbar^2}|\mathcal{V}_{21}|^2\delta(\omega_{21} - \omega) \qquad \left(\omega_{21} = \frac{E_2 - E_1}{\hbar}\right).
\end{aligned}
$$

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

$$
\begin{aligned}
w_{2\to1} = w_{1\to2} &= \frac{2\pi}{\hbar^2}\int|\mathcal{V}_{21}|^2\delta(\omega_{21} - \omega) \cdot \rho(\omega)d\omega \\
&= \frac{2\pi}{\hbar^2}\frac{e^2}{m^2}\,A_0^2(\omega_{21})\rho(\omega_{21})\left|\mathbf{e_k}{\cdot}\langle\psi_2|\widehat{\mathbf{p}}\,e^{i\mathbf{k}{\cdot}\mathbf{r}}|\psi_1\rangle\right|^2.
\end{aligned}
$$

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 $u(\omega)$:

$$
\boxed{w_{2\to1} = w_{1\to2} = \frac{\pi}{\hbar^2}\frac{e^2}{m^2}\frac{u(\omega_{21})}{\epsilon_0\omega_{21}^2}\left|\mathbf{e_k}{\cdot}\langle\psi_2|\widehat{\mathbf{p}}\,e^{i\mathbf{k}{\cdot}\mathbf{r}}|\psi_1\rangle\right|^2.} \tag{T15.22}
$$

15.3.b The dipole approximation

The Bohr frequency ω_{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 $1 \rightarrow 2$ and $2 \rightarrow 1$ 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 ψ_1 and ψ_2. In the matrix element

$$\langle \psi_2 | \widehat{\mathbf{p}} e^{i\mathbf{k}\cdot\mathbf{r}} | \psi_1 \rangle = \int \psi_2^* \widehat{\mathbf{p}} \, e^{i\mathbf{k}\cdot\mathbf{r}} \psi_1 \, d^3r$$

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

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

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 ψ_1 and ψ_2 are eigenstates of the unperturbed part of the Hamiltonian (the "particle part" $\widehat{H}_p$):

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

Secondly, we note that

$$[\widehat{H}_p, x] = \frac{1}{2m}[\widehat{p}_x^2, x] = \frac{1}{2m}\left\{ \widehat{p}_x[\widehat{p}_x, x] + [\widehat{p}_x, x]\widehat{p}_x \right\} = \frac{\hbar}{im} \widehat{p}_x, \tag{T15.24}$$

which can be generalized to

$$\widehat{\mathbf{p}} = \frac{im}{\hbar}[\widehat{H}_p, \mathbf{r}]. \tag{T15.25}$$

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

$$\begin{aligned} \langle \psi_2 | \widehat{\mathbf{p}} \, e^{i\mathbf{k}\cdot\mathbf{r}} | \psi_1 \rangle &\approx \langle \psi_2 | \widehat{\mathbf{p}} | \psi_1 \rangle = \frac{im}{\hbar} \langle \psi_2 | \widehat{H}_p \mathbf{r} - \mathbf{r} \widehat{H}_p | \psi_1 \rangle \\ &= \frac{im}{\hbar} \langle \psi_2 | E_2 \mathbf{r} - \mathbf{r} E_1 | \psi_1 \rangle = im \frac{E_2 - E_1}{\hbar} \langle \psi_2 | \mathbf{r} | \psi_1 \rangle \\ &\equiv im\omega_{21} \, \mathbf{d}_{21}, \end{aligned} \tag{T15.26}$$

where

$$\mathbf{d}_{21} \equiv \langle \psi_2 | \mathbf{r} | \psi_1 \rangle = \int \psi_2^* \, \mathbf{r} \, \psi_1 \, d^3 r \tag{T15.27}$$

is called the **dipole moment** of the transition. Thus, in the dipole approximation, the transition rates for absorption and stimulated emission are given by

$$\boxed{w_{1 \to 2} = w_{2 \to 1} = \frac{\pi e^2}{\hbar^2 \epsilon_0} \, u(\omega_{21}) \left| \mathbf{e_k} \cdot \mathbf{d}_{21} \right|^2 ,} \qquad \left(\begin{array}{c} \text{electric-dipole} \\ \text{approximation} \end{array} \right) \tag{T15.28}$$

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 Lecture notes 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

$$u(\omega) = \frac{u(\nu) d\nu}{d\omega} = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar \omega / kT} - 1}. \tag{T15.29}$$

Furthermore, the ratio between the number of atoms in the states ψ_1 and ψ_2 is given by the Boltzmann factor

$$\frac{N_1}{N_2} = e^{-i(E_1 - E_2)/kT} = e^{\hbar \omega / kT}, \tag{T15.30}$$

where $\omega = \omega_{21}$. For each atom in the state ψ_2, there is a certain transition rate $w_{2 \to 1}^{\mathrm{sp}} = A$ of spontaneous emission and de-excitation to the state ψ_1. This rate is independent of the temperature and thus occurs even in the absence of radiation. The rate of absorption, $B_{1 \to 2} u(\omega)$, on the other hand, is proportional to $u(\omega)$. The same turns out to be the case for the rate of stimulated emission, $B_{2 \to 1} u(\omega)$. This is how the three Einstein coefficients, A, $B_{1 \to 2}$ and $B_{2 \to 1}$, come into play.

induced by $u(\omega)$ independent of $u(\omega)$
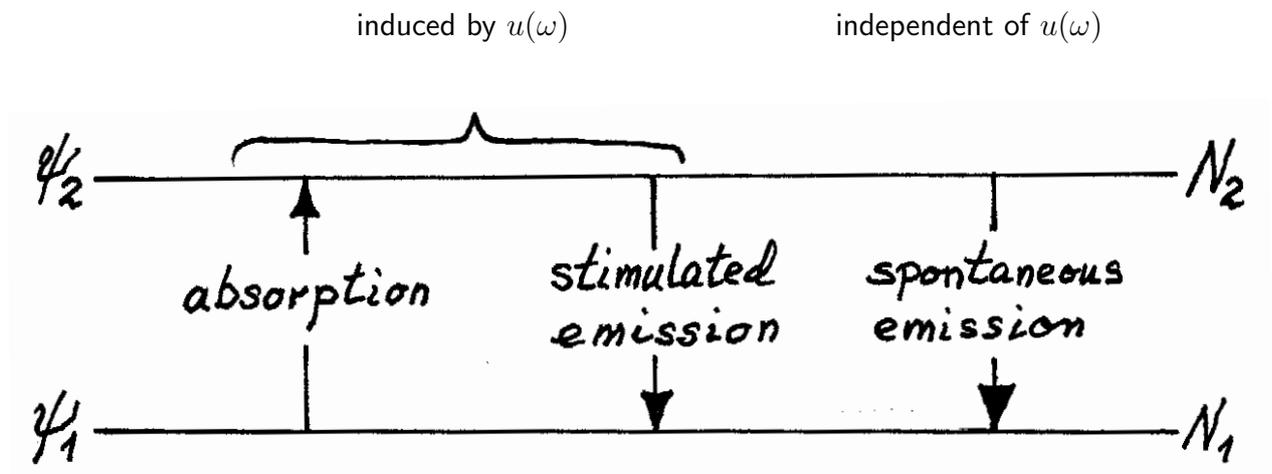
Rates per atom: $B_{1\to2}\, u(\omega)$ $B_{2\to1}\, u(\omega)$ A

Total rates: $N_1 B_{1\to2}\, u(\omega)$ $N_2 B_{2\to1}\, u(\omega)$ $N_2 A$

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

$$
\begin{aligned}
\frac{dN_1}{dt} &= N_2(A + B_{2\to1})\, u(\omega) - N_1 B_{1\to2}\, u(\omega) \\
&= N_2 \left[A + B_{2\to1} u(\omega) - e^{\hbar\omega/kT} B_{1\to2}\, u(\omega) \right] = 0,
\end{aligned}
$$

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

$$
u(\omega) = \frac{A}{B_{1\to2}}\, \frac{1}{e^{\hbar\omega/kT} - B_{2\to1}/B_{1\to2}}.
$$

Comparing with (T15.29), we see that

$$
B_{1\to2} = B_{2\to1} \equiv B \qquad \text{and} \qquad A = \frac{\hbar\omega^3}{\pi^2 c^3} B_{1\to2}. \tag{T15.31}
$$

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

> The transition rate $B_{2\to1}\, u(\omega)$ of stimulated emission is exactly equal to the rate of absorption, $B_{1\to2}\, u(\omega)$, that is, $B_{2\to1} = B_{1\to2}$,

(T15.32)

and

> The ratio between the rates of spontaneous emission and absorption (or stimulated emission) is given by
>
> $$
> \frac{A}{B_{1\to2}\, u(\omega)} = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{u(\omega)} = e^{\hbar\omega/kT} - 1.
> $$

(T15.33)

15.4.b Approximate result for $B_{1\to2} = B_{2\to1}$

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.

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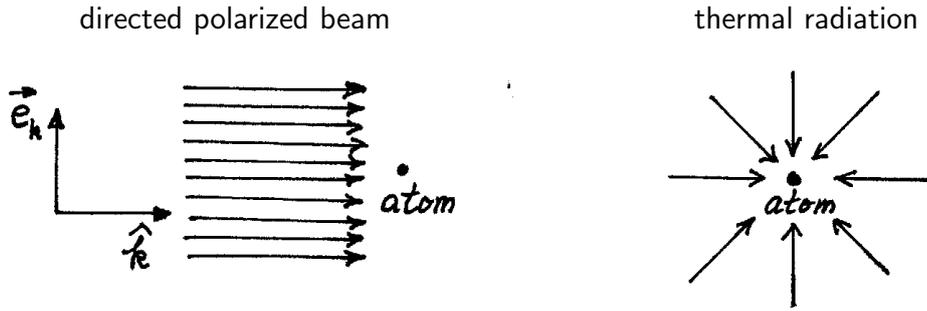
Let us therefore change the scene and consider the case on the right, where the energy density $u(\omega)$ per unit angular frequency is distributed isotropically. We must then take the average of the result for the beam,

$$w_{1\to2} = w_{2\to1} = \frac{\pi e^2}{\hbar^2 \epsilon_0}\, u(\omega_{21}) |\mathbf{e_k}\cdot\mathbf{d}_{21}|^2,$$

over all directions of $\mathbf{k}$ and over polarizations.
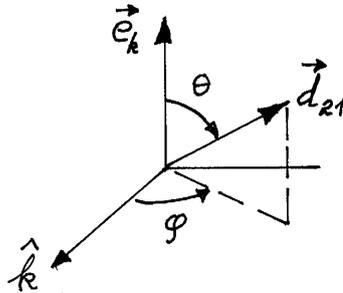
This corresponds to averaging $|\mathbf{e_k}\cdot\mathbf{d}_{21}|^2 = |\mathbf{d}_{21}|^2 \cos^2\theta$ over all directions of $\mathbf{d}_{21}$. With [4]

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

---

[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 (θ_R and θ_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

$$|\Re(\mathbf{d}_{21})|^2 \cdot \frac{1}{3} + |\Im(\mathbf{d}_{21})|^2 \cdot \frac{1}{3} = \frac{1}{3}|\mathbf{d}_{21}|^2, \quad \text{q.e.d.}$$

we simply get the result

$$w_{1 \to 2} = w_{2 \to 1} = \frac{\pi e^2}{3\hbar^2 \epsilon_0} u(\omega_{21}) |\mathbf{d}_{21}|^2 \qquad \text{(isotropic case)} \qquad \text{(T15.34)}$$

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

$$B_{1 \to 2} = \frac{w_{1 \to 2}}{u(\omega_{21})} = \frac{\pi e^2}{3\hbar^2 \epsilon_0} |\langle \psi_2 | \mathbf{r} | \psi_1 \rangle|^2 = B_{2 \to 1}. \qquad \text{(T15.35)}$$

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

$$w_{2 \to 1}^{\text{sp}} = A = \frac{\hbar \omega_{21}^3}{\pi^2 c^3} B_{1 \to 2} = \frac{e^2 \omega_{21}^3}{3\pi \epsilon_0 \hbar c^3} |\mathbf{d}_{21}|^2$$

or, with $\quad \alpha = e^2/(4\pi \epsilon_0 \hbar c) \approx 1/137.036,$

$$\boxed{w_{2 \to 1}^{\text{sp}} = A = \alpha \frac{4\omega_{21}^3}{3c^2} |\langle \psi_2 | \mathbf{r} | \psi_1 \rangle|^2,} \qquad \left(\begin{array}{c} \text{rate of spontaneous} \\ \text{emission} \end{array} \right) \qquad \text{(T15.36)}$$

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 ψ_2 to ψ_1, where a photon with polarization $\mathbf{e_k}$ is emitted into a solid angle $d\Omega$, as

$$\begin{aligned} dw_{2 \to 1}^{\text{sp}} &= \frac{\alpha}{2\pi} \frac{\omega_{21}}{m^2 c^2} \left| \mathbf{e_k^*} \cdot \langle \psi_1 | e^{-i\mathbf{k} \cdot \mathbf{r}} \, \widehat{\mathbf{p}} \, | \psi_2 \rangle \right|^2 d\Omega \\[2mm] &= \frac{\alpha}{2\pi} \frac{\omega_{21}}{m^2 c^2} \left| \mathbf{e_k} \cdot \langle \psi_2 | e^{i\mathbf{k} \cdot \mathbf{r}} \, \widehat{\mathbf{p}} \, | \psi_1 \rangle \right|^2 d\Omega. \end{aligned}$$

Introducing the dipole approximation (cf (T15.26)), $\langle \psi_2 | e^{i\mathbf{k} \cdot \mathbf{r}} \, \widehat{\mathbf{p}} \, | \psi_1 \rangle = im\omega_{21} \langle \psi_2 | \mathbf{r} | \psi_1 \rangle$, we can simplify this to

$$\frac{dw_{2 \to 1}^{\text{sp}}}{d\Omega} = \alpha \frac{\omega_{21}^3}{2\pi c^2} |\mathbf{e_k} \cdot \langle \psi_2 | \mathbf{r} | \psi_1 \rangle|^2 \qquad \text{(dipole approx.).} \qquad \text{(T15.37)}$$

A small exercise:
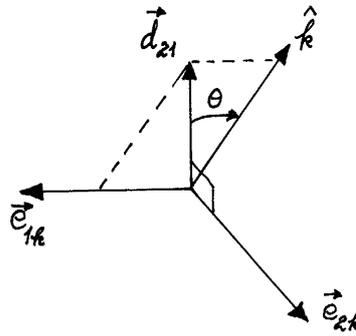
$\mathbf{e}_{1\mathbf{k}}$ in the plane through $\hat{\mathbf{k}}$ and $\mathbf{d}_{21}$ $\implies$ $\mathbf{e}_{2\mathbf{k}} \perp \mathbf{d}_{21}$

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

a) Why is the photon polarized in the plane through $\hat{\mathbf{k}}$ and $\mathbf{d}_{21}$? [Hint: Let $\mathbf{e}_{1\mathbf{k}}$ be a polarization vector *in* this plane, and let $\mathbf{e}_{2\mathbf{k}}$ be orthogonal to $\mathbf{e}_{1\mathbf{k}}$, $\hat{\mathbf{k}}$ and hence to $\mathbf{d}_{21}$. What is then $dw_{2\to1}^{\mathrm{sp}}/d\Omega$ for photons with $\mathbf{e}_{\mathbf{k}} = \mathbf{e}_{1\mathbf{k}}$?]

b) Express $dw_{2\to1}^{\mathrm{sp}}/d\Omega$ in terms of the angle θ_{kd} between $\hat{\mathbf{k}}$ 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")

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

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

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

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

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

such that the *changes* of the quantum numbers are limited to

$$\boxed{\Delta m \equiv m' - m = 0, \pm 1} \quad \text{and} \quad \boxed{\Delta l \equiv l' - l = \pm 1.} \quad \left(\begin{array}{c} \text{selection rules in the electric-} \\ \text{dipole approximation} \end{array} \right)$$

(T15.38)

For transitions which do not satisfy both these conditions, the matrix elements $\mathbf{d}_{fi}$ 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 $\exp(\pm ii\mathbf{k}\cdot\mathbf{r}) = 1 \pm i\mathbf{k}\cdot\mathbf{r} + \cdots$ 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

$$
\begin{aligned}
\mathbf{r} &= \hat{\mathbf{e}}_x\, r\, \sin\theta\cos\phi + \hat{\mathbf{e}}_y\, r\, \sin\theta\sin\phi + \hat{\mathbf{e}}_z\, r\, \cos\theta \\
&= r\sqrt{\frac{4\pi}{3}}\left[\hat{\mathbf{e}}_z\, Y_{10} - \frac{\hat{\mathbf{e}}_x - i\hat{\mathbf{e}}_y}{\sqrt{2}}\, Y_{11} + \frac{\hat{\mathbf{e}}_x + i\hat{\mathbf{e}}_y}{\sqrt{2}}\, Y_{1,-1}\right],
\end{aligned}
\tag{T15.39}
$$

we note that the matrix element $\mathbf{d}_{fi}$ can be written as a radial integral

$$
I_{\mathrm{rad}} \equiv \int_0^\infty R_{n'l'}(r)\, r\, R_{nl}(r) r^2 dr
\tag{T15.40}
$$

multiplied by a linear combination of three angular integrals of the type

$$
J_{m''} \equiv \sqrt{\frac{4\pi}{3}} \int Y_{l'm'}^*\, Y_{1m''} Y_{lm} d\Omega,
\tag{T15.41}
$$

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

$$
(-1)^{l'+1+l} = (-1)^{2l}(-1)^{l'-l+1} = (-1)^{\Delta l+1}.
$$

Thus, the integrand is antisymmetric (and $J_{m''}$ and hence $\mathbf{d}_{fi}$ are equal to zero) <u>unless Δl is odd</u>.
   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 <u>unless $\Delta m = m'' = 0, \pm 1$</u>. This proves the Δm part of the selection rules, and allows us to write the matrix element as

$$
\mathbf{d}_{fi} = I_{\mathrm{rad}}\left(\hat{\mathbf{e}}_z\, J_0\, \delta_{m',m} - \frac{\hat{\mathbf{e}}_x - i\hat{\mathbf{e}}_y}{\sqrt{2}}\, J_1\, \delta_{m',m+1} + \frac{\hat{\mathbf{e}}_x + i\hat{\mathbf{e}}_y}{\sqrt{2}}\, J_{-1}\delta_{m',m-1}\right),
\tag{T15.42}
$$

where J_0, J_1 and J_{-1} are given by (T15.41).
   It remains to show why Δl is restricted to ± 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

$$
J_{m''} = \sqrt{1/3} \int Y_{l'm'}^* Y_{1m''} d\Omega = \sqrt{1/3}\,\delta_{l',1}\delta_{m',m''},
$$

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 $Y_{1m''}Y_{lm}$ 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

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

(There is no term $Y_{l,m+m''}$ on the right because it has the wrong parity.) Inserting this expres-
sion into (T15.41), we see that the rule $\Delta l \equiv l' - l = \pm 1$ 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 $\mathbf{d}_{fi}$ 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.**
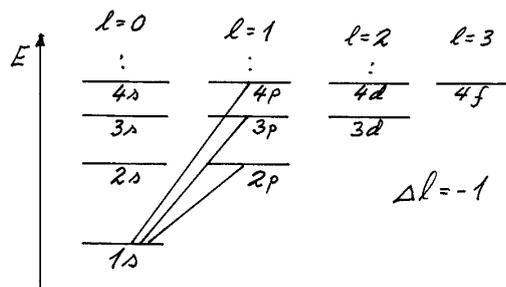

Transitions to $2s$ and $2p$
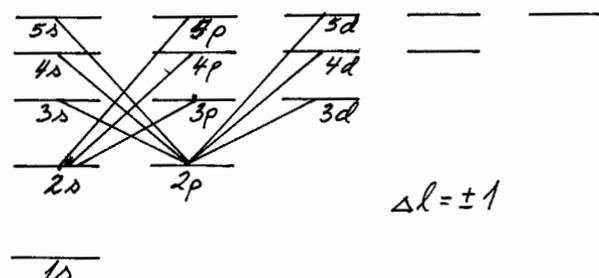
Here the energy differences

$$\Delta E = -\tfrac{1}{2}\alpha^2 mc^2 \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \qquad (n = 3, 4, \cdots)$$

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 Lecture notes 1), which in turn formed part of the background for the Bohr model.

Cascade

As illustrated above, there is no restriction on Δn, 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 $n - 1$.
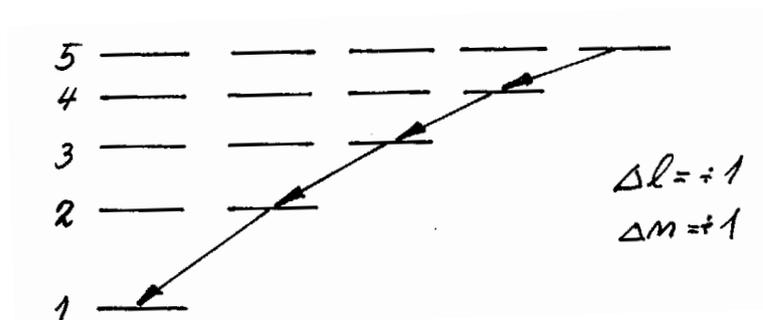
Then, as illustrated in the figure, electric-dipole transitions are only possible for $\Delta n = \Delta l = -1$. This way we get a whole cascade of transitions, with spectral lines corresponding to a whole series of energy differences between neighbouring levels.

15.5.c Lifetime. Line width

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

$$\boxed{ w_{i \to f}^{\text{sp}} = \alpha \, \frac{4\omega_{if}^3}{3c^2} \, |\mathbf{d}_{fi}|^2 , }$$

gives the *probability* per unit time for transition from the state ψ_i to the state ψ_f. This means that we are not able to predict what happens with a single atom in an excited state ψ_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 ψ_i at the time t, the theory predicts that the number that is expected to decay into ψ_f in the time interval $(t, t + dt)$ is

$$dN_f = N(t) w_{i \to f}^{\text{sp}} dt.$$

Summing over the possible final states ψ_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

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

is the total rate of de-excitation for the state ψ_i. Then,

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

which is readily intergrated to

$$N(t) = N(0) \, e^{-w_i t} \equiv N(0) \, e^{-t/\tau_i}; \qquad \tau_i \equiv \frac{1}{w_i}. \tag{T15.44}$$

Here, $\tau_i \equiv 1/w_i$ is called the **lifetime** for the state ψ_i.

> **A small exercise:**
> Show that τ_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 ψ_{100}. With a dipole moment $|\mathbf{d}_{fi}|$ of the order a_0, and a frequency $\omega_{21} \sim 10^{16} \, \mathrm{s}^{-1}$, we then get a transition rate
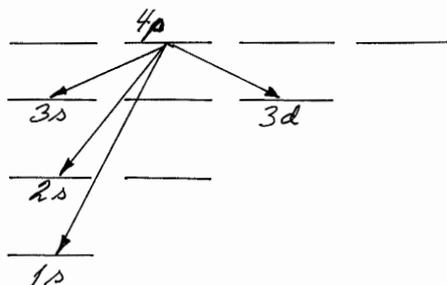
$$w_{i \to f} \sim \alpha \frac{\omega_{21}^3}{c^2} |a_0|^2 \sim 10^{-2} \frac{10^{48}}{10^{17}} 10^{-20} \, \mathrm{s}^{-1} = 10^9 \, \mathrm{s}^{-1}.$$

The lifetime of this state then is of the order of

$$\tau_i = \frac{1}{w_i} \sim 10^{-9} \, \mathrm{s}.$$

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

As another example, let the initial state be ψ_{410}.

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

Note that the transition from ψ_{200} to ψ_{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 ~ 0.1 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 ω_0 and a damping time τ, 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 ω_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 $2p \to 1s$ in hydrogen, the spread in the energy of the emitted photons is[5] $\hbar\Delta\omega = \hbar w_i$, where w_i is the transition rate. More precisely, it can be shown that the probability distribution of the photons emitted goes as

$$P(\hbar\omega) \propto \frac{1}{(\hbar\omega - \hbar\omega_{21})^2 + (\frac{1}{2}\hbar w_i)^2}, \qquad \text{(T15.45)}$$

where $w_i = w_{2\to 1}^{\mathrm{sp}} = 1/\tau_i$ is the spontaneous transition rate from (any of) the $2p$ state(s) to the ground state. This is called a **Lorentzian** probability distribution.
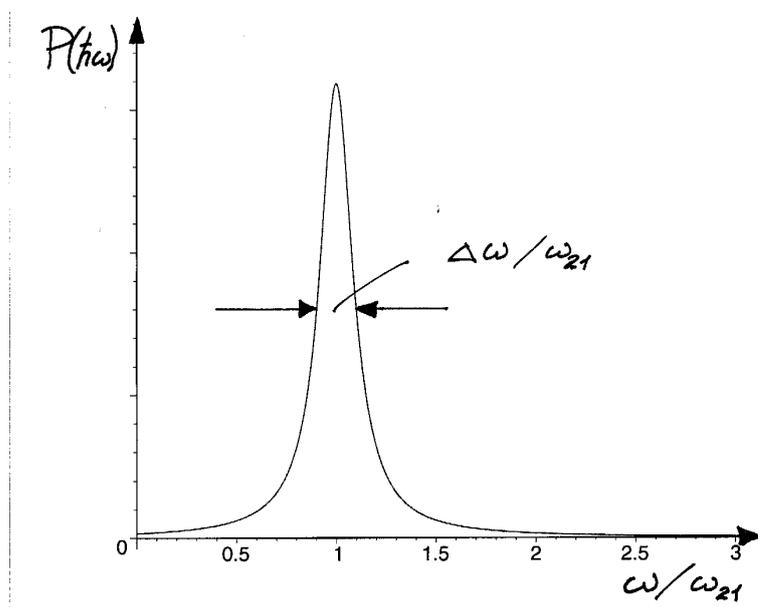
As illustrated in the figure, the "full width at half maximum" of the peak is $\Delta\omega = w_i$. The interpretation of this result (using energy conservation) is that the energy of the initial excited state is not sharp,[6] but has a probability distribution with a width

$$\Delta E_2 = \hbar\Delta\omega = \hbar w_i = \hbar/\tau_i. \qquad \text{(T15.46)}$$

It is fairly common to call the width ΔE_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.[7]

---

[5]See, e.g., section 11.5 in Bransden & Joachain, or W. Heitler, *The Quantum Theory of Radiation* (3$^{\mathrm{rd}}$ edition), Chap. V, §18 p 181..

[6]Note that the initial state ψ_2 is an eigenstate of the "particle part" $\widehat{H}_p$ of the Hamiltonian, but not of the total Hamiltonian $\widehat{H}$. Therefore the initial energy can not be sharp.

[7]Strictly speaking, ΔE 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.

We note that the smaller the liftime 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 widhs 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.