Lecture notes on

Atoms & Clusters

(Theory Part)

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Chapter 1

Matter in an electromagnetic field

1.1 Electromagnetic field

We introduce a scalar and a vector potential such that the electric field is given by

$$\boldsymbol{E}(\boldsymbol{r},t) = -\boldsymbol{\nabla}\phi(\boldsymbol{r},t) - \frac{\partial}{\partial t}\boldsymbol{A}(\boldsymbol{r},t) \tag{1.1}$$

and the magnetic field by

$$\boldsymbol{B}(\boldsymbol{r},t) = \boldsymbol{\nabla} \times \boldsymbol{A}(\boldsymbol{r},t). \tag{1.2}$$

Electric and magnetic field do not change under the *gauge transformation*

$$\boldsymbol{A}(\boldsymbol{r},t) \to \boldsymbol{A}(\boldsymbol{r},t) + \boldsymbol{\nabla}\chi(\boldsymbol{r},t), \tag{1.3}$$

$$\phi(\boldsymbol{r},t) \to \phi(\boldsymbol{r},t) - \frac{\partial}{\partial t}\chi(\boldsymbol{r},t). \tag{1.4}$$

The freedom of choosing χ may be employed to fulfill the *Coulomb gauge* condition

$$\boldsymbol{\nabla} \cdot \boldsymbol{A} = 0 \tag{1.5}$$

so that Maxwell's equations in vacuum (i.e., no charges and currents) boil down to the wave equation

$$\nabla^2 \boldsymbol{A} - \frac{1}{c^2}\frac{\partial^2 \boldsymbol{A}}{\partial t^2} = 0 \tag{1.6}$$

with c the speed of light in vacuum. Plane wave solutions of (1.6) read

$$\boldsymbol{A}(\boldsymbol{r},t) = \hat{A}\boldsymbol{\varepsilon}\cos(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t + \delta_\omega), \tag{1.7}$$

and angular frequency ω and wave number $k = |\boldsymbol{k}|$ satisfy the simple dispersion relation

$$\omega = kc. \tag{1.8}$$

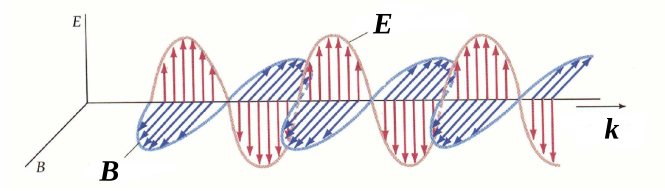

Figure 1.1: Electromagnetic wave.

The vector $\boldsymbol{\varepsilon}$ defines the polarization direction. In the Coulomb gauge (1.5)

$$\boldsymbol{k} \cdot \boldsymbol{\varepsilon} = 0 \tag{1.9}$$

follows. For $\phi = 0$ the fields read

$$\boldsymbol{E}(\boldsymbol{r}, t) = \hat{E} \boldsymbol{\varepsilon} \sin(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t + \delta_\omega), \tag{1.10}$$

$$\boldsymbol{B}(\boldsymbol{r}, t) = \frac{\hat{E}}{\omega} (\boldsymbol{k} \times \boldsymbol{\varepsilon}) \sin(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t + \delta_\omega), \tag{1.11}$$

where

$$\hat{E} = -\omega \hat{A}. \tag{1.12}$$

$\boldsymbol{E}$, $\boldsymbol{B}$, and $\boldsymbol{k}$ are mutually perpendicular (cf. Fig. 1.1). A general, elliptically polarized electromagnetic wave can be constructed as a superposition of two solutions with polarization vectors $\boldsymbol{\varepsilon}_\lambda$, $\lambda = 1, 2$.

The energy density of the electromagnetic field is given by

$$\frac{1}{2} \left(\varepsilon_0 |\boldsymbol{E}|^2 + \mu_0^{-1} |\boldsymbol{B}|^2 \right) = \varepsilon_0 \hat{E}^2 \sin^2(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t + \delta_\omega) \tag{1.13}$$

with $\varepsilon_0 \mu_0 = c^{-2}$. The time-averaged energy density is[1]

$$\rho = \frac{1}{2} \varepsilon_0 \hat{E}^2 = \frac{1}{2} \varepsilon_0 \omega^2 \hat{A}^2. \tag{1.14}$$

On the other hand, thinking in terms of photons yields an energy density

$$\rho = \frac{\hbar \omega N}{V} \tag{1.15}$$

with N the number of photons of energy $\hbar\omega$ and V is the quantization volume. The relation between classical electric field amplitude and number of photons thus reads

$$|\hat{E}| = \sqrt{\frac{2\rho}{\varepsilon_0}} = \sqrt{\frac{2\hbar\omega N}{\varepsilon_0 V}}. \tag{1.16}$$

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[1] Note that the time-average of the $\sin^2$ in (1.13) is $1/2$.

The intensity I is typically defined as the time-average Poynting vector $\langle \boldsymbol{S} \rangle_t$,

$$\boldsymbol{S} = \frac{1}{\mu_0}(\boldsymbol{E} \times \boldsymbol{B}), \tag{1.17}$$

leading to

$$I = \rho c = \frac{1}{2}\varepsilon_0 c \hat{E}^2 = \frac{\hbar\omega N c}{V}. \tag{1.18}$$

The intensity is the field energy transported per time perpendicularly through an unit area (i.e., parallel to the normal vector of the area).

If the phase δ_ω fluctuates randomly, as, e.g., in the case of radiation from a hot gas, the radiation is *incoherent*.

1.2 Coupling to a charged particle

Maxwell's equations do tell us how charges and currents generate electric and magnetic fields. The electromagnetic waves discussed in the previous Section are even supported without any charges and currents because we ignored the fact that they have been generated somewhere sufficiently far away. However, Maxwell's equations do not tell us how charges q move under the influence of electric and magnetic fields. At that point the Lorentz force comes into play:

$$\boldsymbol{F} = q(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}). \tag{1.19}$$

In terms of potentials it reads

$$\boldsymbol{F} = q\left(-\boldsymbol{\nabla}\phi - \frac{\partial}{\partial t}\boldsymbol{A} + \boldsymbol{v} \times (\boldsymbol{\nabla} \times \boldsymbol{A})\right). \tag{1.20}$$

It can be easily shown (→ exercise) that the Lagrangian

$$L = \frac{1}{2}mv^2 - q\phi + q\boldsymbol{v} \cdot \boldsymbol{A} \tag{1.21}$$

yields the equation of motion

$$m\ddot{\boldsymbol{r}} = \boldsymbol{F}. \tag{1.22}$$

The so-called *minimum coupling* Hamiltonian corresponding to the Lagrangian (1.21) reads

$$H = \frac{1}{2m}\left(\boldsymbol{p} - q\boldsymbol{A}\right)^2 + q\phi \tag{1.23}$$

where the canonical momentum $\boldsymbol{p}$ is

$$\boldsymbol{p} = m\boldsymbol{v} + q\boldsymbol{A}. \tag{1.24}$$

So far everything was classical. We assume that the classical Hamiltonian can be used as the corresponding Hamilton operator in a quantum mechanical treatment. As the latter must be Hermitian we assume

$$H = \frac{p^2}{2m} - \frac{q}{2m}(\boldsymbol{A}\cdot\boldsymbol{p} + \boldsymbol{p}\cdot\boldsymbol{A}) + \frac{q^2}{2m}A^2 + q\phi \tag{1.25}$$

(we omit indicating operators explicitly). The time-dependent Schrödinger equation (TDSE)

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{r},t) = H\Psi(\boldsymbol{r},t) \tag{1.26}$$

with H according (1.25) is invariant under the gauge transformation (1.3), (1.4) as long as we also transform the wave function in the proper way:

$$\boldsymbol{A} = \boldsymbol{A}' + \boldsymbol{\nabla}\chi, \tag{1.27}$$

$$\phi = \phi' - \frac{\partial}{\partial t}\chi, \tag{1.28}$$

$$\Psi = \mathrm{e}^{\mathrm{i}q\chi/\hbar}\Psi'. \tag{1.29}$$

We can use the gauge freedom to describe the radiation field entirely by the vector potential so that $\phi = 0$, and using the fact that in Coulomb gauge

$$\boldsymbol{\nabla}\cdot(\boldsymbol{A}\Psi) = \boldsymbol{A}\cdot(\boldsymbol{\nabla}\Psi) + (\boldsymbol{\nabla}\cdot\boldsymbol{A})\Psi = \boldsymbol{A}\cdot(\boldsymbol{\nabla}\Psi) \tag{1.30}$$

the TDSE for a free charge in an electromagnetic field reads

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + \mathrm{i}\hbar\frac{q}{m}\boldsymbol{A}\cdot\boldsymbol{\nabla} + \frac{q^2}{2m}A^2\right)\Psi. \tag{1.31}$$

1.3 One-electron atoms in an electromagnetic field

In order to describe one-electron atoms we have to allow at least for one additional positive charge besides the electron (proton, deuteron, positron ...). Assuming that the positive charge has a much bigger mass than the electron $M \gg m$, as, e.g., in H, He$^+$ … we can disregard the difference between reduced mass and electron mass as well as recoil effects. Hence, the interaction with the nucleus is simply described by an external Coulomb potential

$$V_\mathrm{C}(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \tag{1.32}$$

with e the absolute value of the electron charge ($q = -e$) and Ze the nuclear charge. This external potential is added to the Coulomb-gauge Hamiltonian:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \mathrm{i}\hbar\frac{e}{m}\boldsymbol{A}\cdot\boldsymbol{\nabla} + \frac{e^2}{2m}A^2 + V_\mathrm{C}. \tag{1.33}$$

In the perturbative regime we partition the Hamiltonian in the form

$$H = H_0 + H_{\mathrm{int}}(t) \tag{1.34}$$

with H_0 describing the unperturbed atom,

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 + V_{\mathrm{C}} \tag{1.35}$$

and

$$H_{\mathrm{int}}(t) = -\mathrm{i}\hbar\frac{e}{m}\boldsymbol{A}\cdot\boldsymbol{\nabla} + \frac{e^2}{2m}A^2 \simeq -\mathrm{i}\hbar\frac{e}{m}\boldsymbol{A}\cdot\boldsymbol{\nabla} \tag{1.36}$$

where in the last step we made use of the fact that A^2 is of higher order.[2]

1.3.1 Single-photon absorption and emission

For weak electromagnetic fields we can apply time-dependent perturbation theory. The wave function is expanded in eigenstates ψ_j,

$$E_j\psi_j(\boldsymbol{r}) = H_0\psi_j(\boldsymbol{r}), \tag{1.37}$$

$$\Psi(\boldsymbol{r},t) = \sum_j c_j(t)\psi_j(\boldsymbol{r})\mathrm{e}^{-\mathrm{i}E_jt/\hbar}. \tag{1.38}$$

Inserting this into the TDSE one obtains a coupled set of equations for the coefficients $c_j(t)$. We are interested in transitions between two discrete bound states a, b. We obtain for the change in time of the amplitude $c_b(t)$

$$\dot{c}_b(t) = \frac{1}{\mathrm{i}\hbar}\sum_j \underbrace{\langle\psi_b|H_{\mathrm{int}}(t)\,|\psi_j\rangle}_{H_{\mathrm{int}}^{(bj)}(t)} c_j(t)\mathrm{e}^{\mathrm{i}\omega_{bj}t} \tag{1.39}$$

with $\omega_{bj} = (E_b - E_j)/\hbar$. If the system is for $t \leq 0$ is in the state $|\psi_a\rangle$, i.e.,

$$c_j(t \leq 0) = \delta_{ja}, \tag{1.40}$$

we obtain in first order perturbation theory

$$c_b(t) = \frac{1}{\mathrm{i}\hbar}\int_0^t H_{\mathrm{int}}^{(ba)}(t')\mathrm{e}^{\mathrm{i}\omega_{ba}t'}\,\mathrm{d}t' = -\frac{e}{m}\int_0^t \langle\psi_b|\boldsymbol{A}(\boldsymbol{r},t')\cdot\boldsymbol{\nabla}\,|\psi_a\rangle\,\mathrm{e}^{\mathrm{i}\omega_{ba}t'}\,\mathrm{d}t'. \tag{1.41}$$

Inserting a vector potential of the form

$$\boldsymbol{A}(\boldsymbol{r},t) = \hat{A}\boldsymbol{\varepsilon}\cos(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t + \delta_\omega) \tag{1.42}$$

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[2] We will see later that in dipole approximation the term $\sim A^2$ is purely time-dependent and can be transformed away anyhow.

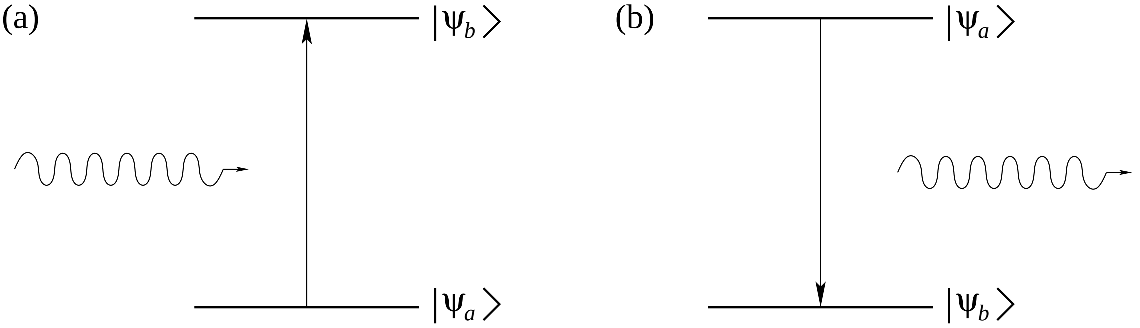

Figure 1.2: Absorption (a) and emission (b) of a photon, involving a transition to a higher (a) or lower (b) atomic level, ensuring energy conservation.

where $\hat{A}$ includes a slowly-varying pulse envelope we obtain

$$\begin{aligned} c_b(t) &= -\frac{e}{2m}\hat{A}\left[\mathrm{e}^{\mathrm{i}\delta_\omega}\langle\psi_b|\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}\cdot\boldsymbol{\nabla}\,|\psi_a\rangle\int_0^t \mathrm{d}t'\,\mathrm{e}^{\mathrm{i}(\omega_{ba}-\omega)t'}\right. \\ &\qquad\left. +\,\mathrm{e}^{-\mathrm{i}\delta_\omega}\langle\psi_b|\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}\cdot\boldsymbol{\nabla}\,|\psi_a\rangle\int_0^t \mathrm{d}t'\,\mathrm{e}^{\mathrm{i}(\omega_{ba}+\omega)t'}\right]. \end{aligned} \tag{1.43}$$

As the pulse duration is much longer than $2\pi/\omega_{ba}$, the time integrals mainly contribute when $\omega_{ba} = \pm\omega$ for the first and the second term, respectively. Obviously the first term describes absorption of a photon, as

$$\omega_{ba} = \omega \qquad \Rightarrow \qquad E_b = E_a + \hbar\omega \tag{1.44}$$

while the second term describes emission of a photon,

$$\omega_{ba} = -\omega \qquad \Rightarrow \qquad E_b = E_a - \hbar\omega \tag{1.45}$$

(see Fig. 1.2).

1.3.2 Absorption

With

$$M_{ba}(\omega) = \langle\psi_b|\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}\cdot\boldsymbol{\nabla}\,|\psi_a\rangle \tag{1.46}$$

we find for the case of absorption[3]

$$\begin{aligned} |c_b(t)|^2 &= \left|-\frac{e}{2m\mathrm{i}}\hat{A}\mathrm{e}^{\mathrm{i}\delta_\omega}M_{ba}(\omega)\frac{\mathrm{e}^{\mathrm{i}(\omega_{ba}-\omega)t}-1}{\omega_{ba}-\omega}\right|^2 && (1.47)\\ &= \frac{1}{2}\left(\frac{e}{m}\right)^2\hat{A}^2|M_{ba}(\omega)|^2F(t,\tilde{\omega}) && (1.48) \end{aligned}$$

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[3] The interference term can be neglected (→ exercise).

with

$$F(t,\tilde{\omega}) = \frac{1-\cos\tilde{\omega}t}{\tilde{\omega}^2}, \qquad \tilde{\omega} = \omega - \omega_{ba}. \tag{1.49}$$

Using

$$F(t,\tilde{\omega}) \to \pi t\,\delta(\tilde{\omega}) \qquad \text{for} \qquad t \to \infty \tag{1.50}$$

we obtain for the rate for times $t \gg 2\pi/\omega_{ba}$

$$W_{ba} = \frac{\mathrm{d}}{\mathrm{d}t}|c_b(t)|^2 = \frac{\pi}{2}\left(\frac{e}{m}\right)^2 \hat{A}^2 |M_{ba}(\omega_{ba})|^2 \delta(\omega-\omega_{ba}). \tag{1.51}$$

Since

$$\hat{A}^2 = \frac{2I}{\varepsilon_0 c\omega^2} \tag{1.52}$$

this can be written in terms of the intensity I as

$$W_{ba} = \frac{4\pi^2}{m^2 c}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{I}{\omega_{ba}^2}|M_{ba}(\omega_{ba})|^2\delta(\omega-\omega_{ba}). \tag{1.53}$$

The *absorption cross section* is found by noting that

$$\hbar\omega_{ba}W_{ba} = I\sigma_{ba} \tag{1.54}$$

from which

$$\sigma_{ba} = \frac{4\pi^2}{m^2 c}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{\hbar}{\omega_{ba}}|M_{ba}(\omega_{ba})|^2\delta(\omega-\omega_{ba}) = \frac{4\pi^2\alpha\hbar^2}{m^2\omega_{ba}}|M_{ba}(\omega_{ba})|^2\delta(\omega-\omega_{ba}) \tag{1.55}$$

follows, and

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \simeq \frac{1}{137} \tag{1.56}$$

is the *fine structure constant.*

A radiation pulse has a finite bandwidth so that the intensity is actually distributed over frequencies,

$$I = \int_0^\infty u(\omega)c\,\mathrm{d}\omega \tag{1.57}$$

where $u(\omega)$ is the *spectral energy density.* As a consequence, not all incoming energy flux interacts resonantly with the atom, and (1.54) is to be replaced by

$$\hbar\omega_{ba}W_{ba} = \int_0^\infty u(\omega)c\,\sigma_{ba}\,\mathrm{d}\omega, \tag{1.58}$$

leading to

$$W_{ba} = \frac{4\pi^2}{m^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{u(\omega_{ba})}{\omega_{ba}^2}|M_{ba}(\omega_{ba})|^2. \tag{1.59}$$

1.3.3 Stimulated emission

We have noted already that the second term in (1.43) describes emission, where the electron drops from level a with energy $E_a > E_b$ down to level b. Interchanging the labels a and b (so that level b is again the higher one) we find for the stimulated emission rate $\bar{W}_{ab}$

$$\bar{W}_{ab} = W_{ba}, \qquad \bar{\sigma}_{ab} = \sigma_{ba}. \tag{1.60}$$

The fact that the rates for absorption and stimulated emission are equal is called the *principle of detailed balancing*. However, how frequently a process occurs also depends on the population of the levels involved. In equilibrium the upper level is less populated according to the Boltzmann factor $\exp(-\hbar\omega_{ba}/k_{\mathrm{B}}T)$ (see also Sec. 1.3.7 below).

1.3.4 Spontaneous emission

So far we have not quantized the electromagnetic field. If we did we would have obtained for the absorption rate

$$W_{ba} = \frac{4\pi^2}{m^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{N(\omega_{ba})\hbar}{V\omega_{ba}}|M_{ba}(\omega_{ba})|^2\delta(\omega-\omega_{ba}), \tag{1.61}$$

where $N(\omega_{ba})$ is the (expectation) number of photons of energy $\hbar\omega_{ba}$. This expression, because of (1.18)

$$I = \frac{\hbar\omega N c}{V},$$

is the same as (1.53).

However, because of the property of the creation operator (when acting on a Fock state)

$$a^\dagger |n\rangle = \sqrt{n+1}\,|n+1\rangle \tag{1.62}$$

the emission rate is different from the one without quantization of the electromagnetic field:

$$\bar{W}_{ab} = \frac{4\pi^2}{m^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{[N(\omega_{ba})+1]\hbar}{V\omega_{ba}}|M_{ba}(\omega_{ba})|^2\delta(\omega-\omega_{ba}). \tag{1.63}$$

Without quantization of the electromagnetic field there is no emission unless there are already photons in the respective mode. In a quantized field an atom in an excited state can also emit a photon into an empty mode, thanks to the 1 in $N(\omega_{ba})+1$ in the numerator on the right hand side of (1.63). For $N(\omega_{ba}) \gg 1$ the extra 1 can be neglected. Instead, for $N(\omega_{ba}) = 0$ *only* spontaneous emission contributes:

$$W^{\mathrm{s}}_{ab} = \frac{4\pi^2}{m^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{\hbar}{V\omega_{ba}}|M_{ba}(\omega_{ba})|^2\delta(\omega-\omega_{ba}). \tag{1.64}$$

Getting rid of the quantization volume via the density of states

Which photons can be emitted in the process of spontaneous emission depends on the boundary conditions. If the atom is placed into a cavity, the electromagnetic field must fit into this cavity. In our case we are interested in radiation propagating in free space. The quantization volume is just introduced as a mathematical trick to identify discrete modes of the radiation field before the continuum limit is taken, but has no physical significance. In all observables the quantization volume cancels out, e.g., by multiplication with the density of states, as we will see now. We impose periodic boundary conditions[4] and thus find for the wave vector components

$$k_x = \frac{2\pi}{L} n_x, \qquad k_y = \frac{2\pi}{L} n_y, \qquad k_z = \frac{2\pi}{L} n_z, \tag{1.65}$$

with n_x, n_y, n_z being positive or negative integers. In the continuum limit

$$\mathrm{d}^3 n = \mathrm{d}n_x \, \mathrm{d}n_y \, \mathrm{d}n_z = \left(\frac{L}{2\pi}\right)^3 \mathrm{d}k_x \, \mathrm{d}k_y \, \mathrm{d}k_z = \left(\frac{L}{2\pi}\right)^3 k^2 \, \mathrm{d}k \, \mathrm{d}\Omega = \frac{V}{(2\pi)^3} \frac{\omega^2}{c^3} \, \mathrm{d}\omega \, \mathrm{d}\Omega, \tag{1.66}$$

using $k = \omega/c$ in the last step. The density of states $\varrho_a(\omega)$ follows from

$$\mathrm{d}^3 n = \varrho_a(\omega) \, \mathrm{d}\omega \, \mathrm{d}\Omega, \tag{1.67}$$

leading to

$$\varrho_a(\omega) = \frac{V}{(2\pi)^3} \frac{\omega^2}{c^3}. \tag{1.68}$$

Multiplying $\varrho_a(\omega) \, \mathrm{d}\omega \, \mathrm{d}\Omega$ to the right hand side of (1.64) and integrating out ω yields the rate at which linearly polarized photons are emitted under an angle (θ, ϕ) into a solid angle element $\mathrm{d}\Omega$:[5]

$$W^{\mathrm{s}}_{ab} \, \mathrm{d}\Omega = \frac{\hbar}{2\pi m^2 c^3} \left(\frac{e^2}{4\pi\varepsilon_0}\right) \omega_{ba} |M_{ba}(\omega_{ba})|^2 \, \mathrm{d}\Omega. \tag{1.69}$$

The quantization volume V canceled, as required. Integration over all emission angles and summation over the two linearly independent polarizations $\boldsymbol{\varepsilon}_\lambda$, $\lambda = 1, 2$ leads to the total rate

$$W^{\mathrm{s}}_{ab} = \frac{\hbar}{2\pi m^2 c^3} \left(\frac{e^2}{4\pi\varepsilon_0}\right) \int \mathrm{d}\Omega \sum_{\lambda=1}^{2} \omega_{ba} |M^{(\lambda)}_{ba}(\omega_{ba})|^2 \tag{1.70}$$

with

$$M^{(\lambda)}_{ba}(\omega) = \langle \psi_b | \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \boldsymbol{\varepsilon}_\lambda \cdot \boldsymbol{\nabla} \, | \psi_a \rangle \, . \tag{1.71}$$

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[4] As it was done in the derivation of (1.61) and (1.63).

[5] In the following, we keep the notation W^{s}_{ab} for what actually is $\int W^{\mathrm{s}}_{ab} \, \varrho_a(\omega) \, \mathrm{d}\omega$.

1.3.5 Dipole approximation

If the wavelength is much greater than the relevant atomic length scale one may cut the expansion

$$\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} = 1 + \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r} + \frac{1}{2!}(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})^2 + \cdots \tag{1.72}$$

already after the first term. As the vector potential then looses its spatial dependence, the magnetic field $\boldsymbol{B} = \boldsymbol{\nabla}\times\boldsymbol{A}(t) = \boldsymbol{0}$ vanishes. The electric field is considered uniform on the atomic length scale so that also retardation effects are neglected. This approximation is called the *dipole approximation.*

In dipole approximation

$$M_{ba} \to M_{ba}^{\mathrm{D}} = \boldsymbol{\varepsilon}\cdot\langle\psi_b|\boldsymbol{\nabla}\,|\psi_a\rangle = \frac{\mathrm{i}}{\hbar}\boldsymbol{\varepsilon}\cdot\langle\psi_b|\boldsymbol{p}\,|\psi_a\rangle \tag{1.73}$$

where in the last step we used the fact that $\boldsymbol{p} = -\mathrm{i}\hbar\boldsymbol{\nabla}$ in position space representation.

1.3.6 Gauge transformations in dipole approximation

As in dipole approximation the A^2-term in (1.33)[6] is purely time-dependent, it can be transformed away by a contact transformation. Substituting

$$\psi = \exp\left(-\frac{\mathrm{i}e^2}{2m\hbar}\int^t A^2(t')\,\mathrm{d}t'\right)\psi' \tag{1.74}$$

one obtains the time-dependent Schrödinger equation in so-called *velocity gauge*,

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi' = \left(H_0 + \frac{e}{m}\boldsymbol{A}(t)\cdot\boldsymbol{p}\right)\psi' \tag{1.75}$$

with H_0 given in (1.35). Another option is

$$\psi = \exp\left(-\frac{\mathrm{i}e}{\hbar}\boldsymbol{A}(t)\cdot\boldsymbol{r}\right)\psi'', \tag{1.76}$$

leading to the *length gauge* Schrödinger equation

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi'' = (H_0 + e\boldsymbol{E}(t)\cdot\boldsymbol{r})\,\psi''. \tag{1.77}$$

Here, the electric field of the electromagnetic wave is $\boldsymbol{E}(t) = -\partial_t\boldsymbol{A}(t)$. Assuming a linearly polarized vector potential (1.42) the polarization vector $\boldsymbol{\varepsilon}$ is the same for $\boldsymbol{E}$

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[6] Repeated here for convenience:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \mathrm{i}\hbar\frac{e}{m}\boldsymbol{A}\cdot\boldsymbol{\nabla} + \frac{e^2}{2m}A^2 + V_{\mathrm{C}}.$$

and $\boldsymbol{A}$. Note that the transformation (1.76) can be interpreted as a translation in momentum space.

If we perform the perturbative treatment of Sec. 1.3.1 in dipole approximation and length gauge we have

$$H_{\text{int}}(t) = e\boldsymbol{E}(t)\cdot\boldsymbol{r} \tag{1.78}$$

and

$$M_{ba}^{\mathrm{D}} = \frac{m\omega_{ba}}{\hbar e}\boldsymbol{\varepsilon}\cdot\boldsymbol{D}_{ba}, \qquad \boldsymbol{D}_{ba} = -e\langle\psi_b|\boldsymbol{r}\,|\psi_a\rangle = -e\boldsymbol{r}_{ba} \tag{1.79}$$

so that, inserted in (1.59),

$$W_{ba}^{\mathrm{D}} = \frac{4\pi^2}{\hbar^2}\left(\frac{1}{4\pi\varepsilon_0}\right)u(\omega_{ba})|\boldsymbol{\varepsilon}\cdot\boldsymbol{D}_{ba}|^2 = \frac{4\pi^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)u(\omega_{ba})|\boldsymbol{\varepsilon}\cdot\boldsymbol{r}_{ba}|^2 \tag{1.80}$$

follows. The dipole transition matrix element $\boldsymbol{D}_{ba}$ or $\boldsymbol{r}_{ba}$ are atomic properties, the polarization vector $\boldsymbol{\varepsilon}$ is a property of the external field. Their orientation with respect to each other is crucial for the probability that a transition takes place in dipole approximation.

If the matrix element M_{ba} vanishes the corresponding transition is forbidden in first-order perturbation theory. If M_{ba}^{D} vanishes, the transition is called “E1 dipole-forbidden”. The next-order term in the expansion (1.72) $\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}$ may give rise to magnetic dipole (M1) or electric quadrupole (E2) transitions.

The last expression in (1.80) can be written as

$$W_{ba}^{\mathrm{D}} = \frac{4\pi^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)u(\omega_{ba})|\boldsymbol{r}_{ba}|^2\cos^2\theta \tag{1.81}$$

with θ being the angle between $\boldsymbol{\varepsilon}$ and $\boldsymbol{r}_{ba}$. If the radiation is unpolarized one has to average $\cos^2\theta$ over all solid angles,

$$\frac{1}{4\pi}\int_0^{2\pi}\mathrm{d}\phi\int_{-1}^{1}\mathrm{d}(\cos\theta)\,\cos^2\theta = \frac{1}{3}, \tag{1.82}$$

leading to

$$\tilde{W}_{ba}^{\mathrm{D}} = \frac{4\pi^2}{3\hbar^2}\left(\frac{1}{4\pi\varepsilon_0}\right)u(\omega_{ba})|\boldsymbol{D}_{ba}|^2 = \frac{4\pi^2}{3\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)u(\omega_{ba})|\boldsymbol{r}_{ba}|^2. \tag{1.83}$$

We know already that the rate for stimulated emission equals that of absorption. The rate for spontaneous emission (1.69) in dipole approximation and length form becomes

$$W_{ab}^{\mathrm{sD}}\,\mathrm{d}\Omega = \frac{1}{2\pi\hbar c^3}\left(\frac{1}{4\pi\varepsilon_0}\right)\omega_{ba}^3|\boldsymbol{\varepsilon}\cdot\boldsymbol{D}_{ba}|^2\,\mathrm{d}\Omega = \frac{1}{2\pi\hbar c^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\omega_{ba}^3|\boldsymbol{\varepsilon}\cdot\boldsymbol{r}_{ba}|^2\,\mathrm{d}\Omega. \tag{1.84}$$

Summation over the two polarization directions and integration over the angles yields the total rate (→ exercise)

$$\tilde{W}_{ab}^{\mathrm{sD}} = \frac{4}{3\hbar c^3}\left(\frac{1}{4\pi\varepsilon_0}\right)\omega_{ba}^3|\boldsymbol{D}_{ba}|^2 = \frac{4\alpha}{3c^2}\omega_{ba}^3|\boldsymbol{r}_{ba}|^2. \tag{1.85}$$

1.3.7 Einstein coefficients

Consider an ensemble of atoms in a container. Only two nondegenerate levels $E_b > E_a$ are assumed to be relevant, and the ensemble is supposed to be in thermal equilibrium at temperature T.

The number of atoms undergoing a transition $a \to b$ per unit time is governed by

$$\dot{N}_{ba} = W_{ba} N_a \tag{1.86}$$

where N_a is the number of atoms in state a. Einstein introduced a coefficient B_{ba} which relates the spectral energy density $u(\omega)$ with the absorption rate according

$$B_{ba} = \frac{\tilde{W}^{\mathrm{D}}_{ba}}{u(\omega)} = \frac{4\pi^2}{3\hbar^2}\left(\frac{1}{4\pi\varepsilon_0}\right)|\boldsymbol{D}_{ba}|^2. \tag{1.87}$$

Hence,

$$\dot{N}_{ba} = B_{ba} N_a u(\omega_{ba}). \tag{1.88}$$

The number of transitions $b \to a$ per unit time, accompanied by the emission of a photon, reads

$$\dot{N}_{ab} = A_{ab} N_b + B_{ab} N_b u(\omega_{ba}). \tag{1.89}$$

A_{ab} is the Einstein coefficient for spontaneous emission, B_{ab} is the Einstein coefficient for stimulated emission. At equilibrium there must be as many “upward” as “downward” transitions, $\dot{N}_{ba} = \dot{N}_{ab}$ so that

$$\frac{N_a}{N_b} = \frac{A_{ab} + B_{ab} u}{B_{ba} u}. \tag{1.90}$$

On the other hand we know that

$$\frac{N_a}{N_b} = \mathrm{e}^{\hbar\omega_{ba}/k_{\mathrm{B}}T}. \tag{1.91}$$

As a consequence, the spectral energy density is

$$u(\omega_{ba}) = \frac{A_{ab}}{B_{ba}\mathrm{e}^{\hbar\omega_{ba}/k_{\mathrm{B}}T} - B_{ab}}. \tag{1.92}$$

Comparing this with Planck’s distribution

$$u(\omega_{ba}) = \frac{\hbar\omega_{ba}^3}{\pi^2 c^3}\frac{1}{\mathrm{e}^{\hbar\omega_{ba}/k_{\mathrm{B}}T} - 1} \tag{1.93}$$

yields the detailed balance and a relation between spontaneous emission and absorption:

$$B_{ba} = B_{ab}, \tag{1.94}$$

$$A_{ab} = \frac{\hbar\omega_{ba}^3}{\pi^2 c^3} B_{ab}. \tag{1.95}$$

It is easily verified that the latter equation agrees with the above derived result (1.85), i.e.,

$$A_{ab} = \tilde{W}^{\mathrm{sD}}_{ab}. \tag{1.96}$$

In the case of degenerate levels (degeneracies g_a, g_b) one obtains

$$g_a B_{ba} = g_b B_{ab} \tag{1.97}$$

whereas Eq. (1.95) remains valid (→ exercise).

1.3.8 Spontaneous emission from the 2p level

As a concrete example we want to evaluate the rate of spontaneous emission (1.85) for the 2p → 1s-transition in hydrogen-like atoms or ions. First we remind ourselves that the energy levels are given by[7]

$$E_n = -\frac{e^2}{4\pi\varepsilon_0 a_0}\frac{Z^2}{2n^2} = -\frac{1}{2}mc^2\frac{(Z\alpha)^2}{n^2}, \qquad n = 1, 2, 3, \ldots \tag{1.98}$$

where

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \tag{1.99}$$

is the Bohr radius and n is the principal quantum number. The transition frequency ω_{ba} that appears in (1.85) thus is

$$\omega_{2\mathrm{p},1\mathrm{s}} = -\frac{1}{2}\frac{mc^2}{\hbar}(Z\alpha)^2\left(\frac{1}{4} - 1\right) = \frac{3}{8}\frac{mc^2}{\hbar}(Z\alpha)^2. \tag{1.100}$$

The matrix element $\boldsymbol{r}_{21m,100}$ (where the indices indicate the $n\ell m$-quantum numbers of the 2p and 1s state involved) needs to be evaluated with the corresponding hydrogenic eigenfunctions. We remember that the hydrogenic eigenfunctions separate into a radial and an angular part,

$$\Psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_\ell^m(\theta, \phi) \tag{1.101}$$

with $Y_\ell^m(\theta, \phi)$ being the spherical harmonics, and the orbital angular momentum and magnetic quantum numbers obey

$$\ell = 0, 1, \ldots, n-1, \qquad m = -\ell, -\ell+1, \ldots, \ell, \tag{1.102}$$

respectively. The bound-state radial wave functions $R_{n\ell}(r)$ are normalized according to

$$\int_0^\infty |R_{n\ell}|^2 r^2 \, \mathrm{d}r = 1 \tag{1.103}$$

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[7] Here, we neglect spin-orbit coupling and other corrections.

and can be expressed in terms of Laguerre polynomials. We give explicitly the first three of them:

$$\begin{aligned} R_{10}(r) &= 2\left(\frac{Z}{a_0}\right)^{3/2} \mathrm{e}^{-Zr/a_0}, && (1.104) \\ R_{20}(r) &= 2\left(\frac{Z}{2a_0}\right)^{3/2} \left(1-\frac{Zr}{2a_0}\right) \mathrm{e}^{-Zr/2a_0}, && (1.105) \\ R_{21}(r) &= \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{a_0} \mathrm{e}^{-Zr/2a_0}. && (1.106) \end{aligned}$$

The spherical harmonics for $\ell = 0$ and 1 read

$$\begin{aligned} Y_0^0 &= \sqrt{\frac{1}{4\pi}}, && (1.107) \\ Y_1^0(\theta) &= \sqrt{\frac{3}{4\pi}} \cos\theta, && (1.108) \\ Y_1^{\pm 1}(\theta,\phi) &= \mp\sqrt{\frac{3}{8\pi}} \sin\theta\, \mathrm{e}^{\pm \mathrm{i}\phi}. && (1.109) \end{aligned}$$

With this we find for the matrix element $\boldsymbol{r}_{21m,100}$

$$\boldsymbol{r}_{21m,100} = \int_0^\infty R_{21}(r) R_{10}(r) r^3 \,\mathrm{d}r \int [Y_1^m(\theta,\phi)]^* \boldsymbol{e}_r(\theta,\phi) Y_0^0 \,\mathrm{d}\Omega. \tag{1.110}$$

The radial integral gives

$$\int_0^\infty R_{21}(r) R_{10}(r) r^3 \,\mathrm{d}r = \left(\frac{Z}{a_0}\right)^4 \frac{1}{\sqrt{6}} \int_0^\infty r^4 \,\mathrm{e}^{-3Zr/2a_0} \,\mathrm{d}r = \frac{a_0}{Z}\frac{24}{\sqrt{6}}\left(\frac{2}{3}\right)^5. \tag{1.111}$$

The angular integration can be performed using

$$\begin{aligned} \boldsymbol{e}_r \cdot \boldsymbol{e}_x = \cos\phi\sin\theta &= \sqrt{\frac{2\pi}{3}}(-Y_1^1 + Y_1^{-1}), && (1.112) \\ \boldsymbol{e}_r \cdot \boldsymbol{e}_y = \sin\phi\sin\theta &= \sqrt{\frac{2\pi}{3}}\mathrm{i}(Y_1^1 + Y_1^{-1}), && (1.113) \\ \boldsymbol{e}_r \cdot \boldsymbol{e}_z = \cos\theta &= \sqrt{\frac{4\pi}{3}} Y_1^0 && (1.114) \end{aligned}$$

(arguments of the Y_ℓ^ms suppressed) and the orthogonality of the spherical harmonics,

$$\int [Y_\ell^m(\theta,\phi)]^* Y_{\ell'}^{m'}(\theta,\phi) \,\mathrm{d}\Omega = \delta_{\ell\ell'}\delta_{mm'}. \tag{1.115}$$

For, e.g., the x-component we find

$$\begin{aligned}\int [Y_1^m(\theta,\phi)]^* \cos\phi \sin\theta \; Y_0^0 \, \mathrm{d}\Omega &= \int [Y_1^m]^* \sqrt{\frac{2\pi}{3}}(-Y_1^1 + Y_1^{-1})\sqrt{\frac{1}{4\pi}}\,\mathrm{d}\Omega \\ &= \sqrt{\frac{1}{6}}\,(-\delta_{m,1} + \delta_{m,-1}) \qquad (1.116)\end{aligned}$$

so that

$$\boldsymbol{r}_{21m,100} \cdot \boldsymbol{e}_x = x_{21m,100} = \frac{a_0}{Z} 4 \left(\frac{2}{3}\right)^5 (-\delta_{m,1} + \delta_{m,-1}) \qquad (1.117)$$

and analogously

$$\begin{aligned} y_{21m,100} &= \frac{a_0}{Z} 4 \left(\frac{2}{3}\right)^5 \mathrm{i}(\delta_{m,1} + \delta_{m,-1}), \qquad (1.118) \\ z_{21m,100} &= \frac{a_0}{Z} \frac{24}{\sqrt{18}} \left(\frac{2}{3}\right)^5 \delta_{m,0}. \qquad (1.119)\end{aligned}$$

Hence,

$$\begin{aligned} |\boldsymbol{r}_{21m,100}|^2 &= \left(\frac{a_0}{Z}\right)^2 \frac{24^2}{18} \left(\frac{2}{3}\right)^{10} \left(\delta_{m,0} + \frac{1}{2}(\delta_{m,1} + \delta_{m,-1}) + \frac{1}{2}(\delta_{m,1} + \delta_{m,-1})\right) \\ &= \left(\frac{a_0}{Z}\right)^2 \frac{2^{15}}{3^{10}} (\delta_{m,0} + \delta_{m,1} + \delta_{m,-1}) \qquad (1.120) \\ &= \frac{1}{Z^2} \left(\frac{\hbar}{mc\alpha}\right)^2 \frac{2^{15}}{3^{10}} (\delta_{m,0} + \delta_{m,1} + \delta_{m,-1}), \qquad (1.121)\end{aligned}$$

and we see (using (1.85)) that all magnetic sublevels contribute with the same partial rate,

$$\begin{aligned} \tilde{W}^{\mathrm{sD}}_{21m,100} &= \frac{4\alpha}{3c^2} \underbrace{\left(\frac{3}{8}\frac{mc^2}{\hbar}(Z\alpha)^2\right)^3}_{\omega_{ba}^3} \underbrace{\frac{1}{Z^2}\left(\frac{\hbar}{mc\alpha}\right)^2 \frac{2^{15}}{3^{10}}}_{|\boldsymbol{r}_{21m,100}|^2 \text{ for any } m} \\ &= \left(\frac{2}{3}\right)^8 \frac{m\alpha^5 Z^4 c^2}{\hbar}. \qquad (1.122)\end{aligned}$$

If all these levels are equally populated the average

$$\langle \tilde{W}^{\mathrm{sD}}_{21m,100} \rangle_m = \frac{1}{3} \sum_{m=-1}^{1} \tilde{W}^{\mathrm{sD}}_{21m,100} \qquad (1.123)$$

yields the same result as (1.122),

$$\langle \tilde{W}^{\mathrm{sD}}_{21m,100} \rangle_m = \left(\frac{2}{3}\right)^8 \frac{m\alpha^5 Z^4 c^2}{\hbar} = 6.27 \times 10^8 \; Z^4 \; \mathrm{s}^{-1}. \qquad (1.124)$$

Table 1.1: Lifetimes of hydrogenic levels.

level	2p	3s	3p	3d	4s	4p	4d	4f
$\tau/10^{-8}\,\mathrm{s}$	0.16	16	0.54	1.56	23	1.24	3.65	7.3

We see that there is a strong Z-dependence of the spontaneous decay rate. For light atoms and ions spontaneous decay is slow compared to, e.g., the pulse duration of picosecond ($10^{-12}\,\mathrm{s}$) or even femtosecond ($10^{-15}\,\mathrm{s}$) laser pulses. This is good news for several reasons. First, it allows the experimentalists to *prepare* atoms in desired states. They can, for instance, create a population inversion (laser), meaning that a higher state is more likely populated than a lower one. If spontaneous emission were faster, such a preparation would be quickly destroyed or simply not feasible to achieve in the first place. Second, the depopulation of excited states by spontaneous emission of photons need not be taken into account when the TDSE is solved numerically.[8]

1.3.9 Atomic lifetimes

The number of atoms $N(t)$ in an excited state b decreases according to the rate equation

$$\dot{N}(t) = -N(t) \sum_k \tilde{W}^{\mathrm{sD}}_{kb} \tag{1.125}$$

where k runs over all states to which the system can decay. Hence,

$$N(t) = N(0)\ \mathrm{e}^{-t/\tau_b} \tag{1.126}$$

where

$$\tau_b = \frac{1}{\sum_k \tilde{W}^{\mathrm{sD}}_{kb}} \tag{1.127}$$

is the *lifetime* of the level b. Lifetimes for hydrogenic levels are given in Table 1.1. Note that the transition rate for the 2s level vanishes in first order in dipole approximation. In fact, $\tau_{2\mathrm{s}} = 0.14\,\mathrm{s}$, which is very slow compared to the values in Table 1.1. The 2s-state is therefore called *metastable*. Two photons are emitted in the 2s → 1s decay, which is less likely and requires second order perturbation theory for a description.

1.3.10 Selection rules

From (1.80) and (1.84) it is apparent that $\boldsymbol{\varepsilon}\cdot\boldsymbol{r}_{ba}$ determines whether a single-photon transition is dipole-allowed or not. This gives rise to so-called *selection rules*. We

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[8] We shall come back to this later on when we study the quantum dynamics in strong and short laser pulses.

choose the quantization axis to be the z-axis[9] and express vectors in the *spherical basis*

$$\begin{aligned} \boldsymbol{e}_{\pm 1} &= \mp\frac{1}{\sqrt{2}}(\boldsymbol{e}_x \pm \mathrm{i}\boldsymbol{e}_y), && (1.128)\\ \boldsymbol{e}_0 &= \boldsymbol{e}_z. && (1.129) \end{aligned}$$

The spherical basis vectors have the property

$$\boldsymbol{e}_q \cdot \boldsymbol{e}^*_{q'} = \delta_{qq'}, \qquad q, q' = -1, 0, 1 \tag{1.130}$$

(→ exercise). The covariant spherical components of the position vector read

$$\begin{aligned} r_{\pm 1} &= \mp\frac{1}{\sqrt{2}}(x \pm \mathrm{i}y) = \mp\frac{1}{\sqrt{2}} r \sin\theta\, \mathrm{e}^{\pm\mathrm{i}\phi} = r\sqrt{\frac{4\pi}{3}} Y_1^{\pm 1}(\theta, \phi), && (1.131)\\ r_0 &= z = r\cos\theta = r\sqrt{\frac{4\pi}{3}} Y_1^0(\theta, \phi), && (1.132) \end{aligned}$$

i.e.,

$$r_q = r\sqrt{\frac{4\pi}{3}} Y_1^q(\theta, \phi). \tag{1.133}$$

It is easy to verify that

$$\boldsymbol{r} = \sum_{q=-1}^{+1} r_q \boldsymbol{e}^*_q = \sum_{q=-1}^{+1} r^*_q \boldsymbol{e}_q. \tag{1.134}$$

The $r^*_q =: r^q$ are the contravariant spherical components of $\boldsymbol{r}$. We also expand the polarization vector

$$\boldsymbol{\varepsilon} = \sum_{q=-1}^{+1} \varepsilon_q \boldsymbol{e}^*_q = \sum_{q=-1}^{+1} \varepsilon^*_q \boldsymbol{e}_q \tag{1.135}$$

and obtain with (1.130)

$$\boldsymbol{\varepsilon} \cdot \boldsymbol{r} = \sum_{q=-1}^{+1} \sum_{q'=-1}^{+1} \varepsilon^*_q r_{q'}\ \boldsymbol{e}_q \cdot \boldsymbol{e}^*_{q'} = \sum_{q=-1}^{+1} \varepsilon^*_q r_q. \tag{1.136}$$

As a consequence,

$$\boldsymbol{\varepsilon} \cdot \boldsymbol{r}_{ba} = \sum_{q=-1}^{+1} \varepsilon^*_q \langle \Psi_b | r_q | \Psi_a \rangle \tag{1.137}$$

results for one-electron atoms, and, with (1.101),

$$\langle \Psi_{n'\ell' m'} | r_q | \Psi_{n\ell m} \rangle = \sqrt{\frac{4\pi}{3}} \int_0^\infty \mathrm{d}r\, r^3 R_{n'\ell' m'} R_{n\ell m} \int \mathrm{d}\Omega\, [Y_{\ell'}^{m'}]^* Y_1^q Y_\ell^m. \tag{1.138}$$

---

[9] This defines the coordinate system for the spherical harmonics.

The integral $\langle\Psi_{n'\ell'm'}|r_q\,|\Psi_{n\ell m}\rangle = \int \mathrm{d}^3r\;\Psi^*_{n'\ell'm'}(\boldsymbol{r})r_q\Psi_{n\ell m}(\boldsymbol{r})$ can as well be performed using the substitution $\boldsymbol{r}\to-\boldsymbol{r}$ (reflection or space inversion) and must lead to the same result. Because under reflection $\boldsymbol{r}\to-\boldsymbol{r}$

$$R_{n\ell}(r)Y_\ell^m(\theta,\phi)\overset{\boldsymbol{r}\to-\boldsymbol{r}}{\longrightarrow}R_{n\ell}(r)Y_\ell^m(\pi-\theta,\phi+\pi)=R_{n\ell}(r)(-1)^\ell Y_\ell^m(\theta,\phi), \tag{1.139}$$

that is, ℓ determines the parity of the wave function and r does not change, we find

$$\langle\Psi_{n'\ell'm'}|r_q\,|\Psi_{n\ell m}\rangle=(-1)^{\ell+\ell'+1}\langle\Psi_{n'\ell'm'}|r_q\,|\Psi_{n\ell m}\rangle \quad\Rightarrow\quad (\ell+\ell'+1)\text{ even} \tag{1.140}$$

unless the matrix element vanishes. This means that the dipole operator only allows for transitions between states of opposite parity. We will now constrain the conditions for a transition being allowed further.

The radial integral in (1.138) never vanishes. Hence, it is the angular integral over the three spherical harmonics defining the selection rules. Because $Y_\ell^m\sim\mathrm{e}^{\mathrm{i}m\phi}$ the integral over the angle ϕ is of the form

$$J(m,m',q)=\int_0^{2\pi}\mathrm{e}^{\mathrm{i}(m+q-m')\phi}\,\mathrm{d}\phi, \tag{1.141}$$

which is nonvanishing only if

$$m'=m+q. \tag{1.142}$$

In case of $q=0$ the polarization vector is in z-direction (linear polarization) and $m'=m$, i.e., $\Delta m=m'-m=0$. In case of $q=\pm1$ the propagation vector $\boldsymbol{k}$ is in z-direction and $m'=m\pm1$, i.e., $\Delta m=\pm1$ (circular polarization, see next Subsection).

In order to extract the selection rule for the orbital angular momentum we need to consider the integral over the product of three spherical harmonics in (1.138),

$$\mathcal{A}(\ell,m,\ell',m',q)=\int\mathrm{d}\Omega\,[Y_{\ell'}^{m'}]^*Y_1^qY_\ell^m, \tag{1.143}$$

which can be expressed in terms of *Clebsch-Gordan coefficients*,

$$\mathcal{A}(\ell,m,\ell',m',q)=\sqrt{\frac{3}{4\pi}\frac{(2\ell+1)}{(2\ell'+1)}}\langle\ell100|\ell'0\rangle\langle\ell1mq|\ell'm'\rangle. \tag{1.144}$$

The Clebsch-Gordan coefficients are tabulated in books on the quantum theory of angular momentum.[10] It is found that $\langle\ell1mq|\ell'm'\rangle$ is only non-vanishing if $m'=m+q$, as observed previously, and

$$\ell'=\ell\pm1, \tag{1.145}$$

i.e., $\Delta\ell=\ell'-\ell=\pm1$. This result can be also established without resorting to Clebsch-Gordan coefficients but just using the orthogonality of the spherical harmonics (1.115) and recurrence relations (→ exercise).

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[10] For instance, D.A. Varshalovich *et al.*, *Quantum Theory of Angular Momentum*, (World Scientific).

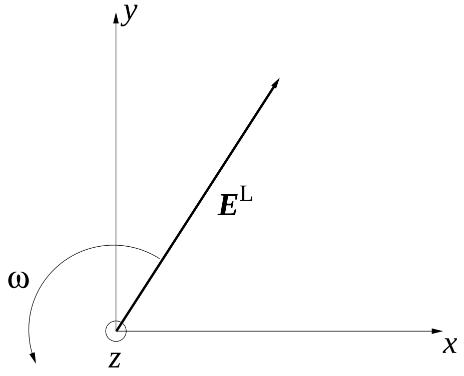

Figure 1.3: How the electric field vector rotates in an anti-clockwise (left-) polarized electromagnetic wave which propagates in z-direction (towards the reader).

Electron spin

The dipole operator does not couple to the electron spin, which is the reason why we have not considered the electron spin in the first place. The electron spin thus remains unaffected by the absorption or emission of dipole radiation.

1.3.11 Helicity of the photon

Let us consider the vector potential

$$\boldsymbol{A}^{\mathrm{L}}(z,t) = \frac{1}{\sqrt{2}}\hat{A}\left(\cos(kz-\omega t)\boldsymbol{e}_x - \sin(kz-\omega t)\boldsymbol{e}_y\right) \tag{1.146}$$

and the corresponding electric field $\boldsymbol{E}^{\mathrm{L}} = -\partial_t \boldsymbol{A}^{\mathrm{L}}$

$$\boldsymbol{E}^{\mathrm{L}}(z,t) = \frac{1}{\sqrt{2}}\hat{A}\omega\left(-\sin(kz-\omega t)\boldsymbol{e}_x - \cos(kz-\omega t)\boldsymbol{e}_y\right). \tag{1.147}$$

Figure 1.3 shows how the electric field vector rotates in the xy-plane, as seen from an observer looking towards the incoming wave.

By projecting onto the spherical basis vectors (1.128) we find

$$\boldsymbol{e}_{\pm 1}\cdot\boldsymbol{A}^{\mathrm{L}} = \mp\frac{1}{2}\hat{A}(\cos\eta \mp \mathrm{i}\sin\eta) = \mp\frac{1}{2}\hat{A}\mathrm{e}^{\mp\mathrm{i}\eta} \tag{1.148}$$

with $\eta = kz-\omega t$. The vector potential can thus be expanded in the form

$$\boldsymbol{A}^{\mathrm{L}} = \frac{1}{2}\hat{A}(\mathrm{e}^{\mathrm{i}\eta}\boldsymbol{e}^*_{-1} - \mathrm{e}^{-\mathrm{i}\eta}\boldsymbol{e}^*_{+1}). \tag{1.149}$$

If we introduce

$$\boldsymbol{e}^*_{-1} = \frac{1}{\sqrt{2}}(\boldsymbol{e}_x + \mathrm{i}\boldsymbol{e}_y) =: \boldsymbol{e}^{\mathrm{L}}, \tag{1.150}$$

$$\boldsymbol{e}^*_{+1} = -\frac{1}{\sqrt{2}}(\boldsymbol{e}_x - \mathrm{i}\boldsymbol{e}_y) =: \boldsymbol{e}^{\mathrm{R}} \tag{1.151}$$

we can write for an anti-clockwise (left-) polarized vector potential

$$\boldsymbol{A}^{\mathrm{L}} = \frac{1}{2}\hat{A}(\boldsymbol{e}^{\mathrm{L}}\mathrm{e}^{\mathrm{i}(kz-\omega t)} + \text{c.c.}) \tag{1.152}$$

and for a clockwise (right-) polarized wave

$$\boldsymbol{A}^{\mathrm{R}} = \frac{1}{2}\hat{A}(\boldsymbol{e}^{\mathrm{R}}\mathrm{e}^{\mathrm{i}(kz-\omega t)} + \text{c.c.}). \tag{1.153}$$

From expression (1.43) we inferred that the term $\sim \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}$ gives rise to absorption and the term $\sim \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}$ gives rise to emission of photons. Therefore the term $\sim \boldsymbol{e}^{\mathrm{L}}\cdot\boldsymbol{r}_{ba}$ describes the absorption of a left-hand circularly polarized photon, and the term $\sim \boldsymbol{e}^{\mathrm{R}}\cdot\boldsymbol{r}_{ba}$ that of a right-hand one. As we interchanged the labels a and b in the emission term in Sec. 1.3.3 we find that $\boldsymbol{e}^{\mathrm{L}^*}\cdot\boldsymbol{r}_{ab} = \boldsymbol{e}^{\mathrm{L}^*}\cdot\boldsymbol{r}^*_{ba}$ describes the emission of a left-hand circularly polarized photon, and $\boldsymbol{e}^{\mathrm{R}^*}\cdot\boldsymbol{r}_{ab} = \boldsymbol{e}^{\mathrm{R}^*}\cdot\boldsymbol{r}^*_{ba}$ that of a right-hand one.

Let us consider the emission of a left-hand circularly polarized photon,

$$\boldsymbol{e}^{\mathrm{L}^*}\cdot\boldsymbol{r}_{ab} = \frac{1}{\sqrt{2}}(\boldsymbol{e}_x - \mathrm{i}\boldsymbol{e}_y)\cdot\boldsymbol{r}_{ab} = \frac{1}{\sqrt{2}}(x_{ab} - \mathrm{i}y_{ab}) = \langle\Psi_a|r_{-1}|\Psi_b\rangle\,. \tag{1.154}$$

In the last step we used (1.131). Because of (1.142) and $q = -1$ in this case, obviously $m' = m - 1$, which means that in the final state the atom lost $1\,\hbar$ of angular momentum projected onto the z-axis (i.e., the quantization axis). With the same line of arguments one arrives at the conclusion that the emission of a right-hand circularly polarized photon increases the m-quantum number by one.

Because of angular momentum conservation of the total system atom + field, a photon has to carry an angular momentum $\pm\hbar$ *in propagation direction.* As there can never be an orbital angular momentum $\boldsymbol{L} = \boldsymbol{r}\times\boldsymbol{p}$ in propagation direction the angular momentum of the photon must be *intrinsic.* We call it the spin of the photon. Its projection onto the propagation direction is called *helicity.* It is $+\hbar$ for left-hand and $-\hbar$ for right-hand circularly polarized photons. There is none with $0\hbar$. This is different from a massive spin-1 particle, for which there would be three values (-1, 0, and $+1\hbar$) for m_s.

1.3.12 Spectrum of one-electron atoms

The non-relativistic expression for the eigenenergies reads

$$E_n = -\frac{e^2}{4\pi\varepsilon_0 a_0}\frac{Z^2}{2n^2} = -\frac{1}{2}mc^2\frac{(Z\alpha)^2}{n^2}, \qquad n = 1,2,3,\ldots \tag{1.155}$$

where

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \tag{1.156}$$

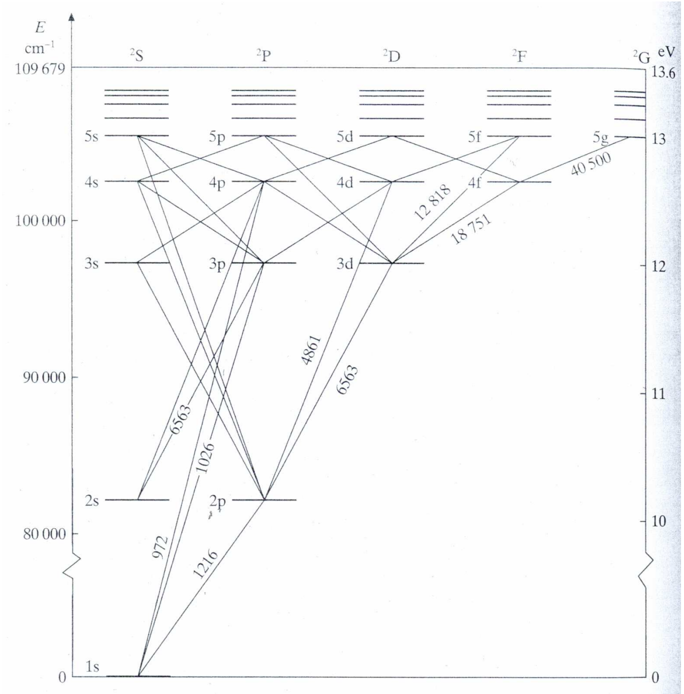

Figure 1.4: Grotrian diagram for atomic hydrogen (from Bransden & Joachain, *Physics of Atoms and Molecules*).

is the Bohr radius and n is the principal quantum number. As these energies only depend on the principal quantum number but the selection rules derived above involve only ℓ and m, the hydrogenic spectrum contains all frequencies

$$\nu_{ab} = \frac{E_{n_b} - E_{n_a}}{h} = \frac{1}{2} mc^2 \frac{\alpha^2}{h} Z^2 \left(\frac{1}{n_a^2} - \frac{1}{n_b^2} \right) \tag{1.157}$$

where $n_b > n_a$. The selection rule (1.145) restricts the possible transitions, as illustrated in the *Grotrian diagram* in Fig. 1.4.

1.3.13 Oscillator strengths

We define the *oscillator strength*

$$f_{ka} = \frac{2m\omega_{ka}}{3\hbar} |\boldsymbol{r}_{ka}|^2 \tag{1.158}$$

where $\omega_{ka} = (E_k - E_a)/\hbar$, $E_k > E_a$ so that $f_{ka} > 0$ for absorption and $f_{ka} < 0$ for emission. We will now show that

$$\sum_k f_{ka} = 1, \tag{1.159}$$

which is the *Thomas-Reiche-Kuhn* sum rule.

We start with

$$\frac{\hbar}{\mathrm{i}} = \langle\psi_a|[p_x, x]\,|\psi_a\rangle\,. \tag{1.160}$$

Inserting unity we obtain

$$\frac{\hbar}{\mathrm{i}} = \sum_k \langle\psi_a|p_x\,|\psi_k\rangle\,\langle\psi_k|x\,|\psi_a\rangle - \sum_k \langle\psi_a|x\,|\psi_k\rangle\,\langle\psi_k|p_x\,|\psi_a\rangle\,. \tag{1.161}$$

Making use of

$$\boldsymbol{p} = m\frac{\mathrm{i}}{\hbar}[H_0, \boldsymbol{r}], \tag{1.162}$$

where H_0 is the atomic Hamiltonian, (1.35) we have

$$\begin{aligned}\frac{\hbar}{\mathrm{i}} &= m\frac{\mathrm{i}}{\hbar}\Big(\sum_k \langle\psi_a|[H_0, x]\,|\psi_k\rangle\,\langle\psi_k|x\,|\psi_a\rangle - \sum_k \langle\psi_a|x\,|\psi_k\rangle\,\langle\psi_k|[H_0, x]\,|\psi_a\rangle\Big) \\ &= m\frac{\mathrm{i}}{\hbar}\Big(\sum_k (E_a - E_k)\langle\psi_a|x\,|\psi_k\rangle\,\langle\psi_k|x\,|\psi_a\rangle - \sum_k (E_k - E_a)\langle\psi_a|x\,|\psi_k\rangle\,\langle\psi_k|x\,|\psi_a\rangle\Big) \\ &= \frac{2m}{\mathrm{i}\hbar}\sum_k \hbar\omega_{ka}|\langle\psi_k|x\,|\psi_a\rangle\,|^2. \end{aligned} \tag{1.163}$$

Hence,

$$1 = \frac{2m}{\hbar}\sum_k \omega_{ka}|\langle\psi_k|x\,|\psi_a\rangle\,|^2. \tag{1.164}$$

The same is obtained for y and z so that

$$3 = \frac{2m}{\hbar}\sum_k \omega_{ka}|\boldsymbol{r}_{ka}|^2, \tag{1.165}$$

and with (1.158) follows (1.159).

If continuum states are involved the sum rule is easily extended to incorporate them as well. Defining

$$\frac{\mathrm{d}f_{Ea}}{\mathrm{d}E} = \frac{2m}{3\hbar}\omega_{Ea}|\boldsymbol{r}_{Ea}|^2 \tag{1.166}$$

where E labels the energy continuum eigenstates $|\psi_E\rangle$ which are supposed to be normalized according to

$$\langle\psi_E|\psi_{E'}\rangle = \delta(E - E') \tag{1.167}$$

and

$$\boldsymbol{r}_{Ea} = \langle\psi_E|\boldsymbol{r}\,|\psi_a\rangle \tag{1.168}$$

one finds

$$\sum_k f_{ka} + \int_0^\infty \frac{\mathrm{d}f_{Ea}}{\mathrm{d}E}\,\mathrm{d}E = 1. \tag{1.169}$$

We derived the Thomas-Reiche-Kuhn sum rule only for one-electron atoms here but it similarly holds for N-electron atoms,

$$\sum_k f_{ka}^{(N)} = N, \tag{1.170}$$

where

$$f_{ka}^{(N)} = \frac{2m\omega_{ka}}{3\hbar}|\boldsymbol{R}_{ka}|^2, \qquad \boldsymbol{R}_{ka} = \sum_{i=1}^{N} \boldsymbol{r}_{ka}^{(i)}, \qquad \boldsymbol{r}_{ka}^{(i)} = \langle\psi_k|\boldsymbol{r}_i\,|\psi_a\rangle \tag{1.171}$$

(→ exercise).

All transition rates in dipole approximation can be expressed in terms of oscillator strengths, e.g.,

$$\tilde{W}_{ab}^{\mathrm{sD}} = \frac{2\alpha\hbar}{mc^2}\omega_{ba}^2|f_{ba}|. \tag{1.172}$$

Sum rules are useful in numerical calculations where basis sets are necessarily restricted. One can then test in how far the sum rules are "exhausted", i.e., how close one is to 1 (or N) when summing up all the oscillator strengths in the numerical implementation.

1.3.14 Spectral lines

What is the energy of a photon being emitted in the process of spontaneous emission? The most likely energy will be $\hbar\omega_{ba}$ because it fits to the energy difference of the levels involved. However, if the lifetime of one of the states (or both) is finite, we expect an uncertainty in the photon energy because of the time-energy uncertainty relation. As a consequence, spectral lines broaden. This leads to a *natural line width* for a given transition, which we will discuss first.

Starting point is (1.39),

$$\dot{c}_b(t) = \frac{1}{\mathrm{i}\hbar}\sum_j \langle\psi_b|H_{\mathrm{int}}(t)\,|\psi_j\rangle\; c_j(t)\mathrm{e}^{\mathrm{i}\omega_{bj}t}. \tag{1.173}$$

We are interested in the spontaneous decay of an initial state b to the ground state a. The final state consists of the emitted photon (characterized by its polarization and the direction of emission) and the electron in the ground state. We characterize the corresponding amplitude by $c_a(\omega,\Omega,\lambda,t)$. Retaining only the two states involved we obtain two equations, namely one where $\dot{c}_b$ is coupled with c_a,

$$\dot{c}_b(t) = -\frac{e}{2m}\frac{V}{(2\pi)^3c^3}\sum_\lambda \int \mathrm{d}\omega\,\omega^2\!\int \mathrm{d}\Omega\;\hat{A}(\omega)M_{ba}^{(\lambda)}(\omega)\mathrm{e}^{\mathrm{i}(\omega_{ba}-\omega)t}c_a(\omega,\Omega,\lambda,t), \tag{1.174}$$

and another one where $\dot{c}_a$ is coupled to c_b,

$$\dot{c}_a(\omega,\Omega,\lambda,t) = \frac{e}{2m}\hat{A}(\omega)M_{ba}^{(\lambda)*}(\omega)\;\mathrm{e}^{\mathrm{i}(\omega-\omega_{ba})t}c_b(t). \tag{1.175}$$

In (1.174), we sum on the right hand side over the polarization of the emitted photon and the direction of emission, and use the density of states (1.68). In (1.175) we made use of the fact that $M_{ab}^{(\lambda)} = -M_{ba}^{(\lambda)*}$. From (1.16) for $N = 1$ photon we infer the vector potential amplitude

$$\hat{A}(\omega) = \sqrt{\frac{2\hbar}{V\varepsilon_0\omega}}. \tag{1.176}$$

In the perturbative treatment of Sec. 1.3.1 we set $c_b = 1$. Now we allow for a decay from time $t = 0$ on:

$$c_b(t) = \Theta(t)\ \mathrm{e}^{-t/(2\tau_b)}. \tag{1.177}$$

The time-evolution of the initial state wavefunction then reads

$$\psi_b(\boldsymbol{r}, t) = c_b(t)\psi_b(\boldsymbol{r})\ \mathrm{e}^{-\mathrm{i}E_b t/\hbar} = \psi_b(\boldsymbol{r})\ \mathrm{e}^{-\mathrm{i}[E_b - \mathrm{i}\hbar/(2\tau_b)]t/\hbar} \tag{1.178}$$

for $t \geq 0$. This resembles the free evolution of a wavefunction with *complex* energy

$$\mathcal{E}_b = E_b - \mathrm{i}\frac{\hbar}{2\tau_b}. \tag{1.179}$$

Inserting (1.177) into (1.175) and integrating over t yields

$$\begin{aligned} c_a(\omega, \Omega, \lambda, t) &= \frac{e}{2m}\hat{A}(\omega)M_{ba}^{(\lambda)*}(\omega)\int_0^t \mathrm{e}^{\mathrm{i}(\omega-\omega_{ba})t' - t'/(2\tau_b)}\ \mathrm{d}t'. \\ &= \frac{e}{2m}\hat{A}(\omega)M_{ba}^{(\lambda)*}(\omega)\ \frac{\mathrm{e}^{\mathrm{i}(\omega-\omega_{ba})t - t/(2\tau_b)} - 1}{\mathrm{i}(\omega - \omega_{ba}) - 1/(2\tau_b)}. \end{aligned} \tag{1.180}$$

For $t \gg \tau_b$ it is seen that the probability $|c_a(\omega, \Omega, \lambda, t)|^2$ for a photon being emitted with polarization $\boldsymbol{\varepsilon}_\lambda$ into the direction Ω is proportional to

$$\left|\frac{1}{\mathrm{i}(\omega - \omega_{ba}) - 1/(2\tau_b)}\right|^2 = \frac{1}{(\omega - \omega_{ba})^2 + 1/(4\tau_b^2)}, \tag{1.181}$$

which is maximal for $\omega = \omega_{ba}$ and half of the maximum at $\omega = \omega_{ba} \pm 1/(2\tau_b)$. Hence, introducing the *natural line width*

$$\Gamma_b = \frac{\hbar}{\tau_b} \tag{1.182}$$

we see that the probability $|c_a(\omega, \Omega, \lambda, t)|^2$ is porportional to the *Lorentzian*

$$f(\omega - \omega_{ba}) = \frac{\Gamma_b^2/(4\hbar^2)}{(\omega - \omega_{ba})^2 + \Gamma_b^2/(4\hbar^2)}, \tag{1.183}$$

whose full width half maximum (FWHM) is $\Gamma_b/\hbar$ and which is shown in Fig. 1.5. The maximum of the function f is unity for all Γ_b so that $\lim_{\Gamma_b\to 0} f = 0$. Instead, with

$$\tilde{f}(\omega - \omega_{ba}) = \frac{1}{\pi}\frac{\Gamma_b/(2\hbar)}{(\omega - \omega_{ba})^2 + \Gamma_b^2/(4\hbar^2)} \tag{1.184}$$

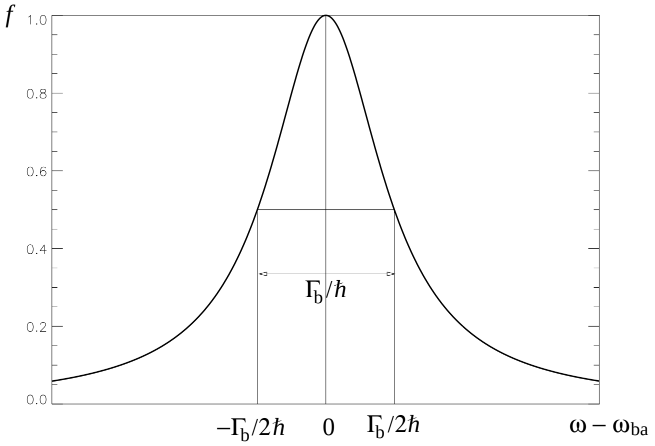

Figure 1.5: Lorentzian Eq. (1.183).

we have

$$\lim_{\Gamma_b\to 0} \tilde{f}(\omega-\omega_{ba}) = \delta(\omega-\omega_{ba}). \tag{1.185}$$

In order to determine the lifetime we insert c_a from (1.180) into the expression for $\dot{c}_b$ (1.174). This gives

$$\begin{aligned} \dot{c}_b(t) &= -\frac{e^2}{4m^2}\frac{V}{(2\pi)^3c^3}\sum_\lambda \int \mathrm{d}\omega\, \omega^2 \int \mathrm{d}\Omega\; \hat{A}^2(\omega)|M_{ba}^{(\lambda)}(\omega)|^2 \frac{\mathrm{e}^{-t/(2\tau_b)} - \mathrm{e}^{\mathrm{i}(\omega_{ba}-\omega)t}}{\mathrm{i}(\omega-\omega_{ba}) - 1/(2\tau_b)}. \\ &= -\frac{\hbar e^2}{2m^2}\frac{1}{\varepsilon_0(2\pi)^3c^3}\sum_\lambda \int \mathrm{d}\omega\, \omega \int \mathrm{d}\Omega\; |M_{ba}^{(\lambda)}(\omega)|^2 \frac{\mathrm{e}^{-t/(2\tau_b)} - \mathrm{e}^{\mathrm{i}(\omega_{ba}-\omega)t}}{\mathrm{i}(\omega-\omega_{ba}) - 1/(2\tau_b)}. \\ &= -\frac{e^2}{4\pi\varepsilon_0}\frac{\hbar}{4\pi^2m^2c^3}\sum_\lambda \int \mathrm{d}\omega\, \omega \int \mathrm{d}\Omega\; |M_{ba}^{(\lambda)}(\omega)|^2 \left\{ \frac{\mathrm{e}^{-t/(2\tau_b)} - \mathrm{e}^{\mathrm{i}(\omega_{ba}-\omega)t}}{\mathrm{i}(\omega-\omega_{ba}) - 1/(2\tau_b)} \right\}. \end{aligned}$$

The last term in brackets peaks sharply around $\omega = \omega_{ba}$ while $\omega|M_{ba}^{(\lambda)}(\omega)|^2$ is only slowly varying as a function of ω. Hence we can take $\omega|M_{ba}^{(\lambda)}(\omega)|^2 \simeq \omega_{ba}|M_{ba}^{(\lambda)}(\omega_{ba})|^2$ and the integral over ω can be performed using contour integration (→ exercise). The result reads

$$\dot{c}_b(t) = -\frac{e^2}{4\pi\varepsilon_0}\frac{\hbar}{4\pi m^2c^3}\sum_\lambda \int \mathrm{d}\Omega\; \omega_{ba}|M_{ba}^{(\lambda)}(\omega_{ba})|^2 \mathrm{e}^{-t/(2\tau_b)}. \tag{1.186}$$

On the other hand, from (1.177) follows

$$\dot{c}_b(t) = -\frac{1}{2\tau_b}\,\mathrm{e}^{-t/(2\tau_b)}, \qquad t > 0. \tag{1.187}$$

Equating this with (1.186) yields

$$\frac{1}{2\tau_b} = \frac{e^2}{4\pi\varepsilon_0}\frac{\hbar}{4\pi m^2 c^3}\sum_\lambda \int \mathrm{d}\Omega \; \omega_{ba}|M_{ba}^{(\lambda)}(\omega_{ba})|^2 \tag{1.188}$$

and because of

$$W_{ab}^{\mathrm{s}} = \frac{1}{\tau_b} \tag{1.189}$$

we see that

$$W_{ab}^{\mathrm{s}} = \frac{e^2}{4\pi\varepsilon_0}\frac{\hbar}{2\pi m^2 c^3}\sum_\lambda \int \mathrm{d}\Omega \; \omega_{ba}|M_{ba}^{(\lambda)}(\omega_{ba})|^2, \tag{1.190}$$

in accordance with the previously derived result (1.70).

One can show that if the state to which the transition takes place also decays the linewidth is given by

$$\Gamma = \hbar\left(\frac{1}{\tau_a} + \frac{1}{\tau_b}\right). \tag{1.191}$$

We saw in Table 1.1 that the lifetimes for hydrogenic levels with $Z = 1$ are on the order of 10^{-8} s. For instance, the energy of the 2p-level is -3.4 eV, the transition energy to the 1s ground state $13.6\,\mathrm{eV} - 3.4\,\mathrm{eV} = 10.2\,\mathrm{eV}$. The linewidth is $\Gamma = \hbar/\tau \simeq 4\times10^{-7}$ eV. In practice, the measured linewidths are usually much greater than the natural line widths, for reasons that will be discussed in the following.

As already suggested by (1.127) the rates of all channels via which a state b may decay should be added up so that

$$\bar{\tau}_b = \frac{1}{W_{\mathrm{tot}}}. \tag{1.192}$$

The same holds for level a and thus

$$\bar{\Gamma} = \hbar\left(\frac{1}{\bar{\tau}_a} + \frac{1}{\bar{\tau}_b}\right). \tag{1.193}$$

This increased linewidth enters (1.183).

Pressure broadening

One reason for an increased decay of levels are *collisions* between atoms. In such a collision the atoms may make transitions between state b and other states without emitting a photon (*radiationless* or *non-radiative transitions*). The collision rate is proportional to the *collision cross section* σ,

$$W_{\mathrm{c}} = nv\sigma \tag{1.194}$$

where nv is the flux, i.e., the density of atoms times their relative velocity. As the density depends (via an equation of state) on pressure, the broadening due to collisions is also called *pressure broadening.* Both v and n depend also on the temperature. Hence, spectral lines contain information about the environment of the emitters. In fact, spectral methods are used in astrophysics to learn about stellar atmospheres and in the lab to charcterize plasmas.

Doppler broadening

Consider an atom that emits a photon of wavelength λ_0 but which moves with a velocity v towards you or away from you. In the nonrelativistic limit $v/c \ll 1$ the wavelength of the radiation will be shifted according

$$\lambda = \lambda_0 \left(1 \pm \frac{v}{c}\right) \tag{1.195}$$

(upper sign for atom moving away, lower sign for atom approaching). The corresponding angular frequency reads

$$\omega = \omega_0 \left(1 \mp \frac{v}{c}\right) . \tag{1.196}$$

We assume that the atoms of mass M obey a Maxwell distribution. As a consequence, the spectral density of the emitted light will be of the form

$$u_{\mathrm{em}}(\omega) = u_{\mathrm{em}}(\omega_0)\ \exp\left[-\frac{Mv^2}{2kT}\right] = u_{\mathrm{em}}(\omega_0)\ \exp\left[-\frac{Mc^2}{2kT}\left(\frac{\omega-\omega_0}{\omega_0}\right)^2\right] . \tag{1.197}$$

The FWHM in this case reads (→ exercise)

$$\Delta\omega = \frac{2\omega_0}{c}\left[\frac{2kT}{M}\ \ln 2\right]^{1/2} . \tag{1.198}$$

As expected, the Doppler linewidth increases with temperature and decreases with the atomic mass. However, note that it also depends on the central frequency ω_0 itself. Unlike the lines due to spontaneous decay and pressure broadening, Doppler broadening generates a *Gaussian* line shape, not a Lorentzian. Because the Gaussian decreases more rapidly as one moves away from the central frequency ω_0 than a Lorentzian, the wings of a spectral line are determined by the Lorentzian (see Fig. 1.6). Methods to eliminate the Doppler broadening are discussed in the experimental part of this lecture.

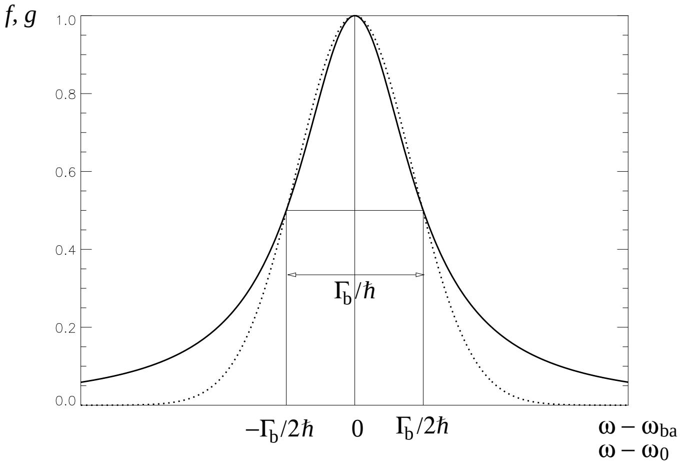

Figure 1.6: Lorentzian (solid) and Gaussian (dotted) with the same FWHM.