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

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

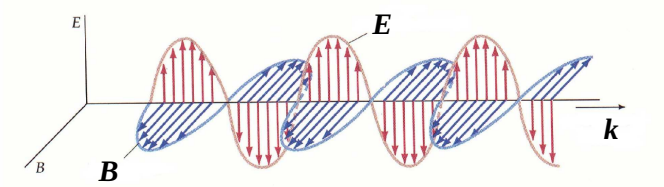

Figure 1.1: Electromagnetic wave.

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

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

[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 ($\rightarrow$ 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

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

with H_0 describing the unperturbed atom,

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

and

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

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,

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

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

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 $c_b(t)$

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

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

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

we obtain in first order perturbation theory

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

Inserting a vector potential of the form

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

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

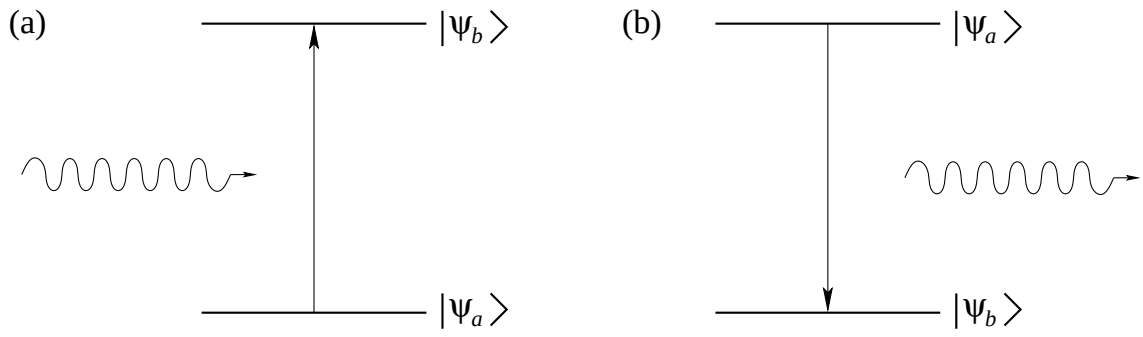

Figure 1.2: Absorption (a) and emission (b) of a photon, involving a transition to a higher (a) or lower (b) atomic level, ensuring energy conservation.

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

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

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]

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

[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. **??** 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

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

[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 $\boldsymbol{E}$

[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

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

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 ($\rightarrow$ exercise)

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