

II Light-matter interaction

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II.1 Reminder on electromagnetic waves

- We start with the homogeneous Maxwell equations:

$$\nabla \cdot \vec{B} = 0 \quad \text{and} \quad \nabla \times \vec{E} + \frac{\partial \vec{B}}{\partial t} = 0.$$

- From the first equation follows that the magnetic field \vec{B} can be written as the curl of another vector field \vec{A} , which is referred to as the vector potential:

$$\vec{B} = \nabla \times \vec{A}, \quad \text{since} \quad \nabla \cdot \nabla \times \vec{A} = 0.$$

- We can thus rewrite the second equation as

$$\nabla \times (\vec{E} + \frac{\partial \vec{A}}{\partial t}) = 0.$$

- Given that the curl of a gradient vanishes, we can thus write the electric field \vec{E} as

$$\vec{E} = -\nabla \phi - \frac{\partial \vec{A}}{\partial t},$$

where ϕ is the scalar potential.

- Let us now express the inhomogeneous Maxwell equations in terms of \vec{A} and ϕ .

$\hookrightarrow \frac{\rho}{\epsilon_0} \xrightarrow{\text{charge density}}$

$$\frac{\rho}{\epsilon_0} = \nabla \cdot \vec{E} = \nabla \cdot \left(-\nabla \phi - \frac{\partial \vec{A}}{\partial t} \right) = -\Delta \phi - \frac{\partial}{\partial t} \nabla \cdot \vec{A}$$

\downarrow
vacuum
permittivity

Laplacian

\downarrow
current density

$$\mu_0 \vec{j} = \nabla \times \vec{B} - \frac{1}{c^2} \frac{\partial \vec{E}}{\partial t} = \nabla \times (\nabla \times \vec{A}) + \frac{1}{c^2} \left(\frac{\partial}{\partial t} \nabla \phi + \frac{\partial^2}{\partial t^2} \vec{A} \right)$$

$$\downarrow \begin{matrix} \text{vacuum} \\ \text{permeability} \end{matrix} = \nabla (\nabla \cdot \vec{A}) - \Delta \vec{A} + \frac{1}{c^2} \left(\frac{\partial}{\partial t} \nabla \phi + \frac{\partial^2}{\partial t^2} \vec{A} \right)$$

$$= \frac{1}{c^2} \frac{\partial^2 \vec{A}}{\partial t^2} - \Delta \vec{A} + \nabla \left(\underbrace{\nabla \cdot \vec{A} + \frac{1}{c^2} \frac{\partial \phi}{\partial t}}_{= \epsilon_0 \mu_0} \right)$$

- In the next step we employ the so-called gauge freedom to simplify the last equation.

- The gauge freedom means that the fields \vec{E} and \vec{B} are invariant under the change of the potentials which is of the form

$$\vec{A} \rightarrow \vec{A}' = \vec{A} + \nabla \chi$$

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

where $\chi = \chi(\vec{r}, t)$ is an arbitrary function.

- The utility of the gauge freedom can be seen as follows:

- Suppose that $\nabla \cdot \vec{A} \neq 0$, but you want to enforce that $\nabla \cdot \vec{A}$ is zero in order to simplify the equations. (This is called Coulomb gauge.)
- Then choose χ such that

$$\nabla \cdot \vec{A}' = \nabla \cdot \vec{A} + \Delta \chi = 0 \rightarrow \Delta \chi = -\nabla \cdot \vec{A}$$

- Within the Coulomb gauge ($\nabla \cdot \vec{A} = 0$) the equations for the potentials become

$$\Delta \phi = -\frac{\rho}{\epsilon_0}$$

$$\frac{1}{c^2} \frac{\partial^2 \vec{A}}{\partial t^2} - \Delta \vec{A} + \frac{1}{c^2} \frac{\partial}{\partial t} \nabla \phi = \mu_0 \vec{j},$$

where the first equation has the solution

$$\phi(\vec{r}, t) = \frac{1}{4\pi\epsilon_0} \int d^3 \vec{r}' \frac{\rho(\vec{r}', t)}{|\vec{r} - \vec{r}'|}.$$

- In the absence of charges and currents ($\rho = 0$, $\vec{j} = \vec{0}$), one has $\phi = 0$ and thus the equation for \vec{A} simplifies to the wave equation

$$\frac{1}{c^2} \frac{\partial^2 \vec{A}}{\partial t^2} - \Delta \vec{A} = 0.$$

- The wave equation has plane wave solutions which are of the form

$$\vec{A}(\vec{r}, t) = a \vec{\epsilon} e^{i(\vec{k} \cdot \vec{r} - \omega t)} + a^* \vec{\epsilon}^* e^{-i(\vec{k} \cdot \vec{r} - \omega t)}$$

\vec{k} ... wave vector

$\vec{\epsilon}$... polarisation vector

$\omega = c|\vec{k}| = ck$... frequency of the wave

- The Coulomb gauge, in which we are working, constrains the solutions:

$$\nabla \cdot \vec{A} = 0 \rightarrow a \vec{\epsilon} \cdot \nabla e^{i(\vec{k} \cdot \vec{r} - \omega t)} = i a \vec{\epsilon} \cdot \vec{k} e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

! $= 0$

$$\hookrightarrow \vec{k} \cdot \vec{\epsilon} = \vec{k} \cdot \vec{\epsilon}^* = 0$$

- This so-called transversality condition means that the polarisation vector has only two free components.

- For example, assuming that $\vec{k} = \begin{pmatrix} 0 \\ 0 \\ k \end{pmatrix}$, we can choose as polarisation bases

linear polarisation

$$\vec{\epsilon}^{(1)} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

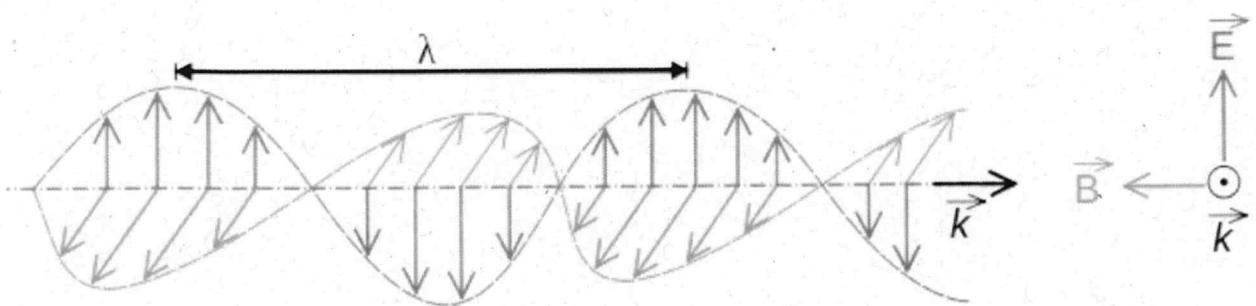
$$\vec{\epsilon}^{(2)} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

circular polarisation

$$\vec{\epsilon}^{(1)} = -\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$$

$$\vec{\epsilon}^{(2)} = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 \\ 1 \\ 0 \end{pmatrix}$$

Plane wave



- Using the plane wave solution one finds for the electric and magnetic fields:

$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} = i\omega (\alpha \vec{\epsilon} e^{i(\vec{k} \cdot \vec{r} - \omega t)} - \alpha^* \vec{\epsilon}^* e^{-i(\vec{k} \cdot \vec{r} - \omega t)})$$

$$\vec{B} = \nabla \times \vec{A} = \alpha (i \vec{k} \times \vec{\epsilon}) e^{i(\vec{k} \cdot \vec{r} - \omega t)} - \alpha^* (i \vec{k} \times \vec{\epsilon}^*) e^{-i(\vec{k} \cdot \vec{r} - \omega t)}$$

- \vec{E} , \vec{B} and \vec{k} are perpendicular to each other.
- We can now generalise the solution of the wave equation to a superposition of many plane waves.
- The amplitude of a wave with wave vector \vec{k} and polarisation vector $\vec{\epsilon}^{(s)}$ is given by $A_s(\vec{k})$.
- With this we can write the general solution as

$$\vec{A}(\vec{r}, t) = \sum_{s=1,2} \underbrace{\int \frac{d^3 \vec{k}}{(2\pi)^3 2\omega}}_{\text{integration measure (different choices possible)}} \left[A_s(\vec{k}) \vec{\epsilon}^{(s)} e^{i(\vec{k} \cdot \vec{r} - \omega t)} + A_s^*(\vec{k}) \vec{\epsilon}^{(s)*} e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right]$$

\downarrow depends also on \vec{k}

- Let us finally consider other important properties of plane wave, such as their energy and momentum.

- The energy density is

$$u = \frac{1}{2} (\epsilon_0 \vec{E}^2 + \frac{1}{\mu_0} \vec{B}^2) = \frac{\epsilon_0}{2} (\vec{E}^2 + c^2 \vec{B}^2) \stackrel{\text{for plane waves}}{=} \epsilon_0 \vec{E}^2$$

$$= \epsilon_0 \omega^2 \underbrace{(\alpha^2 \vec{\epsilon} \cdot \vec{\epsilon} e^{2i(\vec{k} \cdot \vec{r} - \omega t)} - (\alpha^*)^2 \vec{\epsilon}^* \cdot \vec{\epsilon}^* e^{-2i(\vec{k} \cdot \vec{r} - \omega t)})}_{\text{time dependent terms}}$$

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- Averaging over an oscillation period $T = \frac{2\pi}{\omega}$ yields the mean energy density:

$$\bar{u}(\vec{r}) = \frac{1}{T} \int_0^T dt u(\vec{r}, t) = 2 \epsilon_0 \omega^2 |\alpha|^2.$$

- Another important quantity is the pointing vector

$$\vec{s} = \frac{1}{\mu_0} (\vec{E} \times \vec{B}) \stackrel{\text{plane wave}}{=} \frac{1}{\mu_0} |\vec{E}| |\vec{B}| \underbrace{\frac{\vec{k}}{|\vec{k}|}}_{\vec{n}} = \frac{1}{\mu_0 c} \vec{E}^2 \vec{n}.$$

- Averaging over an oscillation period yields

$$\bar{\vec{s}} = \frac{2\omega^2 |\alpha|^2}{\mu_0 c} \vec{n} = \underbrace{\frac{1}{\epsilon_0 \mu_0 c} u \vec{n}}_{\substack{\text{velocity} \\ \text{energy} \\ \text{density}}} = c u \vec{n}$$

$\underbrace{\qquad\qquad\qquad}_{\text{direction}}$

$$= I \cdot \vec{n}$$

\uparrow
intensity

energy flux

- The pointing vector can be used to define a momentum density

$$\vec{p} = \frac{1}{c^2} \vec{s} = \epsilon_0 (\vec{E} \times \vec{B}),$$

whose time average obeys

$$c |\vec{p}| = \bar{u}.$$

II. 2 The hydrogen atom in the (classical) radiation field

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- In the presence of electromagnetic field, characterised by the vector and scalar potential \vec{A}, ϕ , the Hamiltonian of a hydrogen atom reads

\downarrow momentum operator of electron

$$H = \frac{1}{2\mu} (\vec{p} + e \vec{A}(\vec{r}, t))^2 - e \phi(\vec{r}, t) + V(\vec{r})$$

\uparrow
reduced mass

\uparrow
electronic charge: $q = -e$

\uparrow
Coulomb potential

$$\mu = \frac{m_{\text{electron}} m_{\text{proton}}}{m_{\text{electron}} + m_{\text{proton}}}$$

$$V(\vec{r}) = -\frac{e^2}{4\pi\epsilon_0 |\vec{r}|}$$

- Note, that for the moment we do not consider the spin of the electron.
- We can now decompose the Hamiltonian into an unperturbed part H_0 and a perturbation H_1 :

$$H_0 = \frac{\vec{p}^2}{2\mu} + V(\vec{r}) \quad \begin{matrix} \text{electrostatic} \\ \text{interaction} \end{matrix}$$

$$H_1 = \underbrace{\frac{e}{2\mu} (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p})}_{\text{diamagnetic term}} + \underbrace{\frac{e^2}{2\mu} \vec{A}^2}_{\text{paramagnetic term}} - e\phi$$

diamagnetic term

paramagnetic term

- We now use that under the Coulomb gauge, we can write

$$(\vec{p} \cdot \vec{A})\psi = \frac{\hbar}{i} \nabla \cdot (\vec{A}\psi) = \frac{\hbar}{i} \left((\nabla \cdot \vec{A})\psi + \underbrace{\vec{A} \cdot \nabla \psi}_{=0} \right) = \vec{A} \cdot (\vec{p}\psi)$$

and hence

$$\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p} = \vec{A} \cdot \vec{p} + \vec{A} \cdot \vec{p} = 2\vec{A} \cdot \vec{p}.$$

- Moreover, we neglect the diamagnetic term, which for laboratory strength magnetic fields is dominated by the diamagnetic one.

$$\hookrightarrow H_i \approx \frac{e}{\mu} \vec{p} \cdot \vec{A} \quad \leftarrow \text{in a homogeneous static magnetic field this term gives rise to the Zeeman splitting}$$

- We can generalise this interaction Hamiltonian by introducing the probability current density operator

$$\vec{j}(\vec{r}') = \underbrace{\frac{\vec{p}}{2\mu} \delta^3(\vec{r} - \vec{r}') + \delta^3(\vec{r} - \vec{r}') \frac{\vec{p}}{2\mu}}_{\text{symmetrisation in principle needed, since } \vec{p} \text{ and } \vec{r} \text{ are non-commuting quantum mechanical operators}} = "velocity \times (probability density)"$$

symmetrisation in principle needed, since \vec{p} and \vec{r} are non-commuting quantum mechanical operators

- With this definition we have

$$H_i = e \int d^3\vec{r}' \vec{j}(\vec{r}') \cdot \vec{A}(\vec{r}', +).$$

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- The vector potential thus couples to the electric current density: $\vec{j}(\vec{r}) = \vec{v} \times \vec{A}(\vec{r})$
- H_1 is interaction energy of a current density in a magnetic field.
- To proceed, we define the Fourier transform of the probability current density:

$$\begin{aligned}\vec{j}(\vec{k}) &= \int d^3\vec{r}' e^{-i\vec{k} \cdot \vec{r}'} \vec{j}(\vec{r}') = \int d\vec{r}' e^{-i\vec{k} \cdot \vec{r}'} (\hat{\vec{p}} \delta(\vec{r}-\vec{r}') + \delta^3(\vec{r}-\vec{r}') \hat{\vec{p}}) \\ &= e^{-i\vec{k} \cdot \vec{r}} \hat{\vec{p}} + \hat{\vec{p}} e^{-i\vec{k} \cdot \vec{r}}.\end{aligned}$$

- For the interaction of the atom with a monochromatic wave with wave vector \vec{k} and polarisation s ,

$$\vec{A}(\vec{r}, t) = a \vec{\epsilon}^{(s)} e^{i(\vec{k} \cdot \vec{r} - \omega t)} + a^* \vec{\epsilon}^{(s)*} e^{-i(\vec{k} \cdot \vec{r} - \omega t)}$$

we can then write

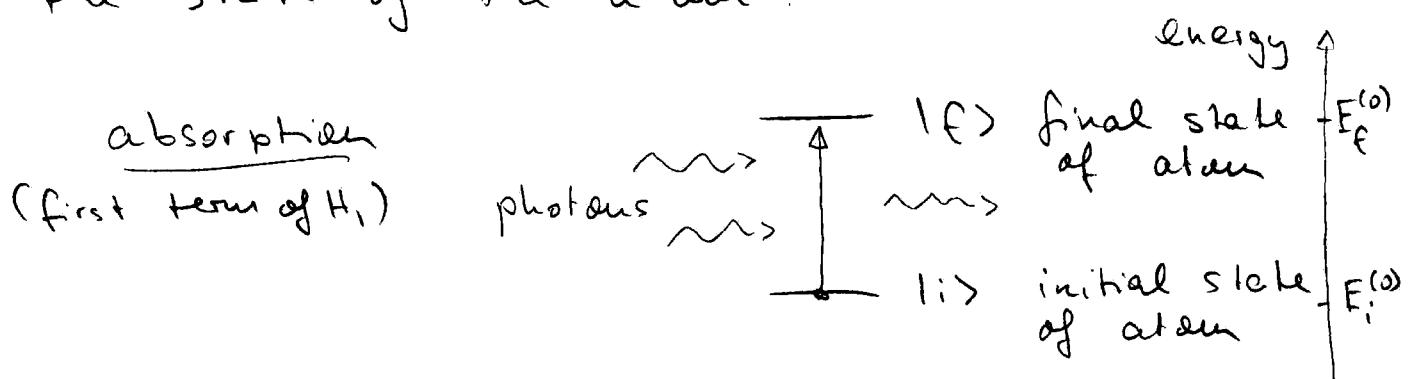
$$\begin{aligned}H_1 &= e [a \vec{\epsilon}^{(s)} \cdot \vec{j}(-\vec{k}) e^{-i\omega t} + a^* \vec{\epsilon}^{(s)*} \cdot \vec{j}(\vec{k}) e^{i\omega t}] \\ &= e [a \vec{\epsilon}^{(s)} \cdot \vec{j}^+(\vec{k}) e^{-i\omega t} + a^* \vec{\epsilon}^{(s)*} \cdot \vec{j}^-(\vec{k}) e^{i\omega t}]\end{aligned}$$

- For calculating this expression one exploits, e.g. that $(\vec{\epsilon}^{(s)} \cdot \vec{p}) e^{i\vec{k} \cdot \vec{r}} = \vec{t}_i (\vec{\epsilon}^{(s)} \cdot \nabla) e^{i\vec{k} \cdot \vec{r}} = \vec{t}_i (\vec{k} \cdot \vec{\epsilon}^{(s)}) e^{i\vec{k} \cdot \vec{r}} = 0$
- H_1 is a hermitian operator

Coulomb
gauge

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- The operator H_1 describes a harmonic perturbation, which was discussed in Sec 1.3.
- It leads to absorption and induced emission of photons from/into the electromagnetic field.
- These processes also lead to a change of the state of the atom:



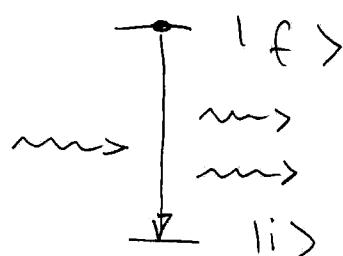
- The corresponding rate is given by Fermi's Golden Rule:

$$\Gamma_{i \rightarrow f}^{\text{abs}} = \frac{2\pi}{\hbar} |\langle f | \alpha \vec{e}^{(s)} \cdot \vec{j}(-\vec{k}) | i \rangle \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega)|$$

$$= \frac{2\pi e^2}{\hbar} |\alpha|^2 |\langle f | \vec{E}^{(s)} \cdot \vec{j}(\vec{k}) | i \rangle \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega)|$$

induced emission

(second term of H_1)



- Here the rate is

$$\Gamma_{f \rightarrow i}^{\text{ind. em.}} = \frac{2\pi e^2}{\hbar} |\alpha|^2 \underbrace{|\langle f | \vec{E}^{(s)} \cdot \vec{j}(\vec{k}) | i \rangle|^2}_{= |\langle i | \vec{E}^{(s)*} \cdot \vec{j}(\vec{k}) | f \rangle|^2} \delta(E_i^{(0)} - E_f^{(0)} + \hbar\omega)$$

$$= \Gamma_{i \rightarrow f}^{\text{abs}}$$

- Both rates are proportional to the factor $|\alpha|^2$, which is the squared modulus of the amplitude of the vector potential \vec{A} . (45)

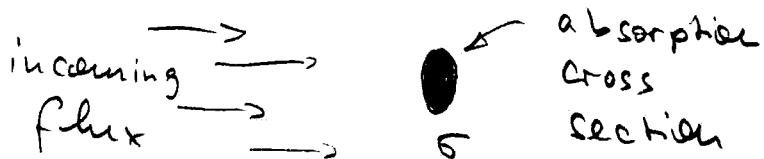
↳ the higher the intensity I of the electromagnetic field, the higher the rates

$$I = 2 \epsilon_0 c \omega^2 |\alpha|^2.$$

- In order to obtain a "normalised" quantity, which describes absorptive and induced emission we define the absorption cross section:

$$\begin{aligned}\sigma_{i \rightarrow f}^{\text{abs}} &= \frac{\text{absorbed energy per time unit}}{\text{incident energy flux}} \\ &= \frac{\hbar \omega \times P_{i \rightarrow f}^{\text{abs}}}{I} \\ &= \frac{\pi e^2}{\epsilon_0 \omega c} | \langle f | \vec{E}^{(e)} \cdot \vec{j}(-t) | i \rangle |^2 \delta(E_f^{(e)} - E_i^{(e)} - \hbar \omega)\end{aligned}$$

- The absorption cross section has the unit 'area', e.g. m^2 .
- It can be interpreted as the size of an effective / fictitious area over which the entire incident current is absorbed.
- It is a quantity that characterises a given absorption process:



- In the following we will focus on the (approximate) calculation of the matrix element $\langle f | \vec{\epsilon}^{(s)} \cdot \vec{j}(-\vec{k}) | i \rangle$, and we will also deal with the δ -function on which $\sigma_{i \rightarrow f}^{\text{abs}}$ (so far) depends.
- The first step consists of realising that the exponential factor $e^{i\vec{k} \cdot \vec{r}}$ in $\vec{j}(-\vec{k})$ varies only weakly over the typical size of an atom, i.e., the region in space where the states $|i\rangle$ (or $|f\rangle$) are non-zero:
- Typical values of $|\vec{k}|$ can be estimated by
$$|\vec{k}| = \frac{\omega}{c} = \frac{E_f^{(s)} - E_i^{(s)}}{hc} < \frac{E_Ry}{hc}$$

$$E_Ry = \frac{\mu e^4}{8\epsilon_0 h^2}$$
- Therefore $|\vec{k}| |\vec{r}| \sim |\vec{k}| \cdot a_0 = \frac{E_Ry a_0}{hc} = \frac{1}{2} \alpha \ll 1$.
$$a_0 = \frac{4\pi\epsilon_0 \hbar}{\mu e^2}$$

$$\alpha = \frac{1}{4\pi\epsilon_0 c} \frac{e^2}{\hbar^2} \approx \frac{1}{137}$$
- We can thus approximate
$$e^{\pm i\vec{k} \cdot \vec{r}} \approx 1 \rightarrow \vec{\epsilon}^{(s)} \cdot \vec{j}(-\vec{k}) \approx \vec{\epsilon}^{(s)} \cdot \vec{p} \mu$$
.

To calculate the matrix element, we use that for the unperturbed Hamiltonian H_0 of the hydrogen atom the following relation holds:

$$[\vec{r}, H_0] = [\vec{r}, \frac{\vec{p}^2}{2\mu}] = \frac{i\hbar}{\mu} \vec{p}.$$

$$\begin{aligned} \langle f | \vec{\epsilon}^{(s)} \cdot \vec{j}(\vec{k}) | i \rangle &\approx \langle f | \vec{\epsilon}^{(s)} \cdot \frac{\vec{p}}{\mu} | i \rangle = \frac{1}{i\hbar} \langle f | \vec{\epsilon}^{(s)} \cdot [\vec{r}, H_0] | i \rangle \\ &= \frac{E_i^{(0)} - E_f^{(0)}}{i\hbar} \langle f | \vec{\epsilon}^{(s)} \cdot \vec{r} | i \rangle \\ &= i\omega \underbrace{\langle f | \vec{\epsilon}^{(s)} \cdot \vec{r} | i \rangle}_{E_i^{(0)} - E_f^{(0)} = -i\omega} \end{aligned}$$

- The last expression depends on the so-called dipole matrix element $\vec{d}_{fi} = \langle f | \vec{r} | i \rangle$
↑ sometimes this is defined with a factor e (electron charge).
- With this definition, we can write for the absorption cross section

$$\sigma_{i \rightarrow f}^{\text{abs}} (\omega, \vec{n}, s) = \frac{\pi e^2 \omega}{\epsilon_0 c} |\vec{d}_{fi} \cdot \vec{\epsilon}^{(s)}(\vec{k})|^2 \delta(E_f^{(0)} - E_i^{(0)} - i\omega).$$

frequency ↑ direction of wave propagation R polarisation
 $\vec{n} = \frac{\vec{k}}{|\vec{k}|}$

- The dipole matrix element is only non zero if the angular momentum quantum numbers of the initial and final states ($|i\rangle$ and $|f\rangle$) obey certain conditions.
- These conditions are called (dipole) selection rules.
- For the following derivation of those rules we consider the non-relativistic hydrogen atom with the initial and final states given by

$$|i\rangle = |n, l, m\rangle \quad |f\rangle = |n', l', m'\rangle$$

[principal quantum number]
 [quantum number of L^2]
 [angular momentum]
 [quantum number of L_z]
 [azimuthal]

- Since the following calculations do not involve the principal quantum numbers n, n' , we omit them to keep the notation compact.
- In order to calculate the selection rules for the azimuthal quantum numbers, we make use of the following commutators:

$$[L_z, z] = 0$$

$$[L_z, x \pm iy] = \pm \hbar (x \pm iy)$$

- The first commutator yields

$$\begin{aligned} 0 &= \langle f | [L_z, z] | i \rangle = \langle e' m' | (L_z z - z L_z) | \ell m \rangle \\ &= \hbar(m' - m) \langle f | z | i \rangle = \hbar \Delta m \langle f | z | i \rangle, \end{aligned}$$

and apparently the z -component of the dipole matrix element can only be non-zero if $\Delta m = m' - m = 0$.

- From the second commutator one obtains

$$\begin{aligned} \pm \hbar \langle f | x \pm iy | i \rangle &= \langle f | [L_z, x \pm iy] | i \rangle \\ &= \hbar(m' - m) \langle f | x \pm iy | i \rangle \end{aligned}$$

$$\hookrightarrow 0 = \hbar(m' - m \mp 1) \langle f | x \pm iy | i \rangle,$$

which yields $\Delta m = \pm 1$.

- Therefore, the selection rules for the azimuthal quantum number for dipole transitions are

$$\Delta m = 0, \pm 1$$

- Note, that $\Delta m = 0$ corresponds to linearly and $\Delta m = \pm 1$ to circularly polarised light.

linear

$$\vec{d}_{fi} \cdot \vec{\epsilon} = \vec{d}_{fi} \cdot \binom{0}{1} = \langle f | z | i \rangle, \quad \overline{\vec{d}_{fi} \cdot \vec{\epsilon}} \propto \vec{d}_{fi} \cdot \binom{\pm 1}{0} = \langle f | x \pm iy | i \rangle$$

circular

In order to calculate the selection rules for the angular momentum quantum number l , we use (50)

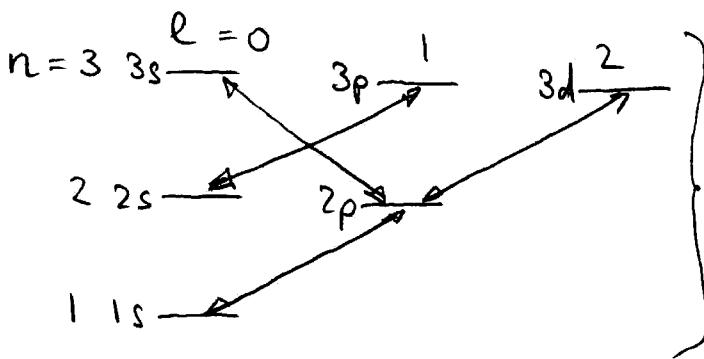
$$[\vec{L}^2, [\vec{L}^2, \vec{r}]] = 2\hbar^2 (\vec{r} \vec{L}^2 + \vec{L}^2 \vec{r}).$$

This yields

$$\begin{aligned} & \underbrace{\langle \ell' |}_{\ell', m'} [\vec{L}^2, [\vec{L}^2, \vec{r}]] \underbrace{| \ell, m \rangle}_{| i \rangle} = \hbar^4 [l'(l'+1) - l(l+1)]^2 \langle \ell' | \vec{r} | i \rangle \\ &= 2\hbar^2 \langle \ell', m' | \vec{r} \vec{L}^2 + \vec{L}^2 \vec{r} | \ell, m \rangle = 2\hbar^4 [l'(l'+1) + l(l+1)] \langle \ell' | \vec{r} | i \rangle \\ & \hookrightarrow (l+l')(l+l'+2)[(l-l')^2 - 1] \langle \ell' | \vec{r} | i \rangle = 0 \end{aligned}$$

Given that $\ell, \ell' \geq 0$, the dipole matrix element can only be non-zero when $\ell = \ell' = 0$ or when $\Delta \ell = \ell' - \ell = \pm 1$.

The first case can be ruled out from symmetry considerations: $\langle 0, 0 | \vec{r} | 0, 0 \rangle \propto \int d^3 r \vec{r} = 0$, and hence, the selection rule is $\Delta \ell = \pm 1$.



transition $2s \rightarrow 1s$ is not dipole allowed;
the $2s$ state has a life time of 0.12 s ,
life time of $2p$ is 1.6 ns

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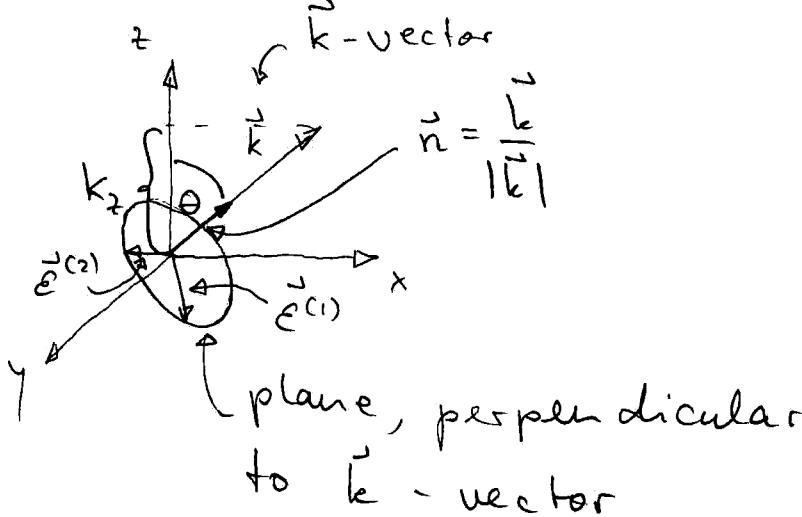
- We are now calculating the total absorptive cross section for electromag. radiation in the dipole approximation.

- This is obtained by averaging $\sigma_{i \rightarrow f}^{\text{abs}}(\omega, \vec{n}, s)$ over all polarisations and incidence angles.

$$\bar{\sigma}_{i \rightarrow f}^{\text{abs}} = \underbrace{\left(\frac{1}{4\pi} \int d\Omega \right)}_{\text{average over solid angle}} \underbrace{\left(\frac{1}{2} \sum_{s=1,2} \right)}_{\text{average over polarisations}} \sigma_{i \rightarrow f}^{\text{abs}}(\omega, \vec{n}, s)$$

$$= \frac{1}{8\pi} \frac{\pi e^2 \omega}{\epsilon_0 c} \int d\Omega \sum_{s=1,2} (\vec{d}_f; \vec{E}^{(s)}) (\vec{d}_f; \vec{E}^{(s)})^* \delta(E_f^{(s)} - E_i^{(s)} + \omega).$$

- We now choose the coordinate system in a convenient fashion so as to simplify the evaluation of the integral over the \vec{k} -direction (\vec{n}) and the sum over the polarisations:



- With this choice, we can now write

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$$\begin{aligned}
 & \int d\Omega \sum_{s=1,2} (\vec{d}_{fi} \cdot \vec{\epsilon}^{(s)}) (\vec{d}_f \cdot \vec{\epsilon}^{(s)})^* = 2\pi \int_0^\pi d\theta \sin\theta \sum_{s=1,2} |\vec{d}_{fi} \cdot \vec{\epsilon}^{(s)}|^2 \\
 &= 2\pi \int_0^\pi d\theta \sin\theta \underbrace{(|\vec{d}_{fi}|^2 - |\vec{d}_{fi} \cdot \vec{n}|^2)}_{= |\vec{d}_{fi} \cdot \vec{\epsilon}^{(1)}|^2 + |\vec{d}_{fi} \cdot \vec{\epsilon}^{(2)}|^2 + |\vec{d}_{fi} \cdot \vec{n}|^2} \\
 &= 2\pi \int_0^\pi d\theta \sin\theta (|\vec{d}_{fi}|^2 - |\vec{d}_{fi}|^2 \cos^2\theta) \\
 &= |\vec{d}_{fi}|^2 \cdot 2\pi \int_0^\pi d\theta \sin\theta (1 - \cos^2\theta) = \frac{8\pi}{3} |\vec{d}_{fi}|^2.
 \end{aligned}$$

- This yields

$$\bar{\sigma}_{i \rightarrow f}^{\text{abs}} = \frac{\pi e^2 \omega}{3 \epsilon_0 c} |\vec{d}_{fi}|^2 \delta(E_f^{(o)} - E_i^{(o)} - \hbar\omega).$$

- So far we have considered only processes in the hydrogen atom that are stimulated by the electromagnetic field, i.e. their rate was proportional to the squared amplitude of the vector potential \vec{A} .

- However, there is also the process of (53) Spontaneous emission, which takes place even when the vector potential is zero.
- The quantisation of the radiation field will ultimately allow us to understand the origin of this.
- Nevertheless, it is possible to derive the rate of spontaneous emission even without it, following an argument put forward by Einstein.
- To this end we consider an atom in the presence of the radiation field of a black body, whose spectral energy density is given by Planck's radiation law

$$u(\omega, T) d\omega = \frac{8\pi\omega^3}{\pi^2 c^3} \frac{1}{e^{\frac{h\omega}{kT}} - 1} d\omega$$

\uparrow
 $\underbrace{\text{energy per volume}}_{\text{energy density}}$ per frequency
- Following the definition of the absorption cross section,

$$\sigma_{i \rightarrow f}^{\text{abs}} = \frac{8\pi}{\bar{n}c} \frac{\Gamma_{i \rightarrow f}^{\text{abs}}}{\uparrow} \leftarrow \begin{array}{l} \text{absorption} \\ \text{rate} \end{array}$$

\uparrow
 $\text{average energy density}$

we can define a average transition rate (54)

frequency as

$$d\bar{\Gamma}_{i \rightarrow f}^{\text{abs}} = \bar{\sigma}_{i \rightarrow f}^{\text{abs}} \frac{c}{4\pi} \frac{u(\omega, T)}{\hbar\omega} d\omega$$

\uparrow T

quantities are
averaged over
polarisations and
directions of \vec{E} -vector

The total absorption rate is then

$$\begin{aligned}\bar{\Gamma}_{i \rightarrow f}^{\text{abs, tot}} &= \int d\bar{\Gamma}_{i \rightarrow f}^{\text{abs}} = \int_0^\infty d\omega \frac{\pi e^2}{3\varepsilon_0 h} |\vec{d}_{fi}|^2 u(\omega, T) \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega) \\ &= \frac{\pi e^2}{3\varepsilon_0 h^2} |\vec{d}_{fi}|^2 u(\omega_{fi}, T),\end{aligned}$$

where $\omega_{fi} = \frac{1}{\hbar} (E_f^{(0)} - E_i^{(0)})$.

The total rate of induced emission is the same as the total absorption rate,

$$\bar{\Gamma}_{f \rightarrow i}^{\text{ind. em, tot}} = \bar{\Gamma}_{i \rightarrow f}^{\text{abs, tot}} = B u(\omega_{fi}, T),$$

where $B = \frac{\pi e^2}{3\varepsilon_0 h^2} |\vec{d}_{fi}|^2$ is the so-called Einstein

B - coefficient.

Einstein now postulated that there should be an additional process - spontaneous emission, whose rate is

$$\bar{\Gamma}_{f \rightarrow i}^{\text{sp. em, tot}} = A \leftarrow \text{Einstein A-coefficient}$$

- Denoting by P_{if} the probabilities of finding an atom in the initial / final state , it should hold in equilibrium that

$$\underbrace{[A + B u(\omega_{fi}, T)] p_f}_{\text{rate for leaving the state } |f\rangle} = \underbrace{B u(\omega_{fi}, T) p_i}_{\text{rate for leaving the state } |i\rangle}.$$

- On the other hand , in thermal equilibrium we find for the probabilities:

$$\frac{p_f}{p_i} = \frac{e^{-E_f^{(0)}/k_B T}}{e^{-E_i^{(0)}/k_B T}} = e^{-\frac{\hbar \omega_{fi}}{k_B T}}$$

- Inserting this into the above expressions allows to obtain the spontaneous emission rate:

$$\begin{aligned} \hookrightarrow A &= B u(\omega_{fi}, T) \left(\frac{p_i}{p_f} - 1 \right) = B u(\omega_{fi}, T) \left(e^{\frac{\hbar \omega_{fi}}{k_B T}} - 1 \right) \\ &= B \frac{\frac{\hbar \omega_{fi}^3}{\pi^2 c^3}}{\pi^2 c^3} \end{aligned}$$

$$\hookrightarrow \Gamma_{f \rightarrow i}^{\text{sp. em., tot}} = \frac{e^2 \omega_{fi}^3}{3 \epsilon_0 \hbar c^3 \pi} |\vec{d}_{fi}|^2.$$

- The fact that all (excited) states can decay spontaneously implies that the energy of these states cannot be determined to an arbitrary accuracy, as we will show now.
- In fact, all these states are characterised by a distribution of energies, i.e. they have a finite natural line width.
- To see this, we come back to a result of Sec. 1.3, which showed that the amplitude for remaining in an initially prepared eigenstate (here $|f\rangle$) is

$$\langle f | \psi(t) \rangle = e^{-\frac{i}{\hbar} E_f t - \frac{\Gamma}{2} t}$$

here this is the
 spontaneous decay
 rate

- This expression can be written in terms of an integral of energies:
- $$-\frac{1}{2\pi i} \int_{-\infty}^{\infty} dE \frac{e^{-\frac{i}{\hbar} Et}}{E - E_f + i\frac{\Gamma}{2}} = \frac{-1}{2\pi i} (-1) 2\pi i \underbrace{\text{Res} \left[\frac{e^{-\frac{i}{\hbar} Et}}{E - E_f + i\frac{\Gamma}{2}} \right]}_{E = E_f - i\frac{\Gamma}{2}}$$
- due to integration along a
 contour with negative orientation
 ↓

$$= e^{-\frac{i}{\hbar} E_f t - \frac{\Gamma}{2} t}$$

residue
 theorem

- The integrand $\frac{1}{E - E_f + i\frac{\Gamma}{2}}$ can be interpreted as the energy spectrum of the excited state (similar to a Fourier transform).

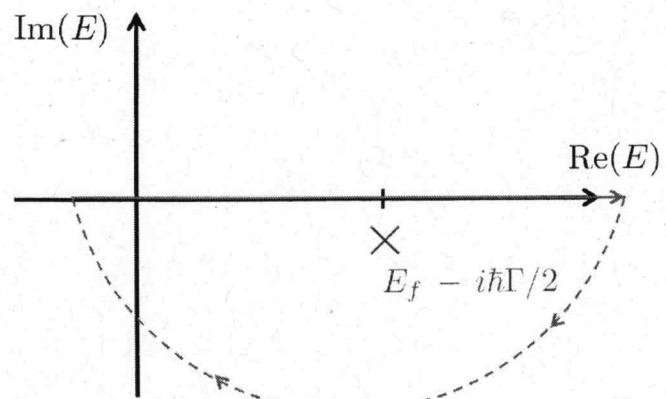
- Moreover, the normalised squared modulus of the integrand can be interpreted as a probability distribution, which states how likely it is to find the atom at energy E :

$$\phi(E) = \frac{\hbar\Gamma}{2\pi} \left| \frac{1}{E - E_f + i\frac{\hbar\Gamma}{2}} \right|^2 = \frac{1}{\pi} \frac{\frac{\hbar\Gamma}{2}}{(E - E_f)^2 + \frac{\hbar^2\Gamma^2}{4}},$$

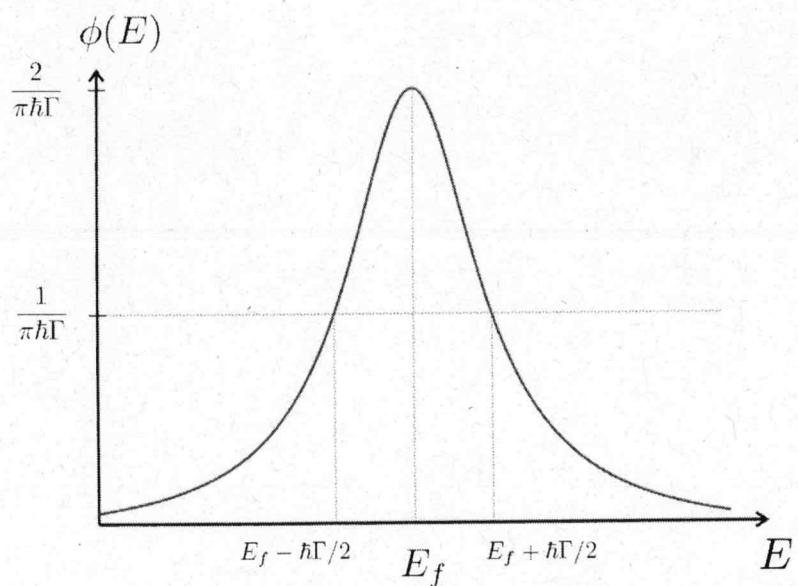
with $\int_{-\infty}^{\infty} dE \phi(E) = 1$.

- The function $\phi(E)$ is a so-called Breit-Wigner profile (or Lorentz curve).
- It is peaked at $E = E_f$ and has a width of $\hbar\Gamma$ (= natural linewidth).
- This width is directly related to the life time τ of the state, via $\tau = \frac{1}{\Gamma}$.
- In the limit $\tau \rightarrow \infty$, i.e. $\Gamma \rightarrow 0$, $\phi(E)$ approaches a Dirac δ -function.
- Since there are apparently no excited states with sharply defined energy, it makes sense to replace in all rates, that we so far calculated $\delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega) \rightarrow \underbrace{\int_{-\infty}^{\infty} dE \phi(E) \delta(E - E_i^{(0)} - \hbar\omega)}_{\text{Integration over a "continuum" of final states}} = \phi(E_i^{(0)} + \hbar\omega)$
- This yields well-defined expressions.

Integration contour for obtaining the Breit-Wigner profile



Breit-Wigner profile



II.3 Quantisation of the radiation field

(58)

- The treatment of radiation and its coupling to atom, as conducted so far, cannot be complete.
- For example, we were not able to derive the effect of spontaneous emission from first principles.
- Moreover, our "semi-classical" treatment of the radiation field revealed first indications hinting towards the existence of photons, i.e. absorption and emission involved an energy change of $\pm \hbar\omega$.
- The quantum theory of radiation will indeed show that this is related to the absorption and emission of discrete quanta, i.e. photons.

- We start from the decomposition of the vector potential into plane waves:

$$\vec{A}(\vec{r}, t) = \sum_{s=1,2} \int \frac{d^3 k}{(2\pi)^3 2\omega} \left[A_s(k) \vec{\epsilon}^{(s)} e^{i(\vec{k} \cdot \vec{r} - \omega t)} + A_s^* \vec{\epsilon}^{(s)*} e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right]$$

- Note, that $\vec{\epsilon}^{(s)} = \vec{\epsilon}^{(s)}(k)$ and $\omega = c|\vec{k}|$.
- For the following discussion it is convenient to introduce a quantisation volume V , which is finite.
- This makes the set of \vec{k} -modes countable, and thereby simplifies the analysis.
- We choose the volume to be a cube whose edges have length L , i.e. $V = L \times L \times L$.
- Moreover, we impose periodic boundary conditions, such that e.g.

$$\vec{A}(x = -\frac{L}{2}, y, z, t) \stackrel{!}{=} \vec{A}(x = \frac{L}{2}, y, z, t).$$

- This means that all plane waves have to satisfy

$$e^{i(k_x \frac{L}{2} + k_y y + k_z z)} = e^{i(k_x \frac{L}{2} + k_y y + k_z z)} \rightarrow e^{-ik_x \frac{L}{2}} = e^{ik_x \frac{L}{2}}$$

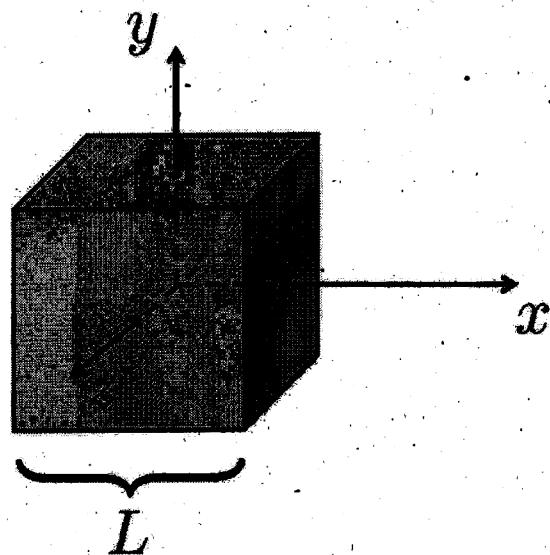
$$\hookrightarrow k_x L = k_x \cdot 2\pi \text{ with } k_x \in \mathbb{Z}$$

- Generalising this to the y and z directions, yields the possible \vec{k} -values:

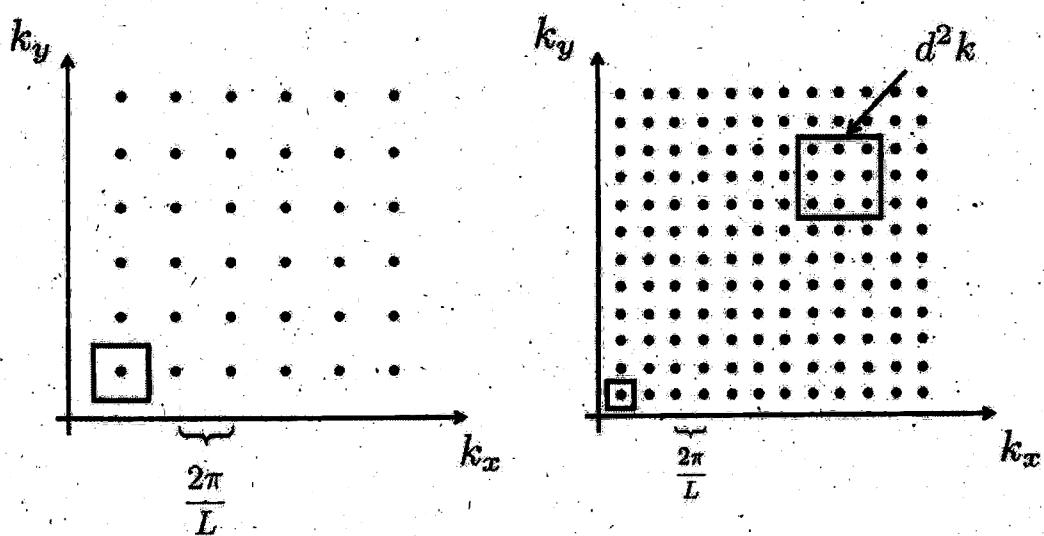
$$\vec{k} = \frac{2\pi}{L} \begin{pmatrix} k_x \\ k_y \\ k_z \end{pmatrix}, \quad k_x, k_y, k_z \in \mathbb{Z}$$

Quantisation of the radiation field

Finite quantisation volume



Discrete countable set of k-modes



(60)

- When switching from the continuous to the discrete \vec{k} -values, we also have to take into account that the integral in the expression for $\tilde{A}(\vec{r}, t)$ becomes a sum

$$\underbrace{\sum_{\vec{k}}}_{\text{discrete}} \longleftrightarrow \underbrace{\frac{1}{(2\pi)^3} \int d^3 k}_{\text{continuous}} = \underbrace{\frac{V}{(2\pi)^3} \int d^3 k}_{\text{continuous}}$$

$$\hookrightarrow \tilde{A}(\vec{r}, t) = \underbrace{\frac{V}{(2\pi)^3}}_{\sum_{\vec{k}, s}} \sum_{\vec{k}, s} \frac{1}{2\omega} \left[A_s(\vec{k}) \tilde{\epsilon}^{(s)} e^{i(\vec{k} \cdot \vec{r} - \omega t)} + A_s^*(\vec{k}) \tilde{\epsilon}^{(s)*} e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right]$$

note, that normalisation constant may be different in different scripts/boots

- Note, that in case of discrete \vec{k} -values the plane waves are actually normalisable and obey

$$\int d^3 r e^{i(\vec{k} \cdot \vec{r})} = V \delta_{\vec{k}, \vec{k}'}$$

Kronecker delta

- After these preliminary considerations we are now in the position to calculate the energy, H_{rad} , of the radiation field using discrete \vec{k} -values.

(61)

$$H_{\text{rad}} = \int d^3 \vec{r} \underbrace{u(\vec{r}, t)}_{\text{energy density}} \\ \frac{\epsilon_0}{2} \left(|\vec{E}(\vec{r}, t)|^2 + c^2 |\vec{B}(\vec{r}, t)|^2 \right)$$

$$(\text{see p. 39}) = \frac{(2\pi)^3}{V} \frac{\epsilon_0}{2} \sum_{\vec{k}, s} \omega \left[A_s(\vec{k}) A_s^*(\vec{k}) + A_s^*(\vec{k}) A_s(\vec{k}) \right]$$

Introducing the quantity

$$\tilde{a}_s(\vec{k}) = \sqrt{\frac{(2\pi)^3 \epsilon_0}{V}} A_s(\vec{k}),$$

one can write this in a more compact way:

$$H_{\text{rad}} = \sum_{\vec{k}, s} \frac{\hbar \omega}{2} \left[\tilde{a}_s(\vec{k}) \tilde{a}_s^*(\vec{k}) + \tilde{a}_s^*(\vec{k}) \tilde{a}_s(\vec{k}) \right]$$

This form of the energy looks similar to the Hamiltonian of a quantum harmonic oscillator, which in terms of creation and annihilation operator, a^+ and a , respectively, has the form

$$H_{\text{osc}} = \hbar \omega (a a^+ + \frac{1}{2}) = \frac{\hbar \omega}{2} (a a^+ + a^+ a)$$

This suggests the following postulate, (62)
which leads to a quantised radiation field: Each mode (characterised by \vec{k} and s) of the radiation field behaves like a harmonic oscillator. The free electromagnetic field is described by an infinite set of quantum harmonic oscillators.

In the corresponding equations this entails the replacement

Fourier coefficient		operator
$\tilde{a}_s(\vec{k})$	\rightarrow	$a_s(\vec{k})$ annihilation operator of mode (\vec{k}, s)
$\tilde{a}^*(\vec{k})$	\rightarrow	$a_s^*(\vec{k})$ creation operator of mode (\vec{k}, s)

Oscillators corresponding to different modes are assumed to be independent, which leads to the following commutation relations:

$$[a_s(\vec{k}), a_{s'}^*(\vec{k}')] = \delta_{ss'} \delta_{\vec{k}\vec{k}'}$$

$$[a_s(\vec{k}), a_{s'}(\vec{k}')] = 0$$

$$[a_s^*(\vec{k}), a_{s'}^*(\vec{k}')] = 0$$

(63)

- The replacement of Fourier coefficients by operators also promotes the vector potential to an operator

$$\vec{A}(\vec{r}, t) = \sum_{\vec{k}, s} \sqrt{\frac{\hbar}{2\epsilon_0\omega V}} \left[a_s(\vec{k}) \epsilon^{(s)} e^{i(\vec{k} \cdot \vec{r} - \omega t)} + a_s^*(\vec{k}) \epsilon^{(s)*} e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right]$$

\uparrow we are not introducing a new symbol for this field operator; often one uses a "hat": $\vec{A} \rightarrow \hat{\vec{A}}$, but we omit the hat when the context is clear

- When expressed in terms of a_s and a_s^* the energy of the radiation field is promoted to a quantum Hamiltonian:

$$\begin{aligned} H_{\text{rad}} &= \sum_{\vec{k}, s} \frac{\hbar\omega}{2} \left[a_s(\vec{k}) a_s^*(\vec{k}) + a_s^*(\vec{k}) a_s(\vec{k}) \right] \\ &= \sum_{\vec{k}, s} \hbar\omega \underbrace{\left(a_s^*(\vec{k}) a_s(\vec{k}) + \frac{1}{2} \right)}_{N_s(\vec{k}) + \frac{1}{2}} = \sum_{\vec{k}, s} \hbar\omega \underbrace{\left(N_s(\vec{k}) + \frac{1}{2} \right)}_{N_s(\vec{k})} \uparrow \\ &= N_s(\vec{k}) \leftarrow \text{number operator} \end{aligned}$$

- The number operator $\hat{n}_{\vec{k}, s}$ obeys the eigenvalue relation (in analogy to the operator $N = \text{ata}$ of the harmonic oscillator):

$$N_s(\vec{k}) |n_{\vec{k}, s}\rangle = n_{\vec{k}, s} |n_{\vec{k}, s}\rangle .$$

(64)

- Here, the number $n_{\vec{k},s}$ can be interpreted as the number of photons that occupy the mode (\vec{k}, s) , i.e. occupation numbers.
- The state $|n_{\vec{k},s}\rangle$, which has a fixed number of photons is called Fock state (= eigenstate of the number operator).
- A state of the electromagnetic field, which contains a fixed number of photons in any of its modes (\vec{k}_j, s_j) with $j = 1 \dots \infty$ reads direct product (tensor product)

$$|\text{photons}\rangle = |\overset{\downarrow}{n_{\vec{k}_1 s_1}}\rangle \otimes |\overset{\downarrow}{n_{\vec{k}_2 s_2}}\rangle \otimes |\overset{\downarrow}{n_{\vec{k}_3 s_3}}\rangle \otimes \dots$$

$$= |\overset{\downarrow}{n_{\vec{k}_1 s_1}}, \overset{\downarrow}{n_{\vec{k}_2 s_2}}, \overset{\downarrow}{n_{\vec{k}_3 s_3}}, \dots\rangle.$$
- These many body Fock states form a complete orthonormal set, e.g.

$$\langle \text{photons} | \text{photons}' \rangle = \underbrace{\langle \overset{\downarrow}{n_{\vec{k}_1 s_1}} | \overset{\downarrow}{n_{\vec{k}_1' s_1'}} \rangle}_{\delta_{n_{\vec{k}_1 s_1}, n_{\vec{k}_1' s_1'}}} \underbrace{\langle \overset{\downarrow}{n_{\vec{k}_2 s_2}} | \overset{\downarrow}{n_{\vec{k}_2' s_2'}} \rangle}_{\delta_{n_{\vec{k}_2 s_2}, n_{\vec{k}_2' s_2'}}} \dots$$

the scalar product is only non-zero when all occupation numbers coincide.

- An important role is taken by the vacuum state:

$$|\text{vac}\rangle = |0\rangle = |0, 0, \dots\rangle.$$

↑ all modes are empty

- States with a well-defined number of photons can then be constructed by the successive application of creation operators:

$$a_s^+(\vec{k}) |0\rangle = |0, 0, \dots, \overset{n_{k_1s}}{\downarrow}, \overset{n_{k_2s}}{\downarrow}, \overset{n_{k_3s}}{\downarrow}, \dots\rangle \quad \left\{ \begin{array}{l} \text{single photon} \\ \text{state} \end{array} \right.$$

$$a_s^+(\vec{k}') a_s^+(\vec{k}) |0\rangle = |0, \dots, \overset{n_{k_1s}}{\downarrow}, 1, \dots, 0, \dots, \overset{n_{k_3s}}{\downarrow}, 1, \dots\rangle \quad \left\{ \begin{array}{l} \text{two photon} \\ \text{states} \end{array} \right.$$

$$a_s^+(\vec{k}) | \dots n_{k_3s} \dots \rangle = \sqrt{n_{k_3s} + 1} | \dots n_{k_3s+1} \dots \rangle$$

$$a_s(\vec{k}) | \dots n_{k_3s} \dots \rangle = \sqrt{n_{k_3s}} | \dots n_{k_3s-1} \dots \rangle$$

in close analogy with the quantum harmonic oscillator.

Note, that the quantisation of the radiation field does not come without conceptual issues.

For example, the energy of the vacuum state is actually infinite:

$$\begin{aligned} H_{\text{rad}} |0\rangle &= \sum_{\vec{k}, s} \hbar\omega (N_s(\vec{k}) + \frac{1}{2}) |0\rangle = \sum_{\vec{k}, s} \hbar\omega \underbrace{(N_s(\vec{k})|0\rangle + \frac{1}{2}|0\rangle)}_0 \\ &= \left(\sum_{\vec{k}, s} \frac{\hbar\omega}{2} \right) |0\rangle = \underset{\text{infinite energy}}{\infty} |0\rangle. \end{aligned}$$

This problem is "cured" by assuming that not absolute energies but merely energy differences are measurable quantities.

Therefore, we will in the following subtract this infinite energy and write

$$H_{\text{rad}} = \sum_{\vec{k}, s} \hbar\omega a_s^*(\vec{k}) a_s(\vec{k}) = \sum_{\vec{k}, s} \hbar\omega N_s(\vec{k})$$

which acts on Fock states according to

$$H_{\text{rad}} |n_{\vec{k}_1, s_1}, n_{\vec{k}_2, s_2} \dots \rangle = \sum_{\vec{k}, s} \hbar\omega n_{\vec{k}, s} |n_{\vec{k}_1, s_1}, n_{\vec{k}_2, s_2}, \dots \rangle.$$

To conclude, we define the momentum operator

$$\begin{aligned} (\text{see p40}) \quad \vec{P}_{\text{rad}} &= \int d^3\vec{r} \vec{p}(\vec{r}, t) \xrightarrow{\text{quant.}} \sum_{\vec{k}, s} \hbar \vec{k} N_s(\vec{k}) \\ &\quad \text{momentum of mode} \qquad \text{number of photons in mode} \end{aligned}$$

- We will now revisit the processes of absorption and emission of radiation by an atom, using the quantised radiation field.

- The interaction Hamiltonian is given by

$$H_i = \frac{e}{\mu} \vec{p} \cdot \vec{A} = e \sum_{\vec{q}, s} \left[\frac{\hbar}{2\epsilon_0 \omega_q} V \left(a_s(\vec{q}) e^{i\omega_q t} \vec{e}^{(s)} \cdot \vec{j}(-\vec{q}) + a_s^*(\vec{q}) e^{i\omega_q t} \vec{e}^{(s)*} \cdot \vec{j}(\vec{q}) \right) \right],$$

with $\omega_q = c|\vec{q}|$ and $\vec{j}(\vec{q}) = \frac{\vec{p}}{\mu} e^{-i\vec{q}\vec{r}}$.

- The quantum states of the atom and the field, which are relevant for absorption and emission, have the structure

$$|\text{atom; photons}\rangle = |\text{atom}\rangle \otimes |\text{photons}\rangle.$$

- E.g. in case of absorption we have

$$\begin{array}{ccc} |i; \dots n_{ks} \dots \rangle & \longrightarrow & |f; \dots n_{ks-1} \dots \rangle \\ \text{atom in state } |i\rangle & & \text{atom in state } |f\rangle \\ \text{and } n_{ks} \text{ photons} & & \text{and } n_{ks-1} \text{ photons} \\ \text{in mode } (\vec{k}, s) & & \text{in mode } (\vec{k}, s) \end{array}$$

- For evaluating the matrix elements of H_i , we use the relations

$$\langle \dots n_{ks-1} \dots | a_s(\vec{q}) | \dots n_{ks} \dots \rangle = \sqrt{n_{ks}} \delta_{ss'} \delta_{\vec{q}, \vec{k}}$$

$$\langle \dots n_{ks-1} \dots | a_s^*(\vec{q}) | \dots n_{ks} \dots \rangle = 0.$$

- Hence, we obtain for an absorptive process the matrix element

$$\langle f; \dots n_{ks}^- \dots | H, | i; \dots n_{ks}^+ \dots \rangle =$$

$$\begin{aligned} &= e \sum_{\vec{q}, s'} \sqrt{\frac{\hbar}{2\epsilon_0 \omega_q V}} \overline{n_{ks}^-} \delta_{ss'} \delta_{\vec{q}\vec{k}} \langle f | \vec{\epsilon}^{(s')} \cdot \vec{j}(-\vec{q}) | i \rangle e^{-i\omega_q t} \\ &= e \sqrt{\frac{\hbar}{2\epsilon_0 \omega V}} \overline{n_{ks}^-} \langle f | \vec{\epsilon}^{(s')} \cdot \vec{j}(-\vec{k}) | i \rangle e^{-i\omega t} \uparrow \\ &\quad \omega = c |\vec{k}| \end{aligned}$$

This yields the transition rate

$$\Gamma_{i \rightarrow f}^{\text{abs}} = \frac{2\pi}{\hbar} \frac{e^2 \hbar}{2\epsilon_0 \omega V} n_{ks}^- | \langle f | \vec{\epsilon}^{(s')} \cdot \vec{j}(-\vec{k}) | i \rangle |^2 \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega)$$

The rate depends on
the number of photons.

- For calculating the emission rate, we need to consider the matrix elements of the states

$$|f; \dots n_{ks}^- \dots \rangle \rightarrow |i; \dots n_{ks}^+ \dots \rangle ,$$

and using

$$\langle \dots n_{ks}^+ \dots | a_s^-(\vec{q}) | \dots n_{ks}^- \dots \rangle = 0 ,$$

$$\langle \dots n_{ks}^+ \dots | a_s^+(\vec{q}) | \dots n_{ks}^- \dots \rangle = \overline{n_{ks}^+} \delta_{ss'} \delta_{\vec{q}\vec{k}}$$

yields

(69)

$$\langle i; \dots k_{is}^{\rightarrow} + \dots | H_i | f; \dots k_{fs}^{\rightarrow} \dots \rangle = c \sqrt{\frac{t}{2\epsilon_0 \omega V}} \sqrt{n_{is}^{\rightarrow} + 1} \langle i | \vec{\epsilon}^{(s)*} \cdot \vec{j}(\vec{k}) | f \rangle e^{i\omega t}$$

The emission rate then becomes

$$\Gamma_{f \rightarrow i}^{\text{em}} = \frac{\pi e^2}{\epsilon_0 \omega V} (n_{is}^{\rightarrow} + 1) \underbrace{|\langle i | \vec{\epsilon}^{(s)*} \cdot \vec{j}(\vec{k}) | f \rangle|^2}_{= |\langle i | \vec{\epsilon}^{(s)*} \cdot \vec{j}(-\vec{k}) | f \rangle|^2} \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega)$$

↑ ↑
spontaneous emission, $\Gamma_{f \rightarrow i}^{\text{sp. em}}$
induced emission, $\Gamma_{f \rightarrow i}^{\text{ind. em}}$

- Apparently, even in the absence of photons the quantised radiation field leads to an emission of a photon together with a deexcitation of the atom.
- The total rate of spontaneous emission is obtained by summing over all wave vectors and polarisations:

$$\begin{aligned} \Gamma_{f \rightarrow i}^{\text{sp. em, tot}} &= \sum_{s=1,2} \sum_{\vec{k}} \frac{\pi e^2 \omega}{\epsilon_0 V} |\vec{d}_{fi} \cdot \vec{\epsilon}^{(s)*}|^2 \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega) \\ &= \sum_s \int \frac{d^3 k}{(2\pi)^3} \frac{\pi e^2 \omega}{\epsilon_0} |\vec{d}_{fi} \cdot \vec{\epsilon}^{(s)*}|^2 \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega) \\ w = c |\vec{k}| &= \sum_s \int d\Omega \int_0^\infty d\omega \omega^2 \frac{\pi e \omega}{\epsilon_0 c^3 (2\pi)^3} |\vec{d}_{fi} \cdot \vec{\epsilon}^{(s)*}|^2 \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega) \\ &= \sum_s \int d\Omega \frac{\pi e^2 \omega_{fi}^3}{\epsilon_0 c^3 (2\pi)^3 \hbar} |\vec{d}_{fi} \cdot \vec{\epsilon}^{(s)*}|^2 \end{aligned}$$

- Using the result from p. 52, i.e. that

$$\sum_s \int d\sigma |\vec{d}_{fi} \cdot \vec{\epsilon}^{(s)}|^2 = \frac{8\pi}{3} |\vec{d}_{fi}|^2, \text{ we find}$$

$$\Gamma_{f \rightarrow}^{\text{sp. em., tot}} = \frac{e^2 \omega_{fi}^3}{3 \epsilon_0 \hbar c^3 \pi} |\vec{d}_{fi}|^2$$

- This result coincides with the one that we obtained previously by following Einstein's argument.

- Let us finally study a bit more closely the vacuum state of the electromagnetic field.
- Using the vector potential of a given mode (\vec{k}, s)

$$A_{ks}(\vec{r}, t) = \sqrt{\frac{t}{2\epsilon_0 \omega V}} [a_s(\vec{k}) \vec{\epsilon}^{(s)} e^{i(\vec{k}\vec{r} - \omega t)} + a_s^+(\vec{k}) \vec{\epsilon}^{(s)*} e^{-i(\vec{k}\vec{r} - \omega t)}],$$

we can calculate the expectation value of the electric field using $\vec{E}_{ks} = -\frac{\partial}{\partial t} \vec{A}_{ks}$:

$$\langle \vec{E}_{ks} \rangle_{\text{vac}} = \langle 0 | \vec{E}_{ks} | 0 \rangle = \dots \underbrace{\langle 0 | a_s(\vec{k}) | 0 \rangle}_0 + \dots \underbrace{\langle 0 | a_s^+(\vec{k}) | 0 \rangle}_0 = 0.$$

- On the other hand one finds

$$\langle \vec{E}_{ks}^2 \rangle_{\text{vac}} = \langle 0 | \vec{E}_{ks}^2 | 0 \rangle = \frac{\hbar \omega}{\epsilon_0 V} \cdot \frac{1}{2}.$$

(71)

- Apparently, the electric field is only on average 0, and it fluctuates around this average value with a variance, that is $(\Delta \tilde{E}_{ls})^2 = \frac{\hbar\omega}{2\epsilon_0 V}$.
- Both, this zero point fluctuation and the spontaneous emission are genuine quantum effects.