IX. Spontaneous emission

Electric dipole transitions

First recall that

$$\langle n'j'm'|\hat{\mathfrak{M}}_{k\varkappa}|njm\rangle = (-1)^{j'-m'}\begin{pmatrix} j' & k & j \\ -m' & \varkappa & m \end{pmatrix}\langle n'j'\|\hat{\mathfrak{M}}_k\|nj\rangle = (-1)^{2k}\, C^{j'm'}_{jmk\varkappa}\frac{\langle n'j'\|\hat{\mathfrak{M}}_k\|nj\rangle}{\sqrt{2j'+1}}$$

and

$$\langle n_1'j_1'n_2'j_2'j'm'\,|\,\hat{P}_{a\alpha}(1)\,|\,n_1j_1n_2j_2jm\rangle = \delta_{j'_2j_2}\delta_{n'_2n_2}(-1)^{j+j'_1+j_2-a}\,\Pi_j\, C^{j'm'}_{jm\,a\alpha}\begin{Bmatrix} j_1 & j_2 & j \\ j' & a & j_1' \end{Bmatrix}\langle n_1'j_1'\|\hat{\mathbf{P}}_a(1)\|n_1j_1\rangle$$

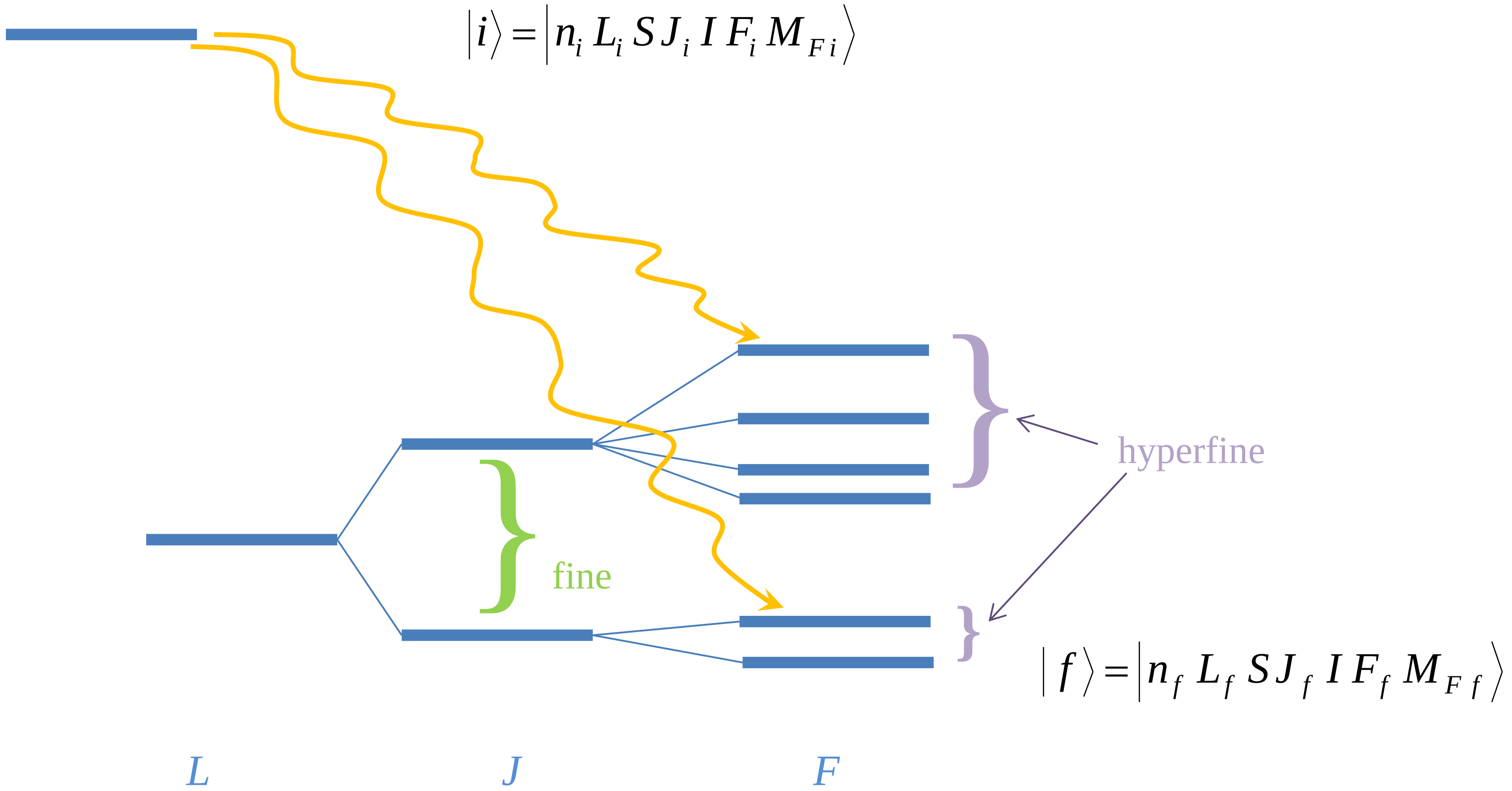
where

$$\Pi_{ab\ldots c} \equiv \sqrt{(2a+1)(2b+1)\ldots(2c+1)}$$

It follows that the reduced matrix element for a composite system is expressed through the reduced matrix element for the 1st subsystem decoupled from the 2nd one as

$$\langle n_1'\, j_1'\, n_2\, j_2\, j'||\hat{P}_a(1)||n_1\, j_1\, n_2\, j_2\, j\rangle =$$

$$= (-1)^{j_1'+j_2+j+a}\sqrt{(2j+1)(2j'+1)}\begin{Bmatrix} j_1 & j_2 & j \\ j' & a & j_1' \end{Bmatrix}\langle n_1'\, j_1'||\hat{P}_a(1)||n_1\, j_1\rangle$$



$2\gamma_{if}$ = decay probability per unit time via the partial channel $|i> \rightarrow |f>$,

γ_{if} = partial width;

$\gamma = \sum_f \gamma_{if}$ = total width, where the sum taken over all states with $E_f < E_i$.

The width appears as an imaginary correction to the energy $E_i - i\hbar\gamma$.

Electric dipole transitions $$\gamma_{if} = \frac{|d_{if}|^2}{6\pi\epsilon_0\hbar}\left(\frac{\omega_{if}}{c}\right)^3$$

Selection rules:

$$P_i = -P_f \qquad \text{(parity)}$$

$\Delta F = 0, \pm 1$, but $F = 0 \rightarrow F' = 0$ transitions are forbidden

(the same selection rules apply for L and J).

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

If $F_i = F_f$ then $M_F = 0 \rightarrow M_F' = 0$ transition is forbidden. Why?

$$d_{fi} = \frac{C^{F_f M_{F\,f}}_{F_i M_{F\,i} 1\mu}}{\sqrt{2F_f+1}} \langle n_f L_f S J_f I F_f || \hat{d} || n_i L_i S J_i I F_i \rangle$$

The dipole momentum operator acts on the radial and orbital-angular degrees of freedom, but not on the electron and nuclear spins.

$$\langle n_f L_f S J_f I F_f || \hat{d} || n_i L_i S J_i I F_i \rangle = (-1)^{J_f+I+F_i+1} \sqrt{(2F_f+1)(2F_i+1)} \times$$

$$\times \begin{Bmatrix} J_i & I & F_i \\ F_f & 1 & J_f \end{Bmatrix} \langle n_f L_f S J_f || \hat{d} || n_i L_i S J_i \rangle$$

$$\langle n_f L_f S J_f || \hat{d} || n_i L_i S J_i \rangle = (-1)^{L_f+S+J_i+1} \sqrt{(2J_f+1)(2J_i+1)} \begin{Bmatrix} L_i & S & J_i \\ J_f & 1 & L_f \end{Bmatrix} \langle n_f L_f || \hat{d} || n_i L_i \rangle$$

$$d_{fi} = (-1)^{L_f+S+J_i+J_f+I+F_i} \sqrt{(2J_f+1)(2J_i+1)(2F_i+1)}\, C^{F_f M_{F\,f}}_{F_i M_{F\,i} 1\mu} \times$$

$$\times \begin{Bmatrix} J_i & I & F_i \\ F_f & 1 & J_f \end{Bmatrix} \begin{Bmatrix} L_i & S & J_i \\ J_f & 1 & L_f \end{Bmatrix} \langle n_f L_f || \hat{d} || n_i L_i \rangle$$

$$\gamma_{if} = \frac{\left|\langle n_f L_f || \hat{d} || n_i L_i \rangle\right|^2}{6\pi\epsilon_0\hbar} \left(\frac{\omega_{if}}{c}\right)^3 (2J_f+1)(2J_i+1)(2F_i+1) \times$$
$$\times \left(C^{F_f M_{Ff}}_{F_i M_{Fi} 1\mu}\right)^2 \begin{Bmatrix} J_i & I & F_i \\ F_f & 1 & J_f \end{Bmatrix}^2 \begin{Bmatrix} L_i & S & J_i \\ J_f & 1 & L_f \end{Bmatrix}^2$$

Now we should perform the summation over final states.
It is instructive to assume the transition frequency ω_{if} is the same for all the sublevels of the fine-structure manifold.
In reality, the fine-structure splitting may reach a few % of the optical transition frequency, but we neglect this difference.

We sum first over the total momentum projections of the final state and cyclic components of the dipole moment operator. Recalling that

$$C^{j_3 m_3}_{j_1 m_1\, j_2 m_2} = (-1)^{j_1 - j_2 + m_3} \sqrt{2j_3+1} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix}$$

we find
$$\sum_{M_{Ff},\,\mu} \left|C^{F_f M_{Ff}}_{F_i M_{Fi} 1\mu}\right|^2 = (2F_f+1) \sum_{M_{Ff},\,\mu} \begin{pmatrix} F_i & 1 & F_f \\ M_{Fi} & \mu & -M_{Ff} \end{pmatrix}^2 =$$
$$= \frac{2F_f+1}{2F_i+1} \sum_{M_{Ff},\,\mu} \left|C^{F_i - M_{Fi}}_{1\mu F_f - M_{Ff}}\right|^2 = \frac{2F_f+1}{2F_i+1}$$

$$\gamma_{i\to F_f} = \frac{\left|\langle n_f L_f || \hat{d} || n_i L_i \rangle\right|^2}{6\pi\epsilon_0\hbar}\left(\frac{\omega_{if}}{c}\right)^3 (2J_f+1)(2J_i+1)(2F_f+1)\begin{Bmatrix} J_i & I & F_i \\ F_f & 1 & J_f \end{Bmatrix}^2 \begin{Bmatrix} L_i & S & J_i \\ J_f & 1 & L_f \end{Bmatrix}^2$$

Before summing over F_f (hyperfine components), recall the definition of the 6j-symbol

$$\langle j_1 j_2 (j_{12}) j_3 j m \mid j_1, j_2 j_3 (j_{23}) j' m' \rangle = \delta_{jj'}\delta_{mm'} U(j_1 j_2 j j_3;\ j_{12} j_{23}) =$$

$$= \delta_{jj'}\delta_{mm'} (-1)^{j_1+j_2+j_3+j}\sqrt{(2j_{12}+1)(2j_{23}+1)}\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{Bmatrix}.$$

and the respective orthogonality property

$$\sum_{j_{12}} (2j_{12}+1)(2j_{23}+1)\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{Bmatrix}\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j & j'_{23} \end{Bmatrix} = \delta_{j_{23}j'_{23}}$$

$$\sum_{j_{23}} (2j_{12}+1)(2j_{23}+1)\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{Bmatrix}\begin{Bmatrix} j_1 & j_2 & j'_{12} \\ j_3 & j & j_{23} \end{Bmatrix} = \delta_{j_{12}j'_{12}}$$

$$\sum_{F_f}(2J_i+1)(2F_f+1)\begin{Bmatrix} J_i & I & F_i \\ F_f & 1 & J_f \end{Bmatrix}^2 = 1$$

$$\gamma_{i\to J_f} = \frac{\left|\langle n_f L_f || \hat{d} || n_i L_i \rangle\right|^2}{6\pi\epsilon_0\hbar} \left(\frac{\omega_{if}}{c}\right)^3 (2J_f+1) \begin{Bmatrix} L_i & S & J_i \\ J_f & 1 & L_f \end{Bmatrix}^2$$

Using the same property of 6*j*-symbols, we sum over J_f (fine structure components)

$$\gamma_{i\to n_f} = \frac{\left|\langle n_f L_f || \hat{d} || n_i L_i \rangle\right|^2}{6\pi\epsilon_0\hbar(2L_i+1)} \left(\frac{\omega_{if}}{c}\right)^3$$

The last expression, obtained in the approximation that neglects differences between the frequencies of transitions to different fine components, does not depend on *S* and *I*.

X. Polarization of the emitted light

and its correlations

Recalling the field polarization definition

Hamiltonian of the electric-dipole interaction:

$$\hat{H}_{dip} = -\hat{\mathbf{d}}\mathbf{E}(t) = -\sum_{\mu} d_\mu E^\mu(t) = -\sum_{\mu} (-1)^\mu d_\mu E_{-\mu}(t)$$

Time-dependent electric field

A linearly (in other words, π-) polarized field causes transitions with $\Delta M_F = 0$, where the quantization axis is directed along the electric field.

For a linearly polarized e.m.wave with $\mathbf{E}(t) = E_{max}\, \mathbf{e}_z \cos(\omega t - kx + \chi) =$

$= (E_{max}/2)\, \mathbf{e}_z \{ \exp[-i(\omega t - kx + \chi)] + \exp[i(\omega t - kx + \chi)] \}$ the intensity is

$$I = c\varepsilon_0 E_{max}^2 / 2 = 2c\varepsilon_0 \,|\, E_{\mu=0} \,|^2,$$

where the $\mu = 0$ cyclic component $E_0 = E_{max}/2$ defined via

$\mathbf{E}(t) = \mathbf{e}_0 \{ E_0 \exp[-i(\omega t - kx)] + \text{c.c} \}$

The (slowly varying, time dependent) prefactor of the exponent $\exp[-i(\omega t - kx + \chi)]$ is considered as E_μ, since the counter-rotating term $\exp[-i(\omega t - kx + \chi)]$ does not contribute to optical excitation from lower-energy to higher-energy atomic level.

For a circularily or ellyptically polarized field it is convenient to choose the propagation direction as the quantization axis.

$$\mathbf{E}\,(t) = E_{\max}\,[\,\mathbf{e}_x \cos(\omega t - kz) + \mathbf{e}_y \sin(\omega t - kz + \varphi)\,]$$

$$\mathbf{E}\,(t) = 2^{-1/2}\,E_{\max}\,\{2^{-1/2}\,[\,\mathbf{e}_x + \mathrm{i}\exp(-\mathrm{i}\,\varphi)\,\mathbf{e}_y\,]\exp[\,-\mathrm{i}\,(\omega t - kz)\,] + \text{c.c.}\,\}$$

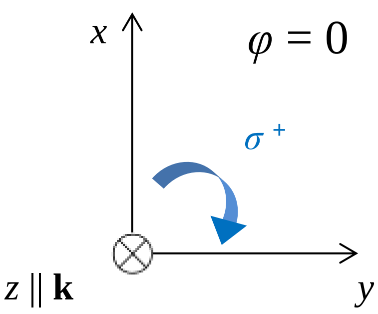
$\omega > 0$

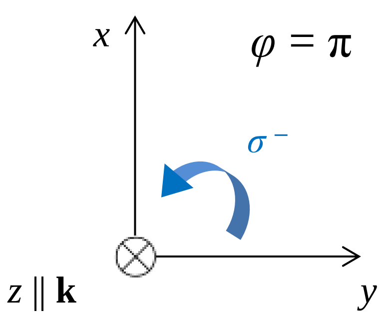
$$\frac{\mathbf{e}_x + \mathrm{i}e^{-\mathrm{i}\varphi}\mathbf{e}_y}{\sqrt{2}} = \begin{cases} -\mathbf{e}_{+1}\,, & \varphi = 0 \\ \mathbf{e}_{-1}\,, & \varphi = \pi \end{cases}$$

If we look in the direction of propagation of a circularly polarized e.m.wave and the electric field rotates

1) clockwise, then this σ^+ - polarized light causes the transitions with $\Delta M_F = +1$,
2) counterclockwise, then this σ^- - polarized light causes the transitions with $\Delta M_F = -1$,

when the atom is being excited (brought to a higher energy state).





$$\mathbf{E}(t) = -(E_{-1}\, \mathbf{e}_{+1} + E_{+1}\, \mathbf{e}_{-1}) \exp[-\mathrm{i}(\omega t - kz)] + \text{c.c.},$$

where

$$E_{\pm 1} = \mp \frac{E_{\max}}{2\sqrt{2}}\left(1 \pm \mathrm{i}\, e^{-\mathrm{i}\varphi}\right)$$

Intensity:

$$I = c\varepsilon_0 E_{\max}^2 = 2c\varepsilon_0 (|E_{-1}|^2 + |E_{+1}|^2)$$

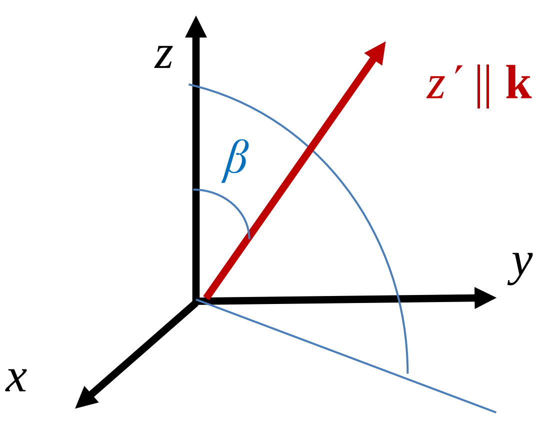
This equations will be needed for calculation of induced transitions.

Angular and polarization distribution of spontaneously emitted photons

Consider a process of decay of an atom from a state | n', F', $M_F'=M_F+\mu$> into |n, F, M_F> , where $\mu = 0, \pm 1$. What is the probability that the emitted photon has a direction $\mathbf{k}/k$, defined by the spherical angles θ and φ, and the polarization λ' with respect to the axis $z' \parallel \mathbf{k}$?
There are two orthogonal polarizations, e.g., $\sigma^{\pm}$.
The decay rate (according to Fermi's Golden Rule):

$$2\gamma_{if} = \frac{2\pi}{\hbar}\sum_{\lambda'}\int \frac{d^3\mathbf{k}}{(2\pi)^3}\frac{ck}{2\epsilon_0}\delta(\omega_{if}-ck)\left|\langle n'F'M_F+\mu|\hat{\mathbf{d}}\mathbf{e}_{\lambda'\mathbf{k}}|n\,F\,M_F\rangle\right|^2$$

The polarization unit vector $\mathbf{e}_{\lambda'\mathbf{k}}$ is defined in a co-ordinate system rotated with respect to (x,y,z) by Euler angles α, β, γ.



$$\mathbf{e}_{\lambda'\mathbf{k}} = \sum_{\lambda}\mathbf{e}_{\lambda}D^{1}_{\lambda\lambda'}(\alpha,\beta,\gamma)$$

$$\langle n'F'M_F+\mu|\hat{d}_{\lambda}|n\,F\,M_F\rangle \propto \delta_{\lambda\mu}$$

$$\left|\langle n'F'M_F+\mu|\hat{\mathbf{d}}\mathbf{e}_{\lambda'\mathbf{k}}|n\,F\,M_F\rangle\right|^2=\left|\langle n'F'M_F+\mu|\hat{d}_\mu|n\,F\,M_F\rangle D^1_{\mu\lambda'}(\alpha,\beta,\gamma)\right|^2=$$

$$=\left|\langle n'F'M_F+\mu|\hat{d}_\mu|n\,F\,M_F\rangle\right|^2\left|d^1_{\mu\lambda'}(\beta)\right|^2$$

$d^1_{MM'}(\beta)$

M \ M'	1	0	−1
1	$\frac{1+\cos\beta}{2}$	$-\frac{\sin\beta}{\sqrt{2}}$	$\frac{1-\cos\beta}{2}$
0	$\frac{\sin\beta}{\sqrt{2}}$	$\cos\beta$	$-\frac{\sin\beta}{\sqrt{2}}$
−1	$\frac{1-\cos\beta}{2}$	$\frac{\sin\beta}{\sqrt{2}}$	$\frac{1+\cos\beta}{2}$

For $\mu = +1$ the probability to detect a photon propagating at the angle β with respect to the old quantization axis z, the azimuthal angle φ, and the polarization $\sigma^{\pm}$ with respect to **k** is

$$\mathcal{P}_{\pm}(\beta)=\frac{3}{16\pi}(1\pm\cos\beta)^2$$

$$2\pi\int_0^\pi d\beta\,\sin\beta\,\mathcal{P}_{\pm}(\beta)=1$$

Calculate them also for $\mu = -1$.

For $\mu = 0$ $$\mathcal{P}_{\pm}(\beta)=\frac{3}{8\pi}\sin^2\beta$$

$$2\gamma_{if}=\frac{|d_{if}|^2}{3\pi\epsilon_0\hbar}\left(\frac{\omega_{if}}{c}\right)^3 2\pi\int_0^\pi d\beta\,\sin\beta\,\frac{1}{2}[\mathcal{P}_+(\beta)+\mathcal{P}_-(\beta)]=\frac{|d_{if}|^2}{3\pi\epsilon_0\hbar}\left(\frac{\omega_{if}}{c}\right)^3$$

Calculate these probabilities for linearly polarized photons (polarized in the plane containing axes z and z' and perpendicular to it).