Above we obtain the transition probability per unit time for an atom interacting with single mode radiation field. When the radiation field contains multiple modes, the transition rate should be the integration result of the number of modes that can interact with the atom times the single mode transition rate. In a unit solid angle $d\Omega$, the mode number is given by

$$dN = \frac{V\omega_k^2}{(2\pi)^3 \hbar c^3} d\Omega\, dE \qquad (218)$$

where E is energy. We use Eq.(218) to time Eq.(213) and Eq.(215), and then integrate over dE. Because of the δ function in Eqs.(213) and (215), only certain energy of the radiation field is choosen, who satisfies the resonance conditions given by the δ function: (we use emission Eq.(215) as an example here)

$$\int W_{A\to B}\cdot dN = \int \frac{\pi e^2(\bar{n}_{k\lambda}+1)}{\mu^2\varepsilon_0 V\omega_k}\frac{V\omega_k^2}{(2\pi)^3\hbar c^3}|\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{p}}\,e^{-i\vec{k}\cdot\vec{r}}|a\rangle|^2 d\Omega \cdot \delta(E_b - E_a + \hbar\omega_k)\, dE$$

$$= \frac{e^2\omega_k(\bar{n}_{k\lambda}+1)}{8\pi^2\mu^2\varepsilon_0\hbar c^3}|\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{p}}\,e^{-i\vec{k}\cdot\vec{r}}|a\rangle|^2 d\Omega$$

Note: we use $\bar{n}_{k\lambda}$ (the mean number of photons of given polarization in the interval of wave vectors $\vec{k}\to\vec{k}+d\vec{k}$) to represent the photon number, $\omega_k = \omega_{ab} = |E_a - E_b|/\hbar = \omega$. Thus, we obtain the transition rate under multi-mode radiation field:

$$dW_{em} = \frac{e^2\omega(\bar{n}_{k\lambda}+1)}{8\pi^2\mu^2\varepsilon_0\hbar c^3}|\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{p}}\,e^{-i\vec{k}\cdot\vec{r}}|a\rangle|^2 d\Omega \qquad (219)$$

$$dW_{ab} = \frac{e^2\omega\,\bar{n}_{k\lambda}}{8\pi^2\mu^2\varepsilon_0\hbar c^3}|\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{p}}\,e^{-i\vec{k}\cdot\vec{r}}|a\rangle|^2 d\Omega \qquad (220)$$

Here, dW corresponds to $d\Omega$ (the unit solid angle).

Thus, under multi-mode radiation field, the spontaneous emission rate is

$$dW_{sp} = \frac{e^2\omega}{8\pi^2\mu^2\varepsilon_0\hbar c^3}\left|\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{p}}\,e^{-i\vec{k}\cdot\hat{\vec{r}}}|a\rangle\right|^2 d\Omega \qquad (221)$$

The stimulated emission and absorption rates are

$$dW_{st} = \frac{e^2\omega\,\bar{n}_{k\lambda}}{8\pi^2\mu^2\varepsilon_0\hbar c^3}\left|\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{p}}\,e^{\mp i\vec{k}\cdot\hat{\vec{r}}}|a\rangle\right|^2 d\Omega \qquad (222)$$

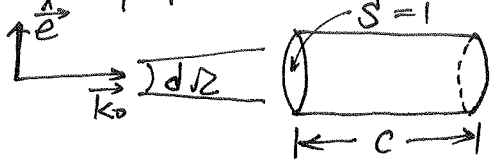
Note: The spontaneous and stimulated emission (absorption) **rates** contain the same matrix element $\left|\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{p}}\,e^{-i\vec{k}\cdot\hat{\vec{r}}}|a\rangle\right|^2$.

Therefore, if this matrix element is zero, then both spontaneous and stimulated emission rates and absorption rates are zero, i.e., such transition is not possible. On the other hand, if this matrix element is non-zero, then spontaneous, stimulated emission and absorption rates are non-zero.

Sometimes it is more convenient to express the photon number $\bar{n}_{k\lambda}$ in terms of **the intensity of radiation**. The intensity is: ① Light power on unit area

or ② Energy flux density

or ③ Light energy passing unit area in unit time



$$V = S\cdot c\cdot\Delta t = 1\cdot c\times 1 = c$$

$$I_{k\lambda}\,d\omega\,d\Omega = \frac{\omega^2 c\,\bar{n}_{k\lambda}\hbar\omega}{(2\pi c)^3}\,d\omega\,d\Omega \qquad (223)$$

$$\Rightarrow\quad \bar{n}_{k\lambda} = \frac{(2\pi)^3 c^2}{\hbar\omega^3}\,I_{k\lambda} \qquad (224)$$

$$\therefore dW_{st} = \frac{\pi e^2 I_{k\lambda}}{\mu^2 \varepsilon_0 \hbar^2 \omega^2 c} |\langle b| \hat{\vec{e}}_{k\lambda} \cdot \hat{\vec{p}}\, e^{\mp i \vec{k}\cdot\hat{\vec{r}}} |a\rangle|^2 d\Omega \qquad (225)$$

With Eqs. (221), (222), and (225), we obtain the transition probability per unit time expressions. Now we need to derive the matrix element. For $e^{i\vec{k}\cdot\hat{\vec{r}}}$ term in these equations, because the radiation field wavelength λ is much longer than the atom dimension,

$$\vec{k}\cdot\vec{r} = \frac{2\pi r}{\lambda} \ll 1.$$

Thus, we can expand $e^{i\vec{k}\cdot\hat{\vec{r}}}$ as

$$e^{i\vec{k}\cdot\hat{\vec{r}}} = 1 + i\vec{k}\cdot\hat{\vec{r}} - \frac{(\vec{k}\cdot\hat{\vec{r}})^2}{2!} + \cdots \qquad (226)$$

When taking different order of approximation, we obtain:

$e^{i\vec{k}\cdot\hat{\vec{r}}} \approx 1$ — electric dipole transition

$i\vec{k}\cdot\hat{\vec{r}}$ — { magnetic dipole transition
electric quadrapole transition.

3. Electric Dipole Transition (Electric Dipole Radiation)

When taking $e^{i\vec{k}\cdot\hat{\vec{r}}} \simeq 1$, Eqs. (221), (222), and (225) give the transition rate for electric dipole transition, called E_1 transition. It is the transition between electron states, e.g., from the ground state to excited states. Electron states are the different states formed by different electron configuration. For example,

Na ground state is $1s^2 2s^2 2p^6 3s^1$.
Na first excited state is $1s^2 2s^2 2p^6 3p^1$ } i.e., electron configuration

changes from $3s \rightarrow 3p$ for the electric dipole transition from the ground state to the 1st excited state.

For E_1 transition,

$$\langle b| \hat{\vec{e}}\cdot\hat{\vec{p}}\, e^{i\vec{k}\cdot\vec{r}} |a\rangle \simeq \langle b| \hat{\vec{e}}\cdot\hat{\vec{p}} |a\rangle \qquad (227)$$

Note: We remove "$k\lambda$" under $\hat{\vec{e}}$ subscript for convenience.

To replace the operator $\hat{\vec{p}}$ with the operator $\hat{\vec{r}}$, we use the commutation relationship: $[x, p_x] = i\hbar$, $[x, p_y] = [x, p_z] = 0$

It is not difficult to obtain

$$[x, p_x^2] = 2i\hbar p_x \qquad (228)$$

Thus, $$[\hat{\vec{r}}, \hat{H}_a] = \frac{i\hbar}{\mu}\hat{\vec{p}}, \qquad (229)$$

Where $\hat{H}_a = \frac{\hat{\vec{p}}^2}{2\mu}$. This will be a homework to prove Eqs. (228) (229).

Thus, $\langle b|\hat{\vec{p}}|a\rangle = \frac{\mu}{i\hbar}\langle b|\hat{\vec{r}}\hat{H}_a - \hat{H}_a\hat{\vec{r}}|a\rangle$

$$= \frac{\mu}{i\hbar}(E_a - E_b)\langle b|\hat{\vec{r}}|a\rangle$$

$$= i\mu\omega_{ba}\langle b|\hat{\vec{r}}|a\rangle \qquad (230)$$

where $\omega_{ba} = (E_b - E_a)/\hbar$.

The matrix element can now be written in terms of $\hat{r}$ operator

$$|\langle b|\hat{e}\cdot\hat{p}\,e^{i\vec{k}\cdot\hat{r}}|a\rangle|^2 \approx |\langle b|\hat{e}\cdot\hat{p}|a\rangle|^2 = |\hat{e}\cdot\langle b|\hat{p}|a\rangle|^2$$
$$= \mu^2\omega^2|\hat{e}\cdot\langle b|\hat{r}|a\rangle|^2$$
$$= \mu^2\omega^2|\langle b|\hat{e}\cdot\hat{r}|a\rangle|^2 \qquad (231)$$

Substitute Eq.(231) into Eq.(221) and Eq.(225), we obtain the transition probability per unit time:

$$dW_{sp} = \frac{e^2\omega^3}{8\pi^2\varepsilon_0\hbar c^3}|\langle b|\hat{e}\cdot\hat{r}|a\rangle|^2$$
$$= \frac{\omega^3}{8\pi^2\varepsilon_0\hbar c^3}|\langle b|\hat{e}\cdot\hat{d}|a\rangle|^2 \qquad (232)$$

$$dW_{st} = \frac{\pi e^2 I_{k\lambda}}{\varepsilon_0\hbar^2 c}|\langle b|\hat{e}\cdot\hat{r}|a\rangle|^2$$
$$= \frac{\pi I_{k\lambda}}{\varepsilon_0\hbar^2 c}|\langle b|\hat{e}\cdot\hat{d}|a\rangle|^2 \qquad (233)$$

Note: We define the electric dipole moment of the atom as

$$\hat{d} = -e\hat{r} \qquad (234)$$

where e is the electron charge, $\hat{r}$ is the electron position relative to the nucleus (i.e., mass center).

Note: In electric dipole transition, the electric dipole moment $\hat{d}$ used in the transition probability is the induced electric dipole moment. The permanent electric dipole moment of an atom is always zero, i.e., $\langle\hat{d}\rangle \equiv \langle\psi_m|-e\hat{r}|\psi_m\rangle = 0$. This is because $\hat{r}$ is antisymmetric, the mean value is zero for any electron orbits. The instantaneous electric dipole moment is nonzero.

(1) Selection Rules derived from 3J-Symbols and Reduced Matrix Elements

To illustrate the selection rules for different kinds of transition, it is important to introduce 3J-symbol and reduced matrix element of "Group Theory". A close inspection of the line intensity, polarization, and angular distribution of emitted and absorbed radiation has to take into account of the orientation of the atoms with respect to a specified direction, called the quantization axis. Therefore, we describe the atomic energy levels $|a\rangle$ and $|b\rangle$ by sets of quantum numbers:

$$(\alpha_a, J_a, M_a) \quad \text{and} \quad (\alpha_b, J_b, M_b)$$

where J stands for the total angular momentum of the electron, M stands for J's projection onto the quantization axis. All other quantum numbers are respesented as a whole by α.

With this representation, the spontaneous transition probability per unit time per unit solid angle is

$$dW_{sp}(\alpha_a J_a M_a \to \alpha_b J_b M_b) = \frac{\omega^3}{8\pi^2 \varepsilon_0 \hbar c^3} |\langle \alpha_b J_b M_b | \hat{\vec{e}} \cdot \hat{\vec{d}} | \alpha_a J_a M_a \rangle|^2 d\Omega \tag{235}$$

The stimulated emission/absorption rate is

$$dW_{st}(\alpha_a J_a M_a \to \alpha_b J_b M_b) = \frac{\pi I_{k\alpha}}{\varepsilon_0 \hbar^2 c} |\langle \alpha_b J_b M_b | \hat{\vec{e}} \cdot \hat{\vec{d}} | \alpha_a J_a M_a \rangle|^2 \tag{236}$$

where the matrix element $\langle \alpha_b J_b M_b | \hat{\vec{e}} \cdot \hat{\vec{d}} | \alpha_a J_a M_a \rangle$ represents the transition from state $|\alpha_a J_a M_a\rangle$ to state $|\alpha_b J_b M_b\rangle$.

This matrix element can be separated into a product of two factors: a "geometrical factor" describing the orientation of the atom, and an "intrinsic factor" which depends on the radiative coupling of the two energy states.

According to Wigner–Eckart theorem, ($\hat{\vec{e}}\cdot\hat{\vec{d}} = \sum_q e_q^* d_q$, $q = 1, 0, -1$)

$$\langle \alpha_b J_b M_b | d_q | \alpha_a J_a M_a \rangle = (-1)^{J_b - M_b} \begin{pmatrix} J_b & 1 & J_a \\ -M_b & q & M_a \end{pmatrix} \langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle \qquad (237)$$

where $\begin{pmatrix} J_b & 1 & J_a \\ -M_b & q & M_a \end{pmatrix}$ is called the "3J-symbol", depending on M_b, M_a; $q = M_b - M_a$. These factors can be expressed by the CG coefficients (Clebsch–Gordan), which describe the coupling of angular momenta for a system initially in a state (J_a, M_a). The photon transfers an angular momentum of $1\hbar$ with projection $m\hbar$ ($m = 0, \pm 1$) and brings the atomic system into another state (J_b, M_b).

The second factor $\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle$ is called the "reduced matrix element". It is independent of the atomic orientation, and gives the "physical part" of the transition probability. The reduced matrix element depends on the atomic wave function $\psi_i(\alpha_a J_a)$ and $\psi_f(\alpha_b J_b)$ in the coordinate frame of the atom.

From the properties of 3J-symbol (CG coefficients), the conditions for nonzero matrix elements are

$$\Delta J = 0, \pm 1, \quad J_a + J_b \geq 1; \quad \Delta M = 0, \pm 1 \qquad (238)$$

where $\Delta J = J_b - J_a$, $\Delta M = M_b - M_a$.

These are the so-called selection rules for E_1 transitions. When considering other quantum numbers, we have

$$\Delta S = 0; \quad \Delta L = 0, \pm 1, \quad L_a + L_b \geq 1 \qquad (239)$$

(for single electron, $\Delta l = \pm 1$)

In addition, the parity of the initial and final states must be opposite, i.e., parity must change.

Furthermore, there is no limitation on the principal quantum number change, i.e., Δn can be arbitrary: $\Delta n = 0$ and $\Delta n \neq 0$

The combination of above four conditions forms the selection rules for the electric dipole (E_1) transitions. Below is a table copied from the book "Atomic and Laser Spectroscopy" by Corney.

TABLE 7.1.

Selection rules for single photon transitions in atomic spectra

Rule	Electric dipole	Magnetic dipole	Electric quadrupole
1.	$\Delta J = 0, \pm 1$ ($0 \not\leftrightarrow 0$)	$\Delta J = 0, \pm 1$ ($0 \not\leftrightarrow 0$)	$\Delta J = 0, \pm 1, \pm 2$ ($0 \not\leftrightarrow 0$; $\frac{1}{2} \not\leftrightarrow \frac{1}{2}$; $0 \not\leftrightarrow 1$)
2.	$\Delta M = 0, \pm 1$	$\Delta M = 0, \pm 1$	$\Delta M = 0, \pm 1, \pm 2$
3.	Parity change	No parity change	No parity change
4.	One electron jump $\Delta l = \pm 1$	No electron jump $\Delta l = 0$, $\Delta n = 0$	One or no electron jump $\Delta l = 0, \pm 2$
5.	$\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
6.	$\Delta L = 0, \pm 1$ ($0 \not\leftrightarrow 0$)	$\Delta L = 0$	$\Delta L = 0, \pm 1, \pm 2$ ($0 \not\leftrightarrow 0$; $0 \not\leftrightarrow 1$)

When hyperfine structures are involved, the additional selection rules are: $\Delta F = 0, \pm 1$, $F = 0 \not\leftrightarrow F = 0$ (240)

$\Delta M_F = 0, \pm 1$

for both E_1 and M_1 transitions.

(2) Intensity, Polarization, and Angular Distribution of Zeeman Spectral Lines

Without external magnetic field, same J but different M levels are degenerate. However, the transition gives polarized light, which enables the discrimination of different components although freqs are the same.

Let us consider in a certain ΔJ transition, the three components $\Delta M = 0, \pm 1$. This will give polarization and angular distribution.

For $\Delta M = 0$, i.e., $M_b = M_a$, $\beta = 0$, $\hat{\vec{e}}_0 = \hat{\vec{e}}_z$,

$$\langle \alpha_b J_b M_b | \hat{\vec{e}} \cdot \hat{\vec{r}} | \alpha_a J_a M_a \rangle = \hat{\vec{e}}_z^{\,*} \langle \alpha_b J_b M_b | r_z | \alpha_a J_a M_a \rangle \quad (241)$$

Radiation propagates in $\vec{k}_0$ direction, and its polarization $\vec{e}_1$ and $\vec{e}_2$ are shown as Figure. $\vec{e}_1$ is in the plane of $(\vec{k}_0, \vec{z})$.

$\therefore e_{1z} = \sin\theta, \quad e_{2z} = 0. \Rightarrow$ linear polarization

$$\therefore dW_{sp}(\alpha_a J_a M \to \alpha_b J_b M) = \frac{e^2\omega^3}{4\pi\varepsilon_0 \, 2\pi\hbar c^3} \left| \langle \alpha_b J_b M | z | \alpha_a J_a M \rangle \right|^2 \sin^2\theta \, d\Omega \quad (242)$$

For $\Delta M = \pm 1$,

$$\langle \alpha_b J_b M_b | \hat{\vec{e}} \cdot \hat{\vec{r}} | \alpha_a J_a M_a \rangle = \vec{e}_{\pm 1}^{\,*} \langle \alpha_b J_b M | r_{\pm 1} | \alpha_a J_a M \mp 1 \rangle$$

$$= \frac{1}{\sqrt{2}} (e_x \mp i e_y) \langle \alpha_b J_b M | \frac{X \pm iY}{\sqrt{2}} | \alpha_a J_a M \mp 1 \rangle \quad (243)$$

$e_{1x} = -\cos\theta, \; e_{1y} = 0$

$e_{2x} = 0, \; e_{2y} = -1.$ $\Rightarrow$ circular polarization.

$$\therefore dW_{sp}(\alpha_a J_a M \to \alpha_b J_b M\pm 1) = \frac{e^2\omega^3}{4\pi\varepsilon_0\, 2\pi\hbar c^3}\left|\langle \alpha_b J_b M\pm 1 \left|\frac{X \pm iY}{\sqrt{2}}\right| \alpha_a J_a M\rangle\right|^2 \times \frac{1}{2}(1+\cos^2\theta)\, d\Omega. \quad (244)$$

Assume we can distinguish $\Delta M = 0, \pm 1$ components. The observed intensity of the fluorescence emitted into the direction θ against the quantization axis is determined by the (product of the angular) transition rate of individual atom dW_{sp} and the number density of atoms on the initial state $|\alpha_a J_a M_a\rangle$. (at a far distance $\rho \gg \lambda$)

$$I(\theta)d\Omega = N(\alpha_a J_a M_a)\cdot dW_{sp}(\alpha_a J_a M_a \to \alpha_b J_b M_b)$$

$$= \frac{d\Omega\cdot e^2\omega^4}{2\varepsilon_0 c^3 4\pi\rho^2} N(\alpha_a J_a M_a)\left|\langle \alpha_b J_b \| \vec{r} \| \alpha_a J_a\rangle\right|^2 * \left|\begin{pmatrix} J_b & 1 & J_a \\ -M_b & q & M_a \end{pmatrix}\right|^2 * \begin{cases} \frac{1}{2}(1+\cos^2\theta) & \text{for } q=\pm 1 \\ \sin^2\theta & \text{for } q=0 \end{cases} \quad (245)$$

This is the intensity for specific transition from $|\alpha_a J_a M_a\rangle \longrightarrow |\alpha_b J_b M_b\rangle$ in unit solid angle.

The $dW_{sp}(\alpha_a J_a M_a \to \alpha_b J_b M_b)$ is the angular transition rate for this specific transition between different Zeeman sublevels.

The angle factor $\begin{cases} \frac{1}{2}(1+\cos^2\theta) & \text{for } q=\pm 1 \\ \sin^2\theta & \text{for } q=0 \end{cases}$ (246)

gives the angular distribution of Zeeman components, shown as the following figure.

Angular Distribution of radiation for E_1 transition $\Delta M = 0, \pm 1$

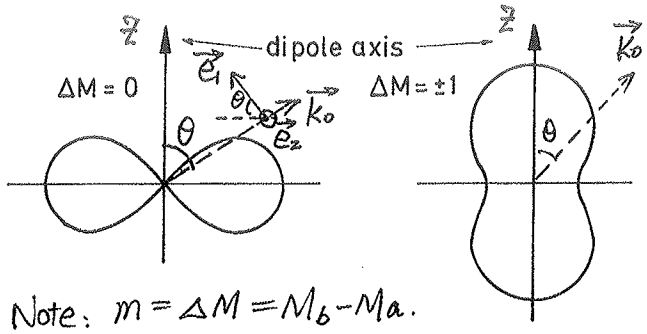


Figure. Angular distribution of the fluorescence emitted on transitions $\Delta M = 0, \pm 1$ between the Zeeman components $|\alpha_a J_a M_a\rangle \rightarrow |\alpha_b J_b M_b\rangle$.

Note: $m = \Delta M = M_b - M_a$.

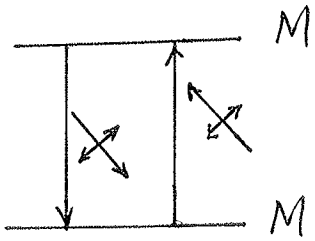
Above figure shows the angular distribution for $\Delta M = 0$ and $\Delta M = \pm 1$ transitions. The polarization characteristics of the emitted fluorescence are different for the two cases.

For $\Delta M = 0$, i.e., $M_b = M_a$. $(m = 0)$,

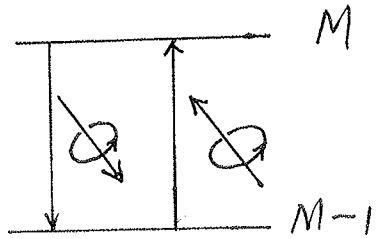
the emitted or absorbed photon is linearly polarized radiation, and its polarization direction is $\vec{e}_1$.

For $\Delta M = \pm 1$,

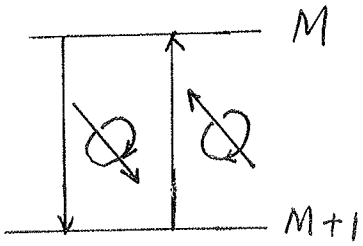
the emitted or absorbed photon is circularly polarized radiation.



Linear Polarization



Circular Polarization (left)



Circular polarization (right)