Atoms in a Radiation field

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Here we discuss the quantum mechanics on the interaction of electrons in atom with the electromagnetic field. The electromagnetic field as well as electrons, are quantized. As a result of the interaction of electrons with photon (quantization of the electromagnetic field), the phenomena of the absorption and emission of photon occur. The emission of photon consists of stimulated emission and spontaneous emission. The spontaneous emission can be derived only if the electromagnetic field is quantized. The A and B coefficients are introduced by Einstein. Although the electromagnetic field is treated classically, the concept of spontaneous emission as well as the absorption and stimulated emission can be well explained qualitatively. Here we show how to calculate the transition rates for the spontaneous emission, stimulated emission, and absorption using the Fermi's golden rule and the Wigner-Eckart theorem. Both the stimulated emission, and absorption are proportional to the number of photon, while the spontaneous emission is independent of the number of photon. The polarization vector of the photon during the transition depends on the selection rule for the matrix element of transition rate. These results are related to the angular momentum conservation; the RHC photon has a spin angular momentum ($+\hbar$) and the LHC photon has a spin angular momentum ($-\hbar$)

The interaction of electrons with an electromagnetic field can be treated by means of time dependent perturbation theory, since the electromagnetic interaction is comparatively weak, as is shown by the smallness of the fine-structure constant $\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$. This smallness of this number is of the fundamental importance in quantum electrodynamics.

1. The interaction of atoms with radiation (quantum mechanics)

The Hamiltonian of the classical radiation field ($\hat{\boldsymbol{p}}$: momentum operator of the system, Quantum mechanical operator) is given by

$$\begin{aligned}
\hat{H} &= \frac{1}{2m}\left(\hat{\boldsymbol{p}} - \frac{q}{c}\boldsymbol{A}\right)^2 \\
&= \frac{1}{2m}\left(\hat{\boldsymbol{p}} + \frac{e}{c}\boldsymbol{A}\right)^2 \\
&= \frac{1}{2m}\left(\hat{\boldsymbol{p}} + \frac{e}{c}\boldsymbol{A}\right)\cdot\left(\hat{\boldsymbol{p}} + \frac{e}{c}\boldsymbol{A}\right) \\
&= \frac{1}{2m}[\hat{\boldsymbol{p}}^2 + \frac{e^2}{c^2}\boldsymbol{A}^2 + \frac{e}{c}(\boldsymbol{A}\cdot\hat{\boldsymbol{p}} + \hat{\boldsymbol{p}}\cdot\boldsymbol{A})]
\end{aligned}$$

where $q = -e$ is the charge of electron (e>0) and $\phi = 0$.

$$\left(\boldsymbol{A}\cdot\hat{\boldsymbol{p}}+\hat{\boldsymbol{p}}\cdot\boldsymbol{A}\right)\psi(\boldsymbol{r}) = \boldsymbol{A}\cdot\frac{\hbar}{i}\nabla\psi(\boldsymbol{r})+\frac{\hbar}{i}\nabla\cdot\left(\boldsymbol{A}\psi(\boldsymbol{r})\right)$$
$$= \boldsymbol{A}\cdot\frac{\hbar}{i}\nabla\psi(\boldsymbol{r})+\frac{\hbar}{i}\left(\nabla\psi(\boldsymbol{r})\cdot\boldsymbol{A}+\psi(\boldsymbol{r})\nabla\cdot\boldsymbol{A}\right)$$
$$= \frac{2\hbar}{i}\boldsymbol{A}\cdot\nabla\psi(\boldsymbol{r})+\frac{\hbar}{i}\psi(\boldsymbol{r})\left(\nabla\cdot\boldsymbol{A}\right)$$

Thus

$$\hat{H} = \frac{1}{2m}\left[\hat{\boldsymbol{p}}^2+\frac{e^2}{c^2}\boldsymbol{A}^2+\frac{2e}{c}\boldsymbol{A}\cdot\hat{\boldsymbol{p}}+\frac{e\hbar}{ic}\left(\nabla\cdot\boldsymbol{A}\right)\right].$$

We use the Coulomb gauge $\nabla\cdot\mathbf{A} = 0$. Then we have the perturbations such that

$$\begin{cases}\hat{H}' = \dfrac{e}{mc}\boldsymbol{A}\cdot\hat{\boldsymbol{p}}\\ \hat{H}'' = \dfrac{e^2}{2mc^2}\boldsymbol{A}^2\end{cases}.$$

where we use the vector potential $\boldsymbol{A}$ for the classical case.

In quantum mechanics, the interaction of atoms with radiation is given by

$$\hat{H}' = \frac{e}{mc}\hat{\boldsymbol{A}}(\boldsymbol{r},t)\cdot\hat{\boldsymbol{p}}$$
$$= \frac{e}{m}\sum_{\boldsymbol{k},s}\sqrt{\frac{2\pi\hbar}{\omega_{\boldsymbol{k}}V}}[\hat{a}_{\boldsymbol{k},s}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}}+\hat{a}_{\boldsymbol{k},s}{}^{+}e^{-i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}}]$$
$$= \sum_{\boldsymbol{k},s}[\hat{H}_1(\boldsymbol{k},\boldsymbol{s})e^{-i\omega_k t}+\hat{H}^{+}{}_1(\boldsymbol{k},\boldsymbol{s})e^{i\omega_k t}]$$

where e>0, and

$$\hat{H}_1(\boldsymbol{k},\boldsymbol{s})e^{-i\omega_k t} = [\frac{e}{m}\sqrt{\frac{2\pi\hbar}{\omega_{\boldsymbol{k}}V}}\hat{a}_{\boldsymbol{k},s}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}}]e^{-i\omega_k t} \qquad \text{(absorption)}$$

and

$$\hat{H}_1{}^{+}(\boldsymbol{k},\boldsymbol{s})e^{i\omega_k t} = [\frac{e}{m}\sqrt{\frac{2\pi\hbar}{\omega_{\boldsymbol{k}} V}}\hat{a}_{\boldsymbol{k},s}{}^{+}e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}}]e^{i\omega_k t} \qquad \text{(emission)}$$

The creation operator and the annihilation operator are defined by

$$\hat{a}_{\boldsymbol{k},s}\left|N_{\boldsymbol{k},s}\right\rangle = \sqrt{N_{\boldsymbol{k},s}}\left|N_{\boldsymbol{k},s}-1\right\rangle,$$

$$\hat{a}_{\boldsymbol{k},s}{}^{+}\left|N_{\boldsymbol{k},s}\right\rangle = \sqrt{N_{\boldsymbol{k},s}+1}\left|N_{\boldsymbol{k},s}+1\right\rangle$$

with

$$\hat{N}_{\boldsymbol{k},s} = \hat{a}_{\boldsymbol{k},s}{}^{+}\hat{a}_{\boldsymbol{k},s}$$

Then we have

$$\begin{aligned}\left\langle N_{\boldsymbol{k},s}-1\right|\hat{H}_1(\boldsymbol{k},\boldsymbol{s})\left|N_{\boldsymbol{k},s}\right\rangle &= \frac{e}{m}\sqrt{\frac{2\pi\hbar}{\omega_{\boldsymbol{k}} V}}\left\langle N_{\boldsymbol{k},s}-1\right|\hat{a}_{\boldsymbol{k},s}\left|N_{\boldsymbol{k},s}\right\rangle e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}} \\ &= \frac{e}{m}\sqrt{\frac{2\pi\hbar}{\omega_{\boldsymbol{k}} V}}\sqrt{N_{\boldsymbol{k},s}}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}} \\ &= \sqrt{N_{\boldsymbol{k},s}}\,\hat{V}(\boldsymbol{k},s)\end{aligned}$$

$$\begin{aligned}\left\langle N_{\boldsymbol{k},s}+1\right|\hat{H}_1{}^{+}(\boldsymbol{k},\boldsymbol{s})\left|N_{\boldsymbol{k},s}\right\rangle &= \frac{e}{m}\sqrt{\frac{2\pi\hbar}{\omega_{\boldsymbol{k}} V}}\left\langle N_{\boldsymbol{k},s}+1\right|\hat{a}_{\boldsymbol{k},s}{}^{+}\left|N_{\boldsymbol{k},s}\right\rangle e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}} \\ &= \frac{e}{m}\sqrt{\frac{2\pi\hbar(N_{\boldsymbol{k},s}+1)}{\omega_{\boldsymbol{k}} V}}e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}} \\ &= \sqrt{N_{\boldsymbol{k},s}+1}\,\hat{V}^{+}(\boldsymbol{k},\boldsymbol{s})\end{aligned}$$

where

$$\hat{V}(\boldsymbol{k},\boldsymbol{s}) = \frac{e}{m}\sqrt{\frac{2\pi\hbar}{\omega_{\boldsymbol{k}} V}}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}}\ ,$$

$$\hat{V}^{+}(\boldsymbol{k},\boldsymbol{s}) = \frac{e}{m}\sqrt{\frac{2\pi\hbar}{\omega_{\boldsymbol{k}} V}}e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}}$$

Here we calculate the transition probability for the absorption and emission of photon by electron. Using the Fermi's golden rule for the sinusoidal time-dependent perturbation, we get the transition rate as

$$\begin{aligned}\Gamma^{abs} &= \frac{2\pi}{\hbar} N_{\boldsymbol{k},s} \left| \langle f | \hat{V}(\boldsymbol{k},s) | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega_k) \\ &= \frac{2\pi}{\hbar} (\frac{2\pi\hbar}{\omega_{\boldsymbol{k}} V} e^2 \omega_{\boldsymbol{k}}{}^2) N_{\boldsymbol{k},s} \left| \langle f | e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \boldsymbol{\varepsilon}(\boldsymbol{k},s) \cdot \hat{\boldsymbol{p}} | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega_k) \\ &= \frac{4\pi^2 e^2 \omega_{\boldsymbol{k}}}{V} N_{\boldsymbol{k},s} \left| \langle f | e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \boldsymbol{\varepsilon}(\boldsymbol{k},s) \cdot \hat{\boldsymbol{p}} | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega_k)\end{aligned}$$

for the absorption, and

$$\begin{aligned}\Gamma^{emi} &= \frac{2\pi}{\hbar} (N_{\boldsymbol{k},s} + 1) \left| \langle f | \hat{V}^{+}(\boldsymbol{k},s) | i \rangle \right|^2 \delta(E_f - E_i + \hbar\omega_k) \\ &= \frac{2\pi}{\hbar} (\frac{2\pi\hbar}{\omega_{\boldsymbol{k}} V} e^2 \omega_{\boldsymbol{k}}{}^2) (N_{\boldsymbol{k},s} + 1) \left| \langle f | e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \boldsymbol{\varepsilon}(\boldsymbol{k},s) \cdot \hat{\boldsymbol{p}} | i \rangle \right|^2 \delta(E_f - E_i + \hbar\omega_k) \\ &= \frac{4\pi^2 e^2 \omega_{\boldsymbol{k}}}{V} N_{\boldsymbol{k},s} \left| \langle f | e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \boldsymbol{\varepsilon}(\boldsymbol{k},s) \cdot \hat{\boldsymbol{p}} | i \rangle \right|^2 \delta(E_f - E_i + \hbar\omega_k) \\ &\quad + \frac{4\pi^2 e^2 \omega_{\boldsymbol{k}}}{V} \left| \langle f | e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \boldsymbol{\varepsilon}(\boldsymbol{k},s) \cdot \hat{\boldsymbol{p}} | i \rangle \right|^2 \delta(E_f - E_i + \hbar\omega_k)\end{aligned}$$

for the emission, where $|i\rangle$ and $|f\rangle$ are the final state and initial state of the atomic system. The first term is the stimulated emission and the second term is the spontaneous emission.

2. Electric dipole approximation

We use the electric dipole approximation. In this approximation we assume

(i) $e^{\pm i\boldsymbol{k}\cdot\boldsymbol{r}} \approx 1$ since $\boldsymbol{k}\cdot\boldsymbol{r} = \frac{2\pi}{\lambda} r_0 << 1$

(ii) $\langle f | \hat{\boldsymbol{p}} | i \rangle = im\omega \langle f | \hat{\boldsymbol{r}} | i \rangle$.

where λ is the wavelength of the light and r_0 is the spacial spread of electron wavefunction, $|f\rangle$ and $|i\rangle$ are the final and initial states of the atomic system. $E_f{}^{(0)} - E_i{}^{(0)} = \hbar\omega = \hbar\omega_{fi}$

((**Note**)) Proof of $\langle f | \hat{\boldsymbol{p}} | i \rangle = im\omega \langle f | \hat{\boldsymbol{r}} | i \rangle$.

In electric dipole transition, the matrix element $\langle f|\hat{\boldsymbol{p}}|i\rangle$ is the decisive quantity that must be evaluated. This can be related to the matrix element of the position operator $\hat{\boldsymbol{r}}$, if the unperturbed Hamiltonian is of the form

$$\hat{H}_0 = \frac{\hat{\boldsymbol{p}}^2}{2m} + V(\hat{\boldsymbol{r}}),$$

and if $V(\hat{\boldsymbol{r}})$ commutes with $\hat{\boldsymbol{r}}$. Under these conditions, we have

$$[\hat{\boldsymbol{r}}, \hat{H}_0] = \frac{1}{2m}[\hat{\boldsymbol{r}}, \hat{\boldsymbol{p}}^2] = \frac{i\hbar}{m}\hat{\boldsymbol{p}}.$$

Using this relation, we get

$$\begin{aligned}
\langle f|\hat{\boldsymbol{p}}|i\rangle &= \frac{m}{i\hbar}\langle f|[\hat{\boldsymbol{r}}, \hat{H}_0]|i\rangle \\
&= \frac{m}{i\hbar}\langle f|\hat{\boldsymbol{r}}\hat{H}_0 - \hat{H}_0\hat{\boldsymbol{r}}|i\rangle \\
&= \frac{m}{i\hbar}(E_i^{(0)} - E_f^{(0)})\langle f|\hat{\boldsymbol{r}}|i\rangle \\
&= \frac{m}{i\hbar}(-\hbar\omega)\langle f|\hat{\boldsymbol{r}}|i\rangle \\
&= im\omega\langle f|\hat{\boldsymbol{r}}|i\rangle
\end{aligned}$$

where

$$E_f^{(0)} - E_i^{(0)} = \hbar\omega = \hbar\omega_{fi},$$

$$\hat{H}_0|i\rangle = E_i^{(0)}|i\rangle, \qquad \hat{H}_0|f\rangle = E_i^{(0)}|f\rangle.$$

Then we have

$$\langle f|\hat{V}(\boldsymbol{k},\boldsymbol{s})|i\rangle \approx \frac{e}{m}\sqrt{\frac{2\pi\hbar}{\omega_{\boldsymbol{k}}V}}\langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}}|i\rangle$$

$$= \frac{e}{m}\sqrt{\frac{2\pi\hbar}{\omega_{\boldsymbol{k}}V}}(im\omega_{\boldsymbol{k}})\langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}}|i\rangle$$

$$= \sqrt{\frac{2\pi\hbar}{\omega_{\boldsymbol{k}}V}}(ie\omega_{\boldsymbol{k}})\langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}}|i\rangle$$

We note that

$$\left|\langle f|\hat{V}^{+}(\boldsymbol{k},\boldsymbol{s})|i\rangle\right|^2 = \left|\langle f|\hat{V}^{+}(\boldsymbol{k},\boldsymbol{s})|i\rangle\right|^2$$

So we obtain the transition rate, within the electric dipole approximation, for the emission and absorption of a photon of the energy $\hbar\omega_k$, by electrons in the atom

$$\Gamma^{emi} = \frac{2\pi}{\hbar}\left(\frac{2\pi\hbar}{\omega_{\boldsymbol{k}}V}e^2\omega_{\boldsymbol{k}}{}^2\right)(N_{\boldsymbol{k},s}+1)\left|\langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}}|i\rangle\right|^2\delta(E_f - E_i + \hbar\omega_k)$$

$$= \frac{4\pi^2e^2\omega_{\boldsymbol{k}}}{V}(N_{\boldsymbol{k},s}+1)\left|\langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}}|i\rangle\right|^2\delta(E_f - E_i + \hbar\omega_k) \qquad \text{(emission)}$$

$$= \frac{4\pi^2e^2\omega_{\boldsymbol{k}}}{V}N_{\boldsymbol{k},s}\left|\langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}}|i\rangle\right|^2\delta(E_f - E_i + \hbar\omega_k)$$

$$+ \frac{4\pi^2e^2\omega_{\boldsymbol{k}}}{V}\left|\langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}}|i\rangle\right|^2\delta(E_f - E_i + \hbar\omega_k)$$

The first term corresponds to the stimulated emission (proportional to $N_{\boldsymbol{k},s}$) and the second term corresponds to the spontaneous emission ($N_{\boldsymbol{k},s}$=0).

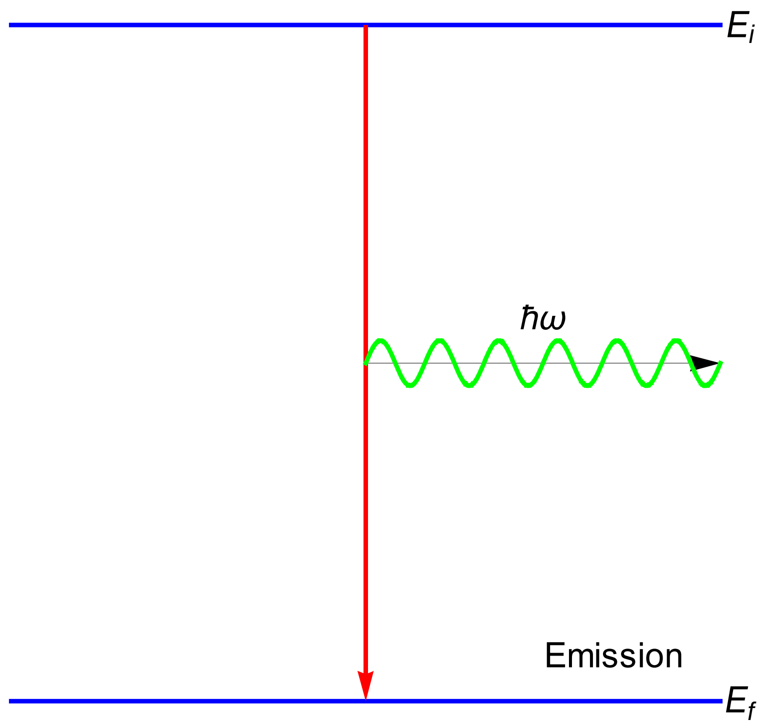


Fig. Stimulated emission process and spontaneous emission . $E_f = E_i - \hbar\omega$.

We also have

$$\Gamma^{abs} = \frac{2\pi}{\hbar}\left(\frac{2\pi\hbar}{\omega_{\boldsymbol{k}} V} e^2 \omega_{\boldsymbol{k}}{}^2\right) N_{\boldsymbol{k},s} \left|\langle f \left| \boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}} \right| i \rangle\right|^2 \delta(E_f - E_i - \hbar\omega_k)$$

$$= \frac{4\pi^2 e^2 \omega_{\boldsymbol{k}}}{V} N_{\boldsymbol{k},s} \left|\langle f \left| \boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}} \right| i \rangle\right|^2 \delta(E_f - E_i - \hbar\omega_k) \qquad \text{(absorption)}$$

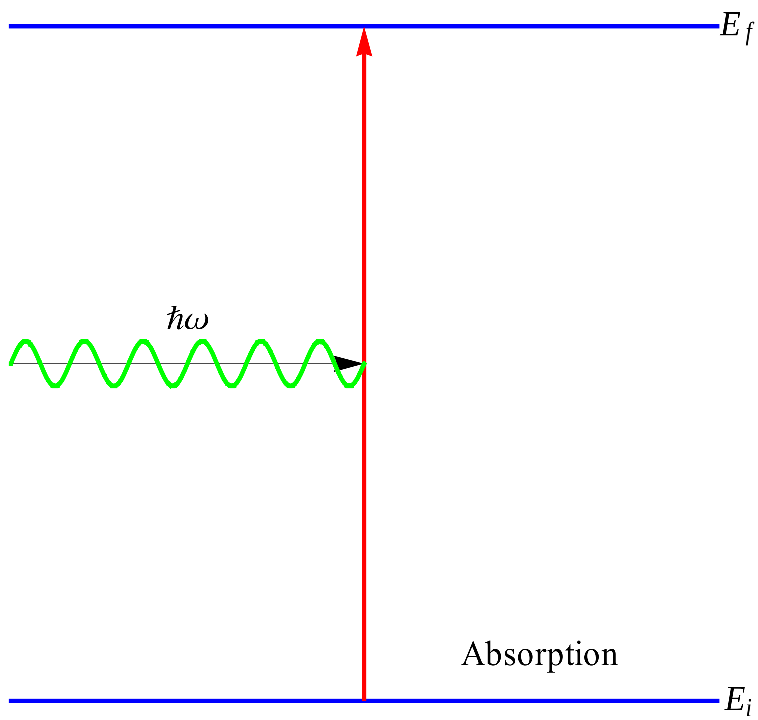


Fig. Absorption process. $E_f = E_i - \hbar\omega$.

The transition rate for the absorption and stimulated emission is given by

$$\frac{4\pi^2 e^2 \omega_k}{V} N_{k,s} \left| \langle f | \boldsymbol{\varepsilon}(\boldsymbol{k}, s) \cdot \hat{\boldsymbol{r}} | i \rangle \right|^2 \delta(E_f - E_i + \hbar\omega_k)$$

and

$$\frac{4\pi^2 e^2 \omega_k}{V} N_{k,s} \left| \langle f | \boldsymbol{\varepsilon}(\boldsymbol{k}, s) \cdot \hat{\boldsymbol{r}} | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega_k)$$

The selection rule is determined from the matrix element

$$\langle f | \boldsymbol{\varepsilon}(\boldsymbol{k}, s) \cdot \hat{\boldsymbol{r}} | i \rangle = \boldsymbol{\varepsilon}(\boldsymbol{k}, s) \cdot \langle f | \hat{\boldsymbol{r}} | i \rangle = \boldsymbol{\varepsilon}(\boldsymbol{k}, s) \cdot \boldsymbol{R}$$

for both cases,

$$\boldsymbol{R} = \langle f | \hat{\boldsymbol{r}} | i \rangle = \langle f | \hat{x} | i \rangle \boldsymbol{e}_x + \langle f | \hat{y} | i \rangle \boldsymbol{e}_y + \langle f | \hat{y} | i \rangle \boldsymbol{e}_z$$

3. Transition rate for emission and absorption

The emitted photon (with a fixed polarization) having a wave number between k and k +dk in the solid angle dΩ is given by

$$\rho d\Omega = \frac{Vk^2 dk d\Omega}{(2\pi)^3} = \frac{V\omega^2 d\omega}{(2\pi)^3 c^3} d\Omega$$

where the dispersion is given by $\omega = ck$. Using the Fermi golden rule, the transition probability per unit time to a particular final state of the atom is given by

$$dW_{fi}{}^{e} = \frac{2\pi}{\hbar} \sum_s N_{\boldsymbol{k},s} \left| \langle f | \hat{V}^+(\boldsymbol{k},s) | i \rangle \right|^2 \rho d\Omega \delta(E_f - E_i + \hbar\omega)$$

(absorption))

$$dW_{fi}{}^{ab} = \frac{2\pi}{\hbar} \sum_s (N_{\boldsymbol{k},s} + 1) \left| \langle f | \hat{V}^+(\boldsymbol{k},s) | i \rangle \right|^2 \rho d\Omega \delta(E_f - E_i + \hbar\omega)$$

(emission)

The transition rate for the emission is

$$dW_{fi}^{e} = \frac{4\pi^2 e^2 \omega_0}{V} \sum_s (N_{\boldsymbol{k},s} + 1) \left| \langle f | \boldsymbol{\varepsilon}(\boldsymbol{k},s) \cdot \hat{\boldsymbol{r}} | i \rangle \right|^2 \delta(E_i - E_f - \hbar\omega_k) \frac{V\omega^2}{(2\pi)^3 c^3} d\omega d\Omega$$

$$W_{fi}^{e} \to \frac{4\pi^2 e^2 \omega_0}{V} \int d\omega \delta(\omega_0 - \omega) \frac{V\omega^2}{(2\pi)^3 c^3 \hbar} (N_{\boldsymbol{k}} + 1) d\Omega \sum_s \left| \langle f | \boldsymbol{\varepsilon}(\boldsymbol{k},s) \cdot \hat{\boldsymbol{r}} | i \rangle \right|^2$$

$$= \frac{4\pi^2 e^2 \omega_0}{V} \frac{V{\omega_0}^2 [\overline{N(\omega_0)} + 1]}{(2\pi)^3 c^3 \hbar} \frac{8\pi}{3} \left| \langle f | \hat{\boldsymbol{r}} | i \rangle \right|^2$$

$$= \frac{4{\omega_0}^3 e^2}{3\hbar c^3} [\overline{N(\omega_0)} + 1] \left| \langle f | \hat{\boldsymbol{r}} | i \rangle \right|^2$$

$\frac{4{\omega_0}^3 e^2}{3\hbar c^3} \overline{N(\omega_0)} \left| \langle f | \hat{\boldsymbol{r}} | i \rangle \right|^2$ Stimulate emission

$\frac{4{\omega_0}^3 e^2}{3\hbar c^3} \left| \langle f | \hat{\boldsymbol{r}} | i \rangle \right|^2$ Spontaneous emission

We note that

$$\delta(E_f - E_i + \hbar\omega_k) = \delta(\frac{E_f - E_i}{\hbar} + \omega_k) = \frac{1}{\hbar}\delta(\omega_0 - \omega).$$

and

$$E_f - E_i = \hbar\omega_0 .$$

The transition rate for the absorption is

$$dW_{fi}^a = \frac{4\pi^2 e^2 \omega_0}{V}\sum_s N_{\boldsymbol{k},s}\left|\langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}}|i\rangle\right|^2 \delta(E_f - E_i - \hbar\omega_k)\frac{V\omega^2}{(2\pi)^3 c^3} d\omega' d\Omega$$

$$W_{fi}^a \to \frac{4\pi^2 e^2 \omega_0}{V}\int d\omega\delta(\omega_0 - \omega)\frac{V\omega^2 \overline{N_{\boldsymbol{k}}}}{(2\pi)^3 c^3 \hbar} d\omega d\Omega \sum_s \left|\langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}}|i\rangle\right|^2$$

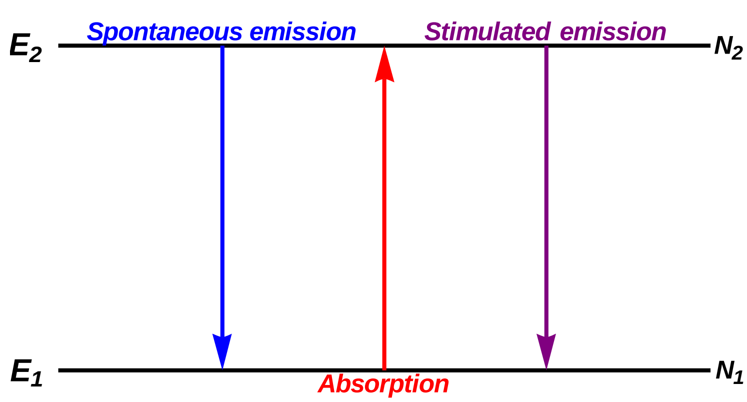
$$= \frac{4\pi^2 e^2 \omega_0}{V}\frac{V\omega_0{}^2\overline{N(\omega_0)}}{(2\pi)^3 c^3 \hbar}\frac{8\pi}{3}\left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2$$

$$= \frac{4\omega_0{}^3 e^2}{3\hbar c^3}\overline{N(\omega_0)}\left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2$$

$$\frac{4\omega_0{}^3 e^2}{3\hbar c^3}\overline{N(\omega_0)}\left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2 \qquad \text{Absorption}$$

4. Planck's radiation law

Planck's radiation law



Let the number of atoms in the state $|1\rangle$ and the state $|2\rangle$ be N_1 and N_2. In the thermal equilibrium, we have

$$\frac{E_2}{E_1} = \exp(-\frac{\hbar\omega_0}{k_B T})$$

where $E_2 - E_1 = \hbar\omega_0$ (>0).

The number of photons undergoing absorption per unit time is

$$\frac{4\omega_0^3 e^2}{3\hbar c^3}\overline{N(\omega_0)}\left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2 N_1$$

The number of photons undergoing emission per unit time is

$$\frac{4\omega_0^3 e^2}{3\hbar c^3}[\overline{N(\omega_0)}+1]\left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2 N_2$$

In thermal equilibrium, the number of photons for the emission is the same as that for the absorption,

$$\frac{4\omega_0^3 e^2}{3\hbar c^3}\overline{N(\omega_0)}\left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2 N_1 = \frac{4\omega_0^3 e^2}{3\hbar c^3}[\overline{N(\omega_0)}+1]\left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2 N_2$$

or

$$\overline{N(\omega_0)}N_1 = [\overline{N(\omega_0)}+1]N_2 \qquad \text{(detailed balance)}$$

Then we get the Planck's distribution function

$$\overline{N(\omega_0)} = \frac{N_2}{N_1 - N_2} = \frac{1}{\frac{N_1}{N_2} - 1} = \frac{1}{e^{\beta\hbar\omega_0} - 1}$$

5. Einsteins' *A* and *B* co-efficients

The coefficients A_{21} and B_{12} are defined as

$$\frac{4\omega_0^3 e^2}{3\hbar c^3}\left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2 = A_{21}$$

$$\frac{4\omega_0{}^3 e^2}{3\hbar c^3}\left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2\overline{N(\omega_0)} = B_{12}\overline{W_T}(\omega_0)$$
$$= A_{21}\overline{N(\omega_0)}$$
$$= A_{21}\frac{\pi^2 c^3}{\hbar\omega_0{}^3}\overline{W_T}(\omega_0)$$
$$= A_{21}\frac{\pi^2 c^3}{\hbar\omega_0{}^3}\overline{W_T}(\omega_0)$$

or

$$B_{12} = A_{21}\frac{\pi^2 c^3}{\hbar\omega_0{}^3}$$

where we use the relation

$$\overline{W_T}(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{\exp(\beta\hbar\omega)-1} = \frac{\hbar\omega^3}{\pi^2 c^3}\overline{N}(\omega)$$

$$A_{21} = \frac{4\omega^3 e^2}{3\hbar c^3}\left|\langle\phi_f|\hat{\boldsymbol{r}}|\phi_i\rangle\right|^2$$

The electromagnetic energy (per unit time) emitted arising from the spontaneous emission, can be obtained as

$$P = \hbar\omega_0 W_{fi}^e = \hbar\omega_0\frac{4\alpha\omega_0{}^3}{3c^2}\left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2 = \frac{4e^2\omega_0{}^4}{3c^3}\left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2. \qquad \text{(cgs unit)},$$

or

$$P = \frac{e^2\omega_0{}^4}{3\pi\varepsilon_0 c^3}\left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2 \qquad \text{(SI units)}$$

6. Calculation of $\sum_s\left|\langle f|\varepsilon(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}}|i\rangle\right|^2$

The unit vectors $\boldsymbol{\varepsilon}(\boldsymbol{k},s=1)$, $\boldsymbol{\varepsilon}(\boldsymbol{k},s=2)$, and $\boldsymbol{k}$ are chosen to point along the *x*-, *y*-, and *z*-axes. We also assume that the wave functions describing states $|i\rangle$ and $|f\rangle$ have been chosen real such that $\langle f|\hat{\boldsymbol{r}}|i\rangle = \boldsymbol{R}$ is a real three-dimensional vector;

$$\boldsymbol{R} = R(\sin\theta\cos\phi\,\boldsymbol{e}_x + \sin\theta\sin\phi\,\boldsymbol{e}_y + \cos\theta\,\boldsymbol{e}_z)$$

$$\begin{aligned}
\sum_s \left|\langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}}|i\rangle\right|^2 &= \sum_s \langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}}|i\rangle\langle i|\hat{\boldsymbol{r}}\cdot\boldsymbol{\varepsilon}(\boldsymbol{k},s)|f\rangle \\
&= \langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s=1)\cdot\hat{\boldsymbol{r}}|i\rangle\langle i|\boldsymbol{\varepsilon}(\boldsymbol{k},s=1)\cdot\hat{\boldsymbol{r}}|f\rangle + \langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s=2)\cdot\hat{\boldsymbol{r}}|i\rangle\langle i|\boldsymbol{\varepsilon}(\boldsymbol{k},s=2)\cdot\hat{\boldsymbol{r}}|f\rangle \\
&= [\boldsymbol{\varepsilon}(\boldsymbol{k},s=1)\cdot\langle f|\hat{\boldsymbol{r}}|i\rangle][\boldsymbol{\varepsilon}(\boldsymbol{k},s=1)\cdot\langle i|\hat{\boldsymbol{r}}|f\rangle] + [\boldsymbol{\varepsilon}(\boldsymbol{k},s=2)\cdot\langle f|\hat{\boldsymbol{r}}|i\rangle]\boldsymbol{\varepsilon}(\boldsymbol{k},s=2)\cdot\boldsymbol{\varepsilon}(\boldsymbol{k},s=2)\cdot\langle i|\hat{\boldsymbol{r}}|f\rangle] \\
&= [\boldsymbol{e}_x\cdot\langle f|\hat{\boldsymbol{r}}|i\rangle][\boldsymbol{e}_x\cdot\langle i|\hat{\boldsymbol{r}}|f\rangle] + [\boldsymbol{e}_y\cdot\langle f|\hat{\boldsymbol{r}}|i\rangle]\cdot[\boldsymbol{e}_y\cdot\langle i|\hat{\boldsymbol{r}}|f\rangle] \\
&= \langle f|\hat{\boldsymbol{r}}|i\rangle\langle i|\hat{\boldsymbol{r}}|f\rangle\sin^2\theta
\end{aligned}$$

We use the notation R (real 3D vector)

$$\langle f|\hat{\boldsymbol{r}}|i\rangle = \boldsymbol{R}, \quad \langle i|\hat{\boldsymbol{r}}|f\rangle = \langle f|\hat{\boldsymbol{r}}|i\rangle^* = \boldsymbol{R}^*$$

$$\begin{aligned}
\sum_s \left|\langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}}|i\rangle\right|^2 &= [\boldsymbol{e}_x\cdot\langle f|\hat{\boldsymbol{r}}|i\rangle][\boldsymbol{e}_x\cdot\langle i|\hat{\boldsymbol{r}}|f\rangle] + [\boldsymbol{e}_y\cdot\langle f|\hat{\boldsymbol{r}}|i\rangle]\cdot[\boldsymbol{e}_y\cdot\langle i|\hat{\boldsymbol{r}}|f\rangle] \\
&= (\boldsymbol{e}_x\cdot\boldsymbol{R})(\boldsymbol{e}_x\cdot\boldsymbol{R})^* + (\boldsymbol{e}_y\cdot\boldsymbol{R})(\boldsymbol{e}y\cdot\boldsymbol{R})^* \\
&= |(\boldsymbol{e}_x\cdot\boldsymbol{R})| + |(\boldsymbol{e}_y\cdot\boldsymbol{R})|^2 \\
&= R^2\sin^2\theta \\
&= \left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2\sin^2\theta
\end{aligned}$$

$$\int d\Omega\sum_s \left|\langle f|\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}}|i\rangle\right|^2 = \left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2 2\pi\int_0^\pi \sin^3\theta d\theta = \frac{8\pi}{3}\left|\langle f|\hat{\boldsymbol{r}}|i\rangle\right|^2$$

where

$$d\Omega = 2\pi\sin\theta d\theta$$

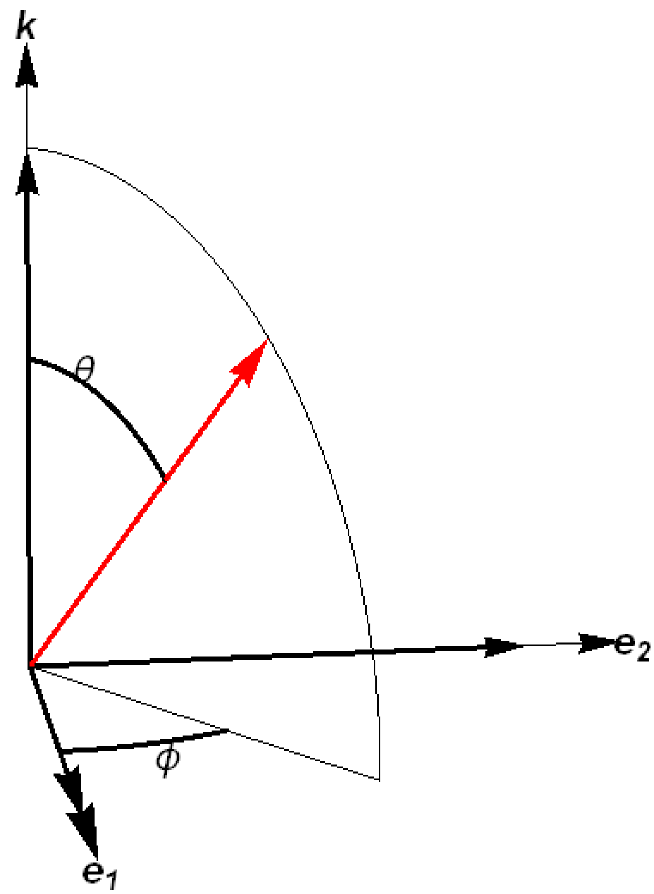


Fig. Two polarization vectors ($\boldsymbol{e}_1$, and $\boldsymbol{e}_2$) perpendicular to the wave vector $\boldsymbol{k}$. The vector $\boldsymbol{R} = \langle f | \hat{\boldsymbol{r}} | i \rangle$ is denoted by a red arrow. $\boldsymbol{R} = \langle f | \hat{\boldsymbol{r}} | i \rangle = |\boldsymbol{R}|(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$.

7. Transition from the 2p state to the 1s state for the hydrogen atom

For the 1s state, we have

$$\langle \boldsymbol{r} | n=1, l=0, m=0 \rangle = \frac{1}{\sqrt{\pi} a^{3/2}} e^{-\frac{r}{a}}$$

For the 2p state, we have

$$\psi_{2,1,1}(\boldsymbol{r}) = \langle \boldsymbol{r} | n=2, l=1, m=1 \rangle = \frac{1}{8\sqrt{\pi} a^{5/2}} r e^{-\frac{r}{2a}} \sin\theta e^{i\phi}$$

$$\psi_{2,1,0}(\boldsymbol{r}) = \langle \boldsymbol{r} | n=2, l=1, m=0 \rangle = \frac{1}{4\sqrt{2\pi} a^{5/2}} r e^{-\frac{r}{2a}} \cos\theta$$

$$\psi_{2,1,-1}(\boldsymbol{r}) = \langle \boldsymbol{r} | n=2, l=1, m=-1\rangle = \frac{1}{8\sqrt{\pi}a^{5/2}} r e^{-\frac{r}{2a}} \sin\theta e^{-i\phi}$$

where a is the Bohr radius,

$$\boldsymbol{r} = \boldsymbol{e}_x r\sin\theta\cos\phi + \boldsymbol{e}_y r\sin\theta\sin\phi + \boldsymbol{e}_z r\cos\theta .$$

$$d\boldsymbol{r} = r^2 \sin\theta dr d\theta d\phi = r^2 dr d\Omega$$

Then we have the integrals

(1) $|2,1,1\rangle \to |1,0,0\rangle$ transition

$$h_{1x} = \int d^3\boldsymbol{r} \psi_{100}{}^*(\boldsymbol{r}) x \psi_{211}(\boldsymbol{r}) = -\frac{128}{243}a$$

$$h_{1y} = \int d\boldsymbol{r} \psi_{100}{}^*(\boldsymbol{r}) y \psi_{211}(\boldsymbol{r}) = -\frac{128}{243}ai$$

$$h_{1z} = \int d\boldsymbol{r} \psi_{100}{}^*(\boldsymbol{r}) z \psi_{211}(\boldsymbol{r}) = 0$$

Note that

$$h_{1x} = \int_0^\infty r^3 R_{10}{}^*(r) R_{21}(r) dr \int d\Omega \sin^2\theta\cos\phi Y_0^{0^*}(\theta,\phi) Y_1^1(\theta,\phi)$$
$$= -\frac{1}{\sqrt{6}} \int_0^\infty r^3 R_{10}{}^*(r) R_{21}(r) dr$$

(ii) $|2,1,0\rangle \to |1,0,0\rangle$ transition

$$h_{2x} = \int d^3\boldsymbol{r} \psi_{100}{}^*(\boldsymbol{r}) x \psi_{210}(\boldsymbol{r}) = 0$$

$$h_{2y} = \int d^3\boldsymbol{r} \psi_{100}{}^*(\boldsymbol{r}) y \psi_{210}(\boldsymbol{r}) = 0$$

$$h_{2z} = \int d^3\boldsymbol{r}\psi_{100}{}^*(\boldsymbol{r})z\psi_{210}(\boldsymbol{r}) = -\frac{128}{243}\sqrt{2}a$$

(iii) $\left|2,1,-1\right\rangle \to \left|1,0,0\right\rangle$ transition

$$h_{3x} = \int d\boldsymbol{r}\psi_{100}{}^*(\boldsymbol{r})x\psi_{21-1}{}^*(\boldsymbol{r}) = \frac{128}{243}a$$

$$h_{3y} = \int d\boldsymbol{r}\psi_{100}{}^*(\boldsymbol{r})y\psi_{21-1}{}^*(\boldsymbol{r}) = -\frac{128}{243}ia$$

$$h_{3z} = \int d\boldsymbol{r}\psi_{100}{}^*(\boldsymbol{r})z\psi_{21-1}{}^*(\boldsymbol{r}) = 0$$

Then we get

$$\sum_m \int d^3\boldsymbol{r}\,\psi_{100}{}^*(r)\boldsymbol{r}\psi_{21m}{}^*(\boldsymbol{r}) = (h_{1y} + h_{2x} + h_{3x})\boldsymbol{e}_x + (h_{1y} + h_{2y} + h_{3y})\boldsymbol{e}_y$$

$$+ (h_{1z} + h_{2z} + h_{3z})\boldsymbol{e}_z$$

$$= \frac{128}{243}a(-2i\boldsymbol{e}_y - \sqrt{2}\boldsymbol{e}_z)$$

$$\frac{1}{3}\left|\sum_m \int dr\psi_{100}{}^*(r)\boldsymbol{r}\psi_{21m}{}^*(\boldsymbol{r})\right|^2 = 2h_{1x}{}^2 = 2\left(\frac{128}{243}a\right)^2 = 2\left(\frac{2^7}{3^5}a\right)^2 = \frac{2^{15}}{3^{10}}a^2$$

where m = 1, 0, and -1. The transition rate is given a formula

$$W_{fi}^e = \frac{4\alpha\omega_0{}^3}{3c^2}\frac{1}{3}\left|\sum_m \int d^3\boldsymbol{r}\psi_{100}{}^*(\boldsymbol{r})\boldsymbol{r}\psi_{21m}(\boldsymbol{r})\right|^2 = \frac{4\alpha\omega_0{}^3}{3c^2}2h_{1x}{}^2$$

or

$$W_{fi}^e = \frac{4\alpha\omega_0{}^3}{3c^2}\frac{2^{15}}{3^{10}}a^2 = \frac{\alpha\omega_0{}^3}{c^2}\frac{2^{17}}{3^{11}}a^2$$

The factor 1/3 is the average over m. Note that

$$\hbar\omega_0 = E_{2p} - E_{1s} = \frac{1}{2}mc^2\alpha^2(1 - \frac{1}{2^2}) = \frac{3}{2^3}mc^2\alpha^2$$

$$W_{fi}^{e} = \frac{\alpha}{c^2}\frac{2^{17}}{3^{11}}a^2\frac{3^3}{2^9}\left(\frac{mc^2\alpha^2}{\hbar}\right)^3 = \left(\frac{2}{3}\right)^8 \alpha^5 \frac{mc^2}{\hbar}$$

where

$$a = \frac{\hbar^2}{me^2}$$

The we can evaluate the lifetime as

$$\tau_{2p\to 1s} = \frac{1}{W_{fi}^{e}} = 1.59531 \text{ x } 10^{-9} \text{ s.}$$

8. Calculation using Mathematica

```
Clear["Global`*"]; Z = 1;
exp_* := exp /. {Complex[re_, im_] :> Complex[re, -im]}

rwave[n_, ℓ_, r_] :=
  1/(√(n + ℓ)!) (2^(1+ℓ) a^(-ℓ-3/2) e^(-(Z r)/(a n)) n^(-ℓ-2) Z^(ℓ+3/2) r^ℓ √(n - ℓ - 1)!
    LaguerreL[-1 + n - ℓ, 1 + 2 ℓ, (2 Z r)/(a n)]);

    ψ[n_, ℓ_, m_, r_, θ_, ϕ_] :=
     SphericalHarmonicY[ℓ, m, θ, ϕ] rwave[n, ℓ, r];

    ψ[1, 0, 0, r, θ, ϕ]
```

$$\frac{e^{-\frac{r}{a}}}{a^{3/2}\sqrt{\pi}}$$

```
    ψ[2, 1, 1, r, θ, ϕ]
```

$$-\frac{e^{-\frac{r}{2a}+i\phi}\, r \,\mathrm{Sin}[\theta]}{8\, a^{5/2}\sqrt{\pi}}$$

```
ψ[2, 1, 0, r, θ, ϕ]
```

$$\frac{e^{-\frac{r}{2a}}\, r \operatorname{Cos}[\theta]}{4\, a^{5/2}\sqrt{2\pi}}$$

```
ψ[2, 1, -1, r, θ, ϕ]
```

$$\frac{e^{-\frac{r}{2a}-i\phi}\, r \operatorname{Sin}[\theta]}{8\, a^{5/2}\sqrt{\pi}}$$

```
f1 =
 r^2 Sin[θ] ψ[1, 0, 0, r, θ, ϕ]*
   (ex r Sin[θ] Cos[ϕ] + ey r Sin[θ] Sin[ϕ] + ez r Cos[θ])
   ψ[2, 1, 1, r, θ, ϕ] // Simplify
```

$$-\frac{e^{-\frac{3r}{2a}+i\phi}\, r^4 \operatorname{Sin}[\theta]^2\, (\text{ez} \operatorname{Cos}[\theta] + \operatorname{Sin}[\theta]\, (\text{ex} \operatorname{Cos}[\phi] + \text{ey} \operatorname{Sin}[\phi]))}{8\, a^4\, \pi}$$

```
f2 =
 r^2 Sin[θ] ψ[1, 0, 0, r, θ, ϕ]*
   (ex r Sin[θ] Cos[ϕ] + ey r Sin[θ] Sin[ϕ] + ez r Cos[θ])
   ψ[2, 1, 0, r, θ, ϕ] // Simplify
```

$$\frac{1}{4\sqrt{2}\,a^4\pi}e^{-\frac{3r}{2a}}r^4\,\text{Cos}[\theta]\,\text{Sin}[\theta]\,(\text{ez Cos}[\theta]+\text{Sin}[\theta]\,(\text{ex Cos}[\phi]+\text{ey Sin}[\phi]))$$

```
f3 =
 r^2 Sin[θ] ψ[1, 0, 0, r, θ, ϕ]*
   (ex r Sin[θ] Cos[ϕ] + ey r Sin[θ] Sin[ϕ] + ez r Cos[θ])
   ψ[2, 1, -1, r, θ, ϕ] // Simplify
```

$$\frac{e^{-\frac{3r}{2a}-i\phi}\,r^4\,\text{Sin}[\theta]^2\,(\text{ez Cos}[\theta]+\text{Sin}[\theta]\,(\text{ex Cos}[\phi]+\text{ey Sin}[\phi]))}{8a^4\pi}$$

```
h1 =
 Integrate[Integrate[Integrate[f1, {ϕ, 0, 2π}],
    {θ, 0, π}], {r, 0, ∞}] // FullSimplify[#, a > 0] &
```

$$-\frac{128}{243}a\,(\text{ex}+i\,\text{ey})$$

```
h2 =
 Integrate[Integrate[Integrate[f2, {ϕ, 0, 2π}], {θ, 0, π}],
   {r, 0, ∞}] // FullSimplify[#, a > 0] &
```

$$\frac{128}{243}\sqrt{2}\,a\,\text{ez}$$

```
h3 =
 Integrate[Integrate[Integrate[f3, {ϕ, 0, 2π}],
    {θ, 0, π}], {r, 0, ∞}] // FullSimplify[#, a > 0] &
```

$$\frac{128}{243}a\,(\text{ex}-i\,\text{ey})$$

9. Larmor's power formula (classical theory)

Classically, any charged particle radiates when accelerated and that the total radiated power is proportional to the square of the acceleration. The Larmor's power formula for an accelerating charge is given by

$$P=\frac{2e^2}{3c^3}\dot{v}^2=\frac{2e^2}{3c^3}a^2. \qquad \text{(erg/s)}$$

where $a = \dot{v}$ is the acceleration. This equation is the basis of the derivations of radiation from a short dipole antenna

(a) Model of simple harmonics (Feynman)

Suppose we have an oscillating system (classical). Let us see what happens if the displacement *x* of the charge is oscillating so that the acceleration a is given by

$$a = -\omega_0^2 x = -\omega_0^2 x_0 \cos(\omega_0 t),$$

where

$$x = x_0 \cos(\omega_0 t).$$

The average of the acceleration squared over a period time $T = \frac{2\pi}{\omega}$ is calculated as

$$\langle a^2 \rangle = \frac{1}{T}\int_0^T \omega_0^4 x_0^2 \cos^2(\omega_0 t) dt = \frac{1}{2}\omega_0^4 x_0^2.$$

Then we have

$$P = \frac{e^2 \omega_0^4 x_0^2}{3c^3}.$$

(b) Model of circular motion

The centripetal acceleration a is given by

$$a = \omega_0^2 r.$$

where *r* is a radius of the circle. Then *P* is obtained as

$$P = \frac{2e^2 \omega_0^4}{3c^3} r^2.$$

which has the same expression derived from that based on the quantum mechanics.

10. The transition rate for stimulated emission and absorption

The transition rate is determined by the matrix element defined by

$$\langle f|\boldsymbol{\varepsilon}\cdot\hat{\boldsymbol{r}}|i\rangle = \boldsymbol{\varepsilon}\cdot\langle f|\hat{\boldsymbol{r}}|i\rangle = \boldsymbol{\varepsilon}\cdot\boldsymbol{R},$$

where $\boldsymbol{R}$ is the vector defined by

$$\boldsymbol{R} = \langle f|\hat{\boldsymbol{r}}|i\rangle .$$

The polarization vector $\boldsymbol{\varepsilon}$ can be expressed by

$$\boldsymbol{\varepsilon} = (\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_+{}^*)\boldsymbol{e}_+ + (\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_-{}^*)\boldsymbol{e}_- + (\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_0{}^*)\boldsymbol{e}_0$$

where we use the unit vectors defined by,

$$\boldsymbol{e}_+ = -\frac{1}{\sqrt{2}}(\boldsymbol{e}_x + i\boldsymbol{e}_y), \qquad \boldsymbol{e}_+{}^* = -\frac{1}{\sqrt{2}}(\boldsymbol{e}_x - i\boldsymbol{e}_y)$$

$$\boldsymbol{e}_- = \frac{1}{\sqrt{2}}(\boldsymbol{e}_x - i\boldsymbol{e}_y), \qquad \boldsymbol{e}_-{}^* = \frac{1}{\sqrt{2}}(\boldsymbol{e}_x + i\boldsymbol{e}_y)$$

$$\boldsymbol{e}_0 = \boldsymbol{e}_z, \qquad \boldsymbol{e}_0{}^* = \boldsymbol{e}_z$$

Here we note that

$$\boldsymbol{e}_+\cdot\boldsymbol{e}_+{}^* = 1, \qquad \boldsymbol{e}_-\cdot\boldsymbol{e}_-{}^* = 1$$

$$\boldsymbol{e}_+\cdot\boldsymbol{e}_-{}^* = 0, \qquad \boldsymbol{e}_-\cdot\boldsymbol{e}_+{}^* = 1$$

We also have the expression for the scalar product

$$\boldsymbol{\varepsilon}\cdot\boldsymbol{R} = (\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_+{}^*)(\boldsymbol{e}_+\cdot\boldsymbol{R}) + (\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_-{}^*)(\boldsymbol{e}_-\cdot\boldsymbol{R}) + (\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_0{}^*)(\boldsymbol{e}_0\cdot\boldsymbol{R})$$

where

$$\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_+{}^* = \frac{1}{\sqrt{2}}\boldsymbol{\varepsilon}\cdot(\boldsymbol{e}_x - i\boldsymbol{e}_y) = -\frac{1}{\sqrt{2}}(\varepsilon_x - i\varepsilon_y),$$

$$\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_-{}^* = \frac{1}{\sqrt{2}}\boldsymbol{\varepsilon}\cdot(\boldsymbol{e}_x + i\boldsymbol{e}_y) = \frac{1}{\sqrt{2}}(\varepsilon_x + i\varepsilon_y)$$

$$\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_0 = \boldsymbol{\varepsilon}\cdot\boldsymbol{e}_z = \varepsilon_z$$

(a) $\boldsymbol{\varepsilon} = \boldsymbol{e}_+$ (RHC photon)

$$\begin{aligned}\boldsymbol{\varepsilon}\cdot\boldsymbol{R} &= (\boldsymbol{e}_+\cdot\boldsymbol{e}_+^*)(\boldsymbol{e}_+\cdot\boldsymbol{R}) + (\boldsymbol{e}_+\cdot\boldsymbol{e}_-^*)(\boldsymbol{e}_-\cdot\boldsymbol{R}) + (\boldsymbol{e}_+\cdot\boldsymbol{e}_0^*)(\boldsymbol{e}_0\cdot\boldsymbol{R})\\ &= \boldsymbol{e}_+\cdot\boldsymbol{R}\\ &= \langle f|\boldsymbol{e}_+\cdot\hat{\boldsymbol{r}}|i\rangle\\ &= -\frac{1}{\sqrt{2}}\langle f|(\boldsymbol{e}_x + i\boldsymbol{e}_y)\cdot\hat{\boldsymbol{r}}|i\rangle\\ &= -\langle f|\frac{\hat{x}+i\hat{y}}{\sqrt{2}}|i\rangle\end{aligned}$$

(b) $\boldsymbol{\varepsilon} = \boldsymbol{e}_-$ (LHC photon)

$$\begin{aligned}\boldsymbol{\varepsilon}\cdot\boldsymbol{R} &= (\boldsymbol{e}_-\cdot\boldsymbol{e}_+^*)(\boldsymbol{e}_+\cdot\boldsymbol{R}) + (\boldsymbol{e}_-\cdot\boldsymbol{e}_-^*)(\boldsymbol{e}_-\cdot\boldsymbol{R}) + (\boldsymbol{e}_-\cdot\boldsymbol{e}_0^*)(\boldsymbol{e}_0\cdot\boldsymbol{R})\\ &= \boldsymbol{e}_-\cdot\boldsymbol{R}\\ &= \langle f|\boldsymbol{e}_-\cdot\hat{\boldsymbol{r}}|i\rangle\\ &= \frac{1}{\sqrt{2}}\langle f|(\boldsymbol{e}_x - i\boldsymbol{e}_y)\cdot\hat{\boldsymbol{r}}|i\rangle\\ &= \langle f|\frac{\hat{x}-i\hat{y}}{\sqrt{2}}|i\rangle\end{aligned}$$

(b) $\boldsymbol{\varepsilon} = \boldsymbol{e}_0$

$$\begin{aligned}\boldsymbol{\varepsilon}\cdot\boldsymbol{R} &= (\boldsymbol{e}_0\cdot\boldsymbol{e}_+^*)(\boldsymbol{e}_+\cdot\boldsymbol{R}) + (\boldsymbol{e}_0\cdot\boldsymbol{e}_-^*)(\boldsymbol{e}_-\cdot\boldsymbol{R}) + (e_0\cdot\boldsymbol{e}_0^*)(\boldsymbol{e}_0\cdot\boldsymbol{R})\\ &= \boldsymbol{e}_0\cdot\boldsymbol{R}\\ &= \langle f|e_z\cdot\hat{\boldsymbol{r}}|i\rangle\\ &= \langle f|\hat{z}|i\rangle\end{aligned}$$

11. Calculation of the matrix element using the Wigner-Eckert theorem

Suppose that

$$\langle \boldsymbol{r}|f\rangle = \langle \boldsymbol{r}|n'l'm'\rangle = R_{n'l'}(r)Y_{l'}^{m'}(\theta,\phi),$$

$$\langle \boldsymbol{r}|i\rangle = \langle \boldsymbol{r}|nlm\rangle = R_{nl}(r)Y_l^m(\theta,\phi)$$

Then we have the matrix element as

$$\begin{aligned}\langle f|\boldsymbol{\varepsilon}\cdot\hat{\boldsymbol{r}}|i\rangle &= \int d\boldsymbol{r}R_{n'l'}{}^*(r)Y_{l'}^{m'^*}(\theta,\phi)(\boldsymbol{\varepsilon}\cdot\boldsymbol{r})R_{nl}(r)Y_l^m(\theta,\phi)\\ &= \int d\boldsymbol{r}R_{n'l'}{}^*(r)Y_{l'}^{m'^*}(\theta,\phi)r(\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_r)R_{nl}(r)Y_l^m(\theta,\phi)\\ &= \int_0^\infty r^3drR_{n'l'}{}^*(r)R_{nl}(r)\int d\Omega Y_{l'}^{m'^*}(\theta,\phi)r(\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_r)Y_l^m(\theta,\phi)\end{aligned}$$

where $\qquad \boldsymbol{r} = r\boldsymbol{e}_r$.

We now evaluate the matrix element

$$\int d\Omega Y_{l'}^{m'^*}(\theta,\phi)r(\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_r)Y_l^m(\theta,\phi) = \frac{1}{r}\langle l',m'|\boldsymbol{\varepsilon}\cdot\hat{\boldsymbol{r}}|l,m\rangle .$$

We note that

$$\begin{aligned}\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_r &= (\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_0{}^*)(\boldsymbol{e}_0\cdot\boldsymbol{e}_r)+(\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_+{}^*)(\boldsymbol{e}_+\cdot\boldsymbol{e}_r)+(\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_-{}^*)(\boldsymbol{e}_-\cdot\boldsymbol{e}_r)\\ &= \varepsilon_z(\boldsymbol{e}_0\cdot\boldsymbol{e}_r)+\frac{-\varepsilon_x+i\varepsilon_y}{\sqrt{2}}(\boldsymbol{e}_+\cdot\boldsymbol{e}_r)+\frac{\varepsilon_x+i\varepsilon_y}{\sqrt{2}}(\boldsymbol{e}_-\cdot\boldsymbol{e}_r)\\ &= \frac{1}{r}\sqrt{\frac{4\pi}{3}}[\varepsilon_z rY_1^0(\theta,\phi)+\frac{-\varepsilon_x+i\varepsilon_y}{\sqrt{2}}rY_1^1(\theta,\phi)+\frac{\varepsilon_x+i\varepsilon_y}{\sqrt{2}}rY_1^{-1}(\theta,\phi)]\end{aligned}$$

where

$$\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_+{}^* = -\boldsymbol{\varepsilon}\cdot(\frac{\boldsymbol{e}_x-i\boldsymbol{e}_y}{\sqrt{2}}) = \frac{-\varepsilon_x+i\varepsilon_y}{\sqrt{2}},$$

$$\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_-{}^* = \boldsymbol{\varepsilon}\cdot(\frac{\boldsymbol{e}_x+i\boldsymbol{e}_y}{\sqrt{2}}) = \frac{\varepsilon_x+i\varepsilon_y}{\sqrt{2}},$$

$$\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_z = \varepsilon_z,$$

and

$$\boldsymbol{e}_+\cdot\boldsymbol{e}_r = \frac{1}{r}(-\frac{x+iy}{\sqrt{2}}) = \frac{1}{r}(-\frac{e^{i\phi}\sin\theta}{\sqrt{2}}) = \frac{1}{r}\sqrt{\frac{4\pi}{3}}Y_1^1(\theta,\phi),$$

$$\boldsymbol{e}_- \cdot \boldsymbol{e}_r = \frac{1}{r}(\frac{x-iy}{\sqrt{2}}) = \frac{e^{-i\phi}\sin\theta}{\sqrt{2}} = \sqrt{\frac{4\pi}{3}} Y_1^{-1}(\theta,\phi),$$

$$\boldsymbol{e}_0 \cdot \boldsymbol{e}_r = \frac{z}{r} = \cos\theta = \sqrt{\frac{4\pi}{3}} Y_1^{0}(\theta,\phi).$$

or

$$Y_1^1(\theta,\phi) = \sqrt{\frac{3}{4\pi}}(-\frac{e^{i\phi}\sin\theta}{\sqrt{2}}) = \sqrt{\frac{3}{4\pi}}(-\frac{x+iy}{\sqrt{2}r}),$$

$$Y_1^{-1}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}(\frac{e^{-i\phi}\sin\theta}{\sqrt{2}}) = \sqrt{\frac{3}{4\pi}}(\frac{x-iy}{\sqrt{2}r}),$$

$$Y_1^0(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta = \sqrt{\frac{3}{4\pi}}\frac{z}{r}.$$

Using the above notations, we have

$$\begin{aligned}
\int d\Omega Y_{l'}^{m'^*}(\theta,\phi) r(\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_r) Y_l^m(\theta,\phi) &= \sqrt{\frac{4\pi}{3}}\int d\Omega Y_{l'}^{m'^*}(\theta,\phi) \\
&\quad [\varepsilon_z Y_1^0(\theta,\phi) + \frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}} Y_1^1(\theta,\phi) + \frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}} Y_1^{-1}(\theta,\phi)] Y_l^m(\theta,\phi) \\
&= \sqrt{\frac{4\pi}{3}}\int d\Omega Y_{l'}^{m'^*}(\theta,\phi) \\
&\quad [(\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_z) Y_1^0(\theta,\phi) + (\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_+^*) Y_1^1(\theta,\phi) + (\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_-^*) Y_1^{-1}(\theta,\phi)] Y_l^m(\theta,\phi)
\end{aligned}$$

The selection rule for the electric dipole moment is determined

$$\int d\Omega Y_{l'}^{m'^*}(\theta,\phi) Y_1^q(\theta,\phi) Y_l^m(\theta,\phi)$$

where q= 1, 0, -1. This matrix can be rewritten in the form (the Wigner-Eckart theorem),

$$\langle n'l'm'|T_q^{(1)}|nlm\rangle$$

where $T_q^{(1)}$ is the spherical tensor of rank-1,

$$T_q^{(1)} = Y_1^q .$$

with

$$T_1^{(1)} = -\frac{\hat{x} + i\hat{y}}{\sqrt{2}} ,$$

$$T_1^{(0)} = \hat{z}$$

$$T_{-1}^{(0)} = \frac{x - iy}{\sqrt{2}}$$

(a) Wigner-Eckart theorem

According to the Wigner-Eckart theorem, we have the selection rule

$$\langle n', l', m' | \hat{T}_q^{(1)} | n, l, m \rangle \neq 0 \text{ for } m' = m + q \text{ and for } l' = l + 1, l, |l - 1|.$$

(b) The parity

$$\hat{\pi} \hat{T}_q^{(1)} \hat{\pi} = -\hat{T}_q^{(1)} , \qquad \text{(odd parity)}$$

$$\hat{\pi} |n'l'm'\rangle = (-1)^{l'} |n'l'm'\rangle . \qquad \hat{\pi} |nlm\rangle = (-1)^{l} |nlm\rangle$$

Thus only the transition is allowed only for

$$l' - l = \text{odd integer}$$

In the case of electric dipole transitions, the final and initial states must have different parities. As a result, the electric dipole transitions like $1s \rightarrow 2s$, $2p \rightarrow 3p$, and so on are forbidden, while the transitions like $1s \rightarrow 2p$, $2p \rightarrow 3s$, and so on are allowed.

((**Conclusion**))

$$\langle n', l', m' | \hat{x} + i\hat{y} | n, l, m \rangle \neq 0 \qquad \text{for } m' = m + 1 ,$$

$$\langle n', l', m' | \hat{x} - i\hat{y} | n, l, m \rangle \neq 0 \qquad \text{for } m' = m - 1 ,$$

$$\langle n',l',m'|\hat{x}-i\hat{y}|n,l,m\rangle \neq 0.$$

12. Selection rule for the transition

The matrix element:

$$I = \frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}}\langle n',l',m'|\hat{T}_1^{(1)}|n,l,m\rangle + \varepsilon_z\langle n',l',m'|\hat{T}_0^{(1)}|n,l,m\rangle$$
$$+\frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}}\langle n',l',m'|\hat{T}_{-1}^{(1)}|n,l,m\rangle$$
$$= \boldsymbol{\varepsilon}\cdot\boldsymbol{e}_+^*\langle n',l',m'|\hat{T}_1^{(1)}|n,l,m\rangle + \boldsymbol{\varepsilon}\cdot\boldsymbol{e}_z\langle n',l',m'|\hat{T}_0^{(1)}|n,l,m\rangle$$
$$+\boldsymbol{\varepsilon}\cdot\boldsymbol{e}_-^*\langle n',l',m'|\hat{T}_{-1}^{(1)}|n,l,m\rangle$$

(a) For the right-hand circularly polarized wave,

$\boldsymbol{\varepsilon} = \boldsymbol{e}_+$ (RHC photon)

$$I = \boldsymbol{e}_+\cdot\boldsymbol{e}_+^*\langle n',l',m'|\hat{T}_1^{(1)}|n,l,m\rangle + \boldsymbol{e}_+\cdot\boldsymbol{e}_z\langle n',l',m'|\hat{T}_0^{(1)}|n,l,m\rangle + \boldsymbol{e}_+\cdot\boldsymbol{e}_-^*\langle n',l',m'|\hat{T}_{-1}^{(1)}|n,l,m\rangle$$
$$= \langle n',l',m'|\hat{T}_1^{(1)}|n,l,m\rangle$$

The selection rule is $m' = m+1$.

(b) For the left-hand circularly polarized wave

$\boldsymbol{\varepsilon} = \boldsymbol{e}_-$ (LHC photon)

$$I = \boldsymbol{e}_-\cdot\boldsymbol{e}_+^*\langle n',l',m'|\hat{T}_1^{(1)}|n,l,m\rangle + \boldsymbol{e}_-\cdot\boldsymbol{e}_z\langle n',l',m'|\hat{T}_0^{(1)}|n,l,m\rangle + \boldsymbol{e}_-\cdot\boldsymbol{e}_-^*\langle n',l',m'|\hat{T}_{-1}^{(1)}|n,l,m\rangle$$
$$= \langle n',l',m'|\hat{T}_{-1}^{(1)}|n,l,m\rangle$$

The selection rule is $m' = m-1$.

(c) For the linearly polarized wave

$\boldsymbol{\varepsilon} = \boldsymbol{e}_z$

$$I = \boldsymbol{e}_z \cdot \boldsymbol{e}_+^* \langle n',l',m' | \hat{T}_1^{(1)} | n,l,m \rangle + \boldsymbol{e}_z \cdot \boldsymbol{e}_z \langle n',l',m' | \hat{T}_0^{(1)} | n,l,m \rangle + \boldsymbol{e}_z \cdot \boldsymbol{e}_-^* \langle n',l',m' | \hat{T}_{-1}^{(1)} | n,l,m \rangle$$
$$= \langle n',l',m' | \hat{T}_0^{(1)} | n,l,m \rangle$$

The selection rule is $m' = m$.

12. Formula for the spontaneous emission (electric dipole, magnetic dipole, and electric quadrupole)

The constant A for the spontaneous emission is given by

$$\frac{4\pi^2 e^2}{Vm^2\omega_0} \int d\omega \delta(\omega_0 - \omega) \frac{V\omega^2}{(2\pi)^3 c^3 \hbar} d\Omega \sum_s \left| \langle f | [(\boldsymbol{\varepsilon}(\boldsymbol{k},s) \cdot \hat{\boldsymbol{p}} + i(\boldsymbol{k}\cdot\boldsymbol{r})(\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}})] | i \rangle \right|^2$$
$$= \frac{4\pi^2 e^2}{Vm^2\omega_0} \int d\omega \delta(\omega_0 - \omega) \frac{V\omega^2}{(2\pi)^3 c^3 \hbar} d\Omega$$
$$\times \sum_s \left| \langle f | (\boldsymbol{\varepsilon}(\boldsymbol{k},s) \cdot \hat{\boldsymbol{p}} + i \frac{(\boldsymbol{k}\cdot\hat{\boldsymbol{r}})(\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}}) - (\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}})(i\boldsymbol{k}\cdot\hat{\boldsymbol{p}})}{2} + i \frac{(\boldsymbol{k}\cdot\hat{\boldsymbol{r}})(\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}}) + (\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}})(i\boldsymbol{k}\cdot\hat{\boldsymbol{p}})}{2} | i \rangle \right|^2$$

(a) Electric dipole contribution

$$A_{ed} = \frac{4\pi^2 e^2}{Vm^2\omega_0} \int d\omega \delta(\omega_0 - \omega) \frac{V\omega^2}{(2\pi)^3 c^3 \hbar} d\Omega \sum_s \left| \langle f | (\boldsymbol{\varepsilon}(\boldsymbol{k},s) \cdot \hat{\boldsymbol{p}} | i \rangle \right|^2$$
$$= \frac{4\pi^2 e^2}{Vm^2\omega_0} \int d\omega \delta(\omega_0 - \omega) \frac{V\omega^2}{(2\pi)^3 c^3 \hbar} \frac{8\pi}{3} \left| \langle f | \hat{\boldsymbol{p}} | i \rangle \right|^2$$
$$= \frac{4\pi^2 e^2}{Vm^2\omega_0} \frac{V\omega_0^2}{(2\pi)^3 c^3 \hbar} \frac{8\pi}{3} \left| \langle f | \hat{\boldsymbol{p}} | i \rangle \right|^2$$
$$= \frac{4e^2\omega_0}{3m^2 c^3 \hbar} \left| \langle f | \hat{\boldsymbol{p}} | i \rangle \right|^2$$
$$= \frac{4e^2\omega_0^3}{3\hbar c^3} \left| \langle f | \hat{\boldsymbol{r}} | i \rangle \right|^2$$
$$= \frac{4\omega_0^3}{3\hbar c^3} \left| \langle f | e\hat{\boldsymbol{r}} | i \rangle \right|^2$$

or

$$A_{ed} = \frac{4\omega_0^3}{3\hbar c^3} \left| \langle f | e\hat{\boldsymbol{r}} | i \rangle \right|^2$$

(b) Magnetic dipole contribution

The contribution from the magnetic dipole is given by

$$A_{mag} = \frac{4\pi^2 e^2}{Vm^2\omega_0}\int d\omega\delta(\omega_0-\omega)\frac{V\omega^2}{(2\pi)^3 c^3\hbar}d\Omega\sum_s\left|\langle f|(i\frac{(\boldsymbol{k}\cdot\hat{\boldsymbol{r}})(\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}})-(\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}})(i\boldsymbol{k}\cdot\hat{\boldsymbol{p}})}{2}|i\rangle\right|^2$$

We note that

$$\begin{aligned}
\langle\boldsymbol{r}|(\boldsymbol{k}\cdot\hat{\boldsymbol{r}})(\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}})-(\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}})(\boldsymbol{k}\cdot\hat{\boldsymbol{p}})|\psi\rangle &= \frac{\hbar}{i}(\boldsymbol{k}\cdot\boldsymbol{r})[\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\nabla\psi(\boldsymbol{r})]-\frac{\hbar}{i}(\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\boldsymbol{r})[\boldsymbol{k}\cdot\nabla\psi(\boldsymbol{r})]\\
&= \frac{\hbar}{i}\{(\boldsymbol{k}\cdot\boldsymbol{r})[\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\nabla\psi(\boldsymbol{r})]-[\boldsymbol{k}\cdot\nabla\psi(\boldsymbol{r})](\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\boldsymbol{r})\}\\
&= \frac{\hbar}{i}(\boldsymbol{k}\times\boldsymbol{\varepsilon}(\boldsymbol{k},s))[\boldsymbol{r}\times\nabla\psi(\boldsymbol{r})]\\
&= (\boldsymbol{k}\times\boldsymbol{\varepsilon}(\boldsymbol{k},s))\langle\boldsymbol{r}|\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}}|\psi\rangle\\
&= (\boldsymbol{k}\times\boldsymbol{\varepsilon}(\boldsymbol{k},s))\langle\boldsymbol{r}|\hat{\boldsymbol{L}}|\psi\rangle
\end{aligned}$$

The orbital magnetic moment is defined by

$$\boldsymbol{\mu}_L = -\frac{\mu_B}{\hbar}\boldsymbol{L} = -\frac{e}{2mc}\boldsymbol{L}$$

leading to

$$\langle\boldsymbol{r}|(\boldsymbol{k}\cdot\hat{\boldsymbol{r}})(\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}})-(\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}})(\boldsymbol{k}\cdot\hat{\boldsymbol{p}})|\psi\rangle = (\boldsymbol{k}\times\boldsymbol{\varepsilon}(\boldsymbol{k},s))(-\frac{2mc}{e})\langle\boldsymbol{r}|\hat{\boldsymbol{\mu}}|\psi\rangle$$

or

$$(\boldsymbol{k}\cdot\hat{\boldsymbol{r}})(\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{p}})-(\boldsymbol{\varepsilon}(\boldsymbol{k},s)\cdot\hat{\boldsymbol{r}})(\boldsymbol{k}\cdot\hat{\boldsymbol{p}}) = -\frac{2mc}{e}(\boldsymbol{k}\times\boldsymbol{\varepsilon}(\boldsymbol{k},s))\hat{\boldsymbol{\mu}}\,,$$

Thus we have

$$
\begin{aligned}
A_{mag} &= \frac{4\pi^2 e^2}{Vm^2\omega_0}\int d\omega\delta(\omega_0-\omega)\frac{V\omega^2}{(2\pi)^3 c^3\hbar}d\Omega\sum_s\left|\langle f|-\frac{imc}{e}(\boldsymbol{k}\times\boldsymbol{\varepsilon}(\boldsymbol{k},s))\hat{\boldsymbol{\mu}}|i\rangle\right|^2 \\
&= \frac{4\pi^2 e^2}{Vm^2\omega_0}\int d\omega\delta(\omega_0-\omega)\frac{V\omega^2}{(2\pi)^3 c^3\hbar}\frac{m^2c^2}{e^2}\frac{\omega^2}{c^2}d\Omega\sum_s\left|\langle f|(\boldsymbol{e}_z\times\boldsymbol{\varepsilon}(\boldsymbol{k},s))\hat{\boldsymbol{\mu}}|i\rangle\right|^2 \\
&= \frac{4\pi^2 e^2}{Vm^2\omega_0}\frac{V\omega_0^{\ 2}}{(2\pi)^3 c^3\hbar}\frac{m^2c^2}{e^2}\frac{\omega_0^{\ 3}}{c^2}\frac{8\pi}{3}\left|\langle f|\hat{\boldsymbol{\mu}}|i\rangle\right|^2 \\
&= \frac{4\omega_0^{\ 3}}{3\hbar c^3}\left|\langle f|\hat{\boldsymbol{\mu}}|i\rangle\right|^2
\end{aligned}
$$

or

$$
A_{mag} = \frac{4\omega_0^{\ 3}}{3\hbar c^3}\left|\langle f|\hat{\boldsymbol{\mu}}|i\rangle\right|^2
$$

(c) Electric quadrupole contribution

The contribution from the electric quadrupole is given by

$$
A_{eq} = \frac{4\pi^2 e^2}{Vm^2\omega_0}\int d\omega\delta(\omega_0-\omega)\frac{V\omega^2}{(2\pi)^3 c^3\hbar}d\Omega\sum_s\left|\langle f|(i\frac{(\boldsymbol{k}\cdot\hat{\boldsymbol{r}})(\boldsymbol{\varepsilon}\cdot\hat{\boldsymbol{p}})+(\boldsymbol{\varepsilon}\cdot\hat{\boldsymbol{r}})(i\boldsymbol{k}\cdot\hat{\boldsymbol{p}})}{2}|i\rangle\right|^2
$$

Note that

$$
\begin{aligned}
\langle f|(\boldsymbol{k}\cdot\hat{\boldsymbol{r}})(\boldsymbol{\varepsilon}\cdot\hat{\boldsymbol{p}})+(\boldsymbol{\varepsilon}\cdot\hat{\boldsymbol{r}})(\boldsymbol{k}\cdot\hat{\boldsymbol{p}})|i\rangle &= i\frac{m}{\hbar}\sum_{i,j}\varepsilon_i k_j\langle f|[\hat{H}_0,\hat{x}_i\hat{x}_i]|i\rangle \\
&= im\sum_{i,j}\varepsilon_i k_j\omega_{fi}\langle f|\hat{x}_i\hat{x}_j|i\rangle
\end{aligned}
$$

where

$$
[\hat{H}_0,\hat{x}_i\hat{x}_j] = \hat{x}_j[\hat{H}_0,\hat{x}_i]+[\hat{H}_0,\hat{x}_j]\hat{x}_i\,.
$$

and

$$
\langle f|[\hat{H}_0,\hat{x}_i\hat{x}_j]|i\rangle = (E_f-E_i)\langle f|\hat{x}_i\hat{x}_j|i\rangle = \hbar\omega_{fi}\langle f|\hat{x}_i\hat{x}_j|i\rangle,
$$

We note that the electric quadrupole moment is defined as

$$\hat{Q}_{ij} = q(\hat{x}_i \hat{x}_j - \frac{1}{3}|\hat{\boldsymbol{r}}|^2 \delta_{i,j}), \qquad (1)$$

where $q = -e$ ($e>0$) for the electron. The extra term proportional to $\delta_{i,j}$ in Eq.(1) does not matter because it gets multiplied by $\varepsilon_i k_j$ giving $\boldsymbol{\varepsilon} \cdot \boldsymbol{k}$ which is zero. We interpret this as an electric quadrupole transition. Its transition probability is of the same order of magnitude as the one from the magnetic dipole moment and much smaller than the transition probability from the electric dipole moment.

Thus we have

$$A_{eq} = \frac{4\pi^2 e^2}{Vm^2\omega_0} \int d\omega \delta(\omega_0 - \omega) \frac{V\omega^2}{(2\pi)^3 c^3 \hbar} \frac{\omega^2 m^2}{4} d\Omega \sum_s \left| \sum_{i,j} \varepsilon_i k_j \langle f | \hat{x}_i \hat{x}_j | i \rangle \right|^2$$

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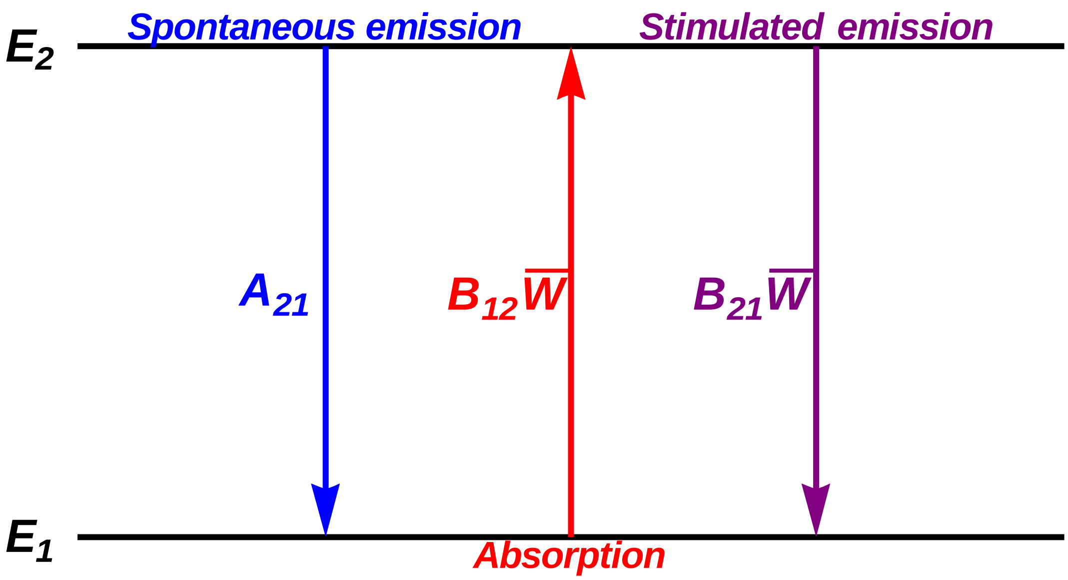
APPENDIX *Einstein A-B co-efficient*

Einstein coefficients (A and B) are mathematical quantities which are a measure of the probability of absorption or emission of light by an atom or molecule. The Einstein A coefficient is related to the rate of spontaneous emission of light and the Einstein B coefficients are related to the absorption and stimulated emission of light.

Here we discuss the transition rate for the two-level system. The absorption and emission of photons occur due to the transition between two levels. According to Einstein, we set up the rate equations for N_1 and N_2



$$\begin{cases} \dfrac{dN_1}{dt} = A_{21}N_2 - N_1B_{12}\overline{W}(\omega) + N_2B_{21}\overline{W}(\omega) \\ \dfrac{dN_2}{dt} = -A_{21}N_2 + N_1B_{12}\overline{W}(\omega) - N_2B_{21}\overline{W}(\omega) \end{cases}$$

where N_1 and N_2 are the number of occupancy for the level 1 and level 2. Note that the spontaneous emission is independent of $\overline{W}(\omega)$. In the case of thermal equilibrium, we have

$$\frac{dN_1}{dt} = \frac{dN_2}{dt} = 0,$$

or

$$N_2A_{21} - N_1B_{12}\overline{W}(\omega) + N_2B_{21}\overline{W}(\omega) = 0.$$

For thermal equilibrium with no external radiation introduced into the cavity

$$\overline{W}(\omega) = \overline{W_T}(\omega)$$

with

$$\overline{W_T}(\omega) = \frac{A_{21}}{\dfrac{N_1}{N_2}B_{12} - B_{21}}.$$

The level populations N_1 and N_2 are related in thermal equilibrium by Boltzman's law

$$\frac{N_1}{N_2} = \frac{e^{-\beta E_1}}{e^{-\beta E_2}} = \exp(\beta\hbar\omega), \qquad (\beta = 1/k_B T)$$

Then

$$\overline{W}_T(\omega) = \frac{A_{21}}{B_{12}e^{\beta\hbar\omega} - B_{21}} = \frac{\dfrac{A_{21}}{B_{21}}}{e^{\beta\hbar\omega} - \dfrac{B_{21}}{B_{12}}},$$

which is compared with the Planck's law,

$$\overline{W}_T(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\beta\hbar\omega} - 1},$$

with

$$\begin{cases} B_{12} = B_{21} \\ \dfrac{A_{21}}{B_{12}} = \dfrac{\hbar\omega^3}{\pi^2 c^3} \end{cases}$$

$$\overline{W}_T(\omega) = \frac{A_{21}}{B_{12}}\overline{n},$$

The energy density in thermal equilibrium between ω and $\omega + d\omega$ is given by $\overline{W}_T(\omega)d\omega$. We know that the Planck's law for the radiative energy density is given by

$$\overline{n} = \frac{1}{e^{\beta\hbar\omega} - 1}.$$

We note that A_{21} can be evaluated from the quantum mechanics,

$$A_{21} = \frac{4e^2\omega^2}{3\hbar c^3}\left|\langle f|\hat{r}|i\rangle\right|^2 = \frac{4\alpha\omega^2}{3c^2}\left|\langle f|\hat{r}|i\rangle\right|^2, \qquad \text{(derived from the quantum mechanics)}$$

We also note that

$$\frac{A_{21}}{B_{12}} = \frac{\hbar\omega_0^{\ 3}}{\pi^2 c^3}. \qquad \text{(Einstein } A\text{-}B \text{ coefficient relation}$$

where

$$\Delta E = E_2 - E_1 = \hbar\omega = h\nu.$$

((**Note**)) **The expression for $\overline{W}(\nu)$**

Since

$$\overline{W}(\omega)d\omega = \overline{W}(\nu)d\nu$$

we have

$$2\pi\overline{W}(\omega)d\nu = \overline{W}(\nu)d\nu\,,$$

or

$$\overline{W}(\nu) = 2\pi\overline{W}(\omega) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\beta h\nu}-1},$$

where

$$\frac{\hbar\omega^3}{\pi^2c^3} = \frac{\frac{h}{2\pi}(2\pi\nu)^3}{\pi^2c^3} = \frac{1}{2\pi}\frac{8\pi h\nu^3}{c^3}\,.$$
