What sets $\Gamma$ (spontaneous decay rate)?

Einstein's argument - determination of Einstein A + B coefficients.

For a simple 2-level system, we can have 3 processes occur (6 first order):

\[ B_{21} : \text{stimulated absorption} \]
\[ B_{21} : \text{stimulated emission} \]
\[ A_{21} : \text{spontaneous emission} \]

How are the rates of these 3 processes related?

w/ no "applied" radiation, we have simply $A_{21}$

\[ N_e = -A_{21} N_e = -N_e/\tau \]
\[ N_g = +A_{21} N_e \]

w/ applied radiation, having energy density $p(\omega) \Theta \omega g$, we have

\[ N_e = B_{12} N_g p(\omega g) - B_{21} N_e p(\omega g) - A_{21} N_e \]
\[ N_g = -N_e \]
Einstein's idea - assume our 2-level system is in a thermal blackbody environment w/ temp. $T$.

(2 expressions for equilibrium)

**First**, find $N_g = N_e = 0$ condition

$$\psi(w) = \frac{\hbar \omega^3}{\pi c^3} \frac{1}{e^{\frac{\hbar \omega}{kT}} - 1}$$

$$\Rightarrow \text{leads to condition } \psi(w) = \frac{A_{21}}{B_{21}} \frac{1}{(\frac{N_g}{N_e})(\frac{B_{22}}{B_{21}})} - 1$$

**Second**, apply Boltzmann

$$\frac{N_e}{g_e} = \frac{N_g}{g_g} e^{-\frac{\hbar \omega}{kT}}$$

degeneracy factor

Combining yields

$$B_{12} = \frac{g_e}{g_g} B_{21}$$

and

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

This result is general, depends only on the 2-level system and not the radiation field.
Finally, getting the magnitude of $\Gamma$ (see Foot Sec. 7.2)

$$S_\omega = e E_0 \frac{\langle e \hat{r} \cdot \hat{E} \rangle}{t}$$

let $\text{Deg} = \langle e \hat{r} \rangle$ (typically ~ few)

where $\left| \frac{\langle e(\hat{r} \cdot \hat{E}) \rangle}{\langle e \hat{r} \rangle} \right|^2 = \frac{1}{3}$

for random polarization

Assuming spectral function

$$p(\omega) \omega \, d\omega = \frac{E_0^2}{2}$$

Can relate excitation rate as

$$B_{12} = \frac{e^2}{\varepsilon_0 \hbar^2} \frac{\pi}{3} |\text{Deg}|^2 = B_{21} \frac{g_e}{g_j}$$

$$A_{21} = \frac{g_j}{g_e} \frac{\pi e^2}{3 \varepsilon_0 \hbar^2} \frac{t \omega^3}{\pi^2 c^2} |\text{Deg}|^2 = \frac{g_j}{g_e} \frac{4 \alpha}{3} \omega^3 \frac{\hbar^2}{c^3}$$

$$A_{21} = \frac{g_j}{g_e} \frac{e^2 \omega^3}{3 \pi \varepsilon_0 \hbar^2 c^2} |\text{Deg}|^2$$

Key:
- $\omega^3$ scaling
- overlap integral
- dipole moments
- element
What sets the value of $\Gamma$? Another argument tied to dissipation

[Roland/Unser/Weisskopf theory]

\[ t = 0 \]

\[
\begin{array}{c}
\text{atom} \\
\text{--|--} \quad \text{time} \quad \text{w/ "environment"} \\
\text{--|--} \\
\text{lq}
\end{array}
\]

devolved of photons

\[ |\Psi(t=0)\rangle = |lq \rangle \otimes |\text{Vac}\rangle \]

Let's assume that the atom can decay and emit a photon at freq. \( \omega \) [note: \( \omega \) does not have to equal \( \omega_g \)] with polarization \( \vec{E} \) along some direction \( \hat{K} = \frac{\vec{K}}{|\vec{K}|} \). Let's denote the photon state by \( S = (\omega, \hat{K}, \vec{E}) \). The decay for a specific state \( |lq\rangle \otimes |1s\rangle \) has a probability \( C_{ls}(t) \) at time \( t \).

We can express the state of the total system [atom + env.] as

\[
|\Psi(t)\rangle = \sum_{S} C_{ls} \ e^{-i(\omega_{ls} - \frac{\omega}{2})t} \ |lq; 1s\rangle + C_{0} \ e^{i\omega_{0} t} \ |l0, 0\rangle
\]

To describe how \( C_{ls}(t) \) grows over time, we need some description of the light-matter interaction. The right way to do this is by quantizing the field, etc.
We'll instead assume some semi-classical coupling of the form

\[
\begin{align*}
\dot{C}_{gs} &= -i \epsilon_0 \Delta S e^{i(w-w_0)t} \quad (1) \\
\text{and} \quad \epsilon_0 &= i \frac{\Delta S}{S} C_{gs} S \quad (2)
\end{align*}
\]

Here, \( \Delta S \) is the vacuum Rabi frequency associated with zero point energy in the field.

Let \(-\Delta S = -\mathbf{d} \cdot \mathbf{E}_w\), with \( \mathbf{d} = e \langle \mathbf{e}_1 \mathbf{e}_2 \rangle \)

and \( \mathbf{E}_w = \sqrt{\frac{k w}{2 \epsilon_0 V}} \mathbf{E} \)

\( V \) is the volume of space (necessary for quantization, will drop out). The total energy of the vacuum field at freq. \( w \) is \( \frac{\epsilon_0}{2} \) for a given mode.

Solving for \( \epsilon_0(t) \) by integration and substitution gives

\[
\epsilon_0(t) = -\frac{\Delta S}{S} |S|^2 \int_0^t e^{-i(w-w_0)(t-t')} \epsilon_0(t') \, dt'
\]

This relates to an exponential decay, where rate will depend on \( \Delta S \) and how many modes we couple to.
Counting modes \( S = (w, \hat{k}, \hat{e}) \) \[\text{[sum \to integral]}\]

Cube of volume \( V = L \times L \times L \)

\( \hat{k}_x = \frac{2\pi n_x}{L} \quad w/ \quad \sigma = \chi y, z \)

\( dn_\sigma = \left( \frac{L}{2\pi} \right) dK_x \quad \text{and} \quad dn = \left( \frac{L}{2\pi} \right)^3 d^3K \)

\( \omega = cK \)

Switching to \( \omega \) and spherical coordinates, we get

\( dn = 2 \times \frac{V}{8\pi^3 c^3} \quad w^2 \sin \theta \quad dw \quad d\theta \quad d\phi \)

Due to 2 polarizations for every \( \hat{k} \)

\( C_{eo}(\theta) = \mathcal{F}_{eo} \left( \frac{e^{\frac{i}{2}}}{2\varepsilon_0 c}\frac{x}{4\pi^2 c^3} w^2 \right) \quad dw \quad \int_{0}^{\pi} \left( \int_{0}^{2\pi} \frac{d^3q}{4\pi^2 c^3} \right) \int_{0}^{t} C_{eo}(\theta') e^{-i(w-w')c(t-t')} \quad dt' \)

\[\frac{4\pi e^2 k_e |\Delta g|^2}{3} \quad \text{--- random polarization}\]

\( C_{eo}(\theta) = -\frac{e^2}{6\pi^2 \varepsilon_0 c^3} \int_{0}^{t} \omega^2 dw \quad \int_{0}^{t} C_{eo}(\theta') e^{-i(w-w')c(t-t')} \quad dt' \)

Some simple assumptions (\( \Delta g \) roughly independent of frequency near \( w' \), etc.) gives \( C_{eo}(\theta) = -\frac{\Gamma}{2} C_{eo}(\theta) \quad w/ \quad \Gamma = \frac{e^2 |\Delta g|^2 \omega^3}{3\pi \varepsilon_0 c^3} \)
Recall our Optical Bloch Equations (OBEs) for excited state decay.

Start with a coupled 2-level system in interaction picture with \( H_0 = h \omega \delta \).

Redefine
\[
\tilde{c}_g = c_g e^{i \delta t/2}, \quad \tilde{c}_e = e^{-i \delta t/2} c_e
\]

With \( \delta = \omega - \omega_0 \)
\[
\tilde{P}_{gg} = P_{gg}, \quad \tilde{P}_{ge} = e^{-i \delta} P_{ge}, \quad \tilde{P}_{ee} = P_{ee}, \quad \tilde{P}_{eg} = e^{i \delta} P_{eg}
\]

Include loss \( \rightarrow \) replace
\[
\tilde{c}_e = \ldots - \frac{1}{2} \frac{P_{ge}}{C_{pe}}
\]

Equivalently
\[
T_2 = 2 T_1, \quad T_1 = \frac{1}{\Gamma}
\]

Or
\[
\dot{U} = \delta U - \frac{P_{ge}}{2} U
\]
\[
\dot{V} = - \delta U + \omega W - \frac{P_{ge}}{2} V
\]
\[
\dot{W} = - \delta V - \Gamma (W - 1)
\]

With
\[
U = \tilde{P}_{eg} + \tilde{P}_{ge}, \quad V = i (\tilde{P}_{eg} - \tilde{P}_{ge}), \quad W = (\tilde{P}_{ee} - \tilde{P}_{gg})
\]

\[
\begin{cases}
\dot{P}_{gg} = \Gamma P_{ee} + \frac{i}{2} \left( \Lambda^2 \tilde{P}_{eg} - \Lambda^2 \tilde{P}_{ge} \right) \\
\dot{P}_{ee} = - \Gamma P_{ee} + \frac{i}{2} \left( \Omega \tilde{P}_{ge} - \Omega \tilde{P}_{eg} \right) \\
\dot{P}_{ge} = - (\frac{\Gamma}{2} + i \delta) P_{ge} + \frac{i}{2} \Lambda^2 P_{ee} - \frac{i}{2} \Lambda P_{gg} \\
\dot{P}_{eg} = - (\frac{\Gamma}{2} - i \delta) P_{eg} - \frac{i}{2} \Lambda P_{ee} - \frac{i}{2} \Lambda P_{gg}
\end{cases}
\]
$\Sigma, \Gamma$ processes are fast generally.

Typically observe "long-time" equilibrium conditions

set $u = v = w = 0$

\[
\begin{pmatrix}
U \\
V \\
W
\end{pmatrix} = \frac{1}{\delta^2 + \frac{\omega_r^2}{2} + \frac{p_r^2}{4}} \begin{pmatrix}
-\omega & 0 & 0 \\
0 & -\omega & 0 \\
0 & 0 & -\delta - \frac{\omega_r^2}{2} + \frac{p_r^2}{4}
\end{pmatrix}
\]

recall $\text{Pee} = \frac{1 + W}{2}$

\[
\text{Pee} = \frac{1}{2} \left[ 1 - \frac{\delta^2 + \frac{p_r^2}{4}}{\delta^2 + \frac{\omega_r^2}{2} + \frac{p_r^2}{4}} \right] = \frac{1}{2} \frac{S}{1 + S + \gamma \frac{\delta^2}{p_r^2}}
\]

let

\[
S = \frac{2 \omega^2}{p_r^2} = \frac{I}{I_{\text{sat}}}
\]

saturation parameter

if $I = \frac{E_0}{2} \frac{1}{E_0^2}$

\[
I_{\text{sat}} = \frac{\hbar c \pi}{3 \lambda^2} \frac{E_0^2}{p_r^2}
\]

typically

few mW/cm$^2$ for alkalis

rate of spontaneous emission $\Rightarrow \Gamma \text{ Pee} = R$

(saturation)

in strong-driving limit ($\omega >> p, \delta >> 1$) with $\delta = 0$,

$R \rightarrow \Gamma/2$

$\text{Pee} \rightarrow \frac{1}{2}$

at long times, atoms spend at most half their time in the excited state.
A typical observable, rate of spontaneous emission.

How is this affected by properties of the light?

\[ R = \frac{\Gamma}{2} \frac{s}{1 + s + \frac{4s^2}{\Gamma^2}} \quad \text{w/} \quad s = \frac{2 \delta^2}{\Gamma^2} \]

\[ R = \frac{\Gamma}{2} s \times \frac{\Gamma^2/4}{\left(\frac{\Gamma^2}{4}\right)(1 + s) + \delta^2} \]

For low \( s \):

- Lorentzian line shape

For large \( s \):

- Still Lorentzian

Qualitatively:

- Gets broader with large \( s \)

Rate of excitation/fluorescence is saturated (by large \( s \)) near resonance; less saturation for large \( \delta \).
What about absorption?

incident beam

$N = \# \text{density}$

$n \, dz = \frac{\# \text{atoms}}{\text{area}}$

no $dz \sim$ fraction of surface covered by atoms

We know the scattered power per unit volume will be

$\frac{\dot{E}}{V} = \frac{N \bar{E}_0}{V} = \frac{kwRn}{2}$

Using $I_{sat} = \frac{hc\pi}{3\lambda^2} = \frac{hc\pi}{3\lambda^2} P$

$\delta = 0$

we can combine $1$ and $2$ to get

$\sigma (\omega = \omega_0) = \frac{3\lambda^2}{2\pi} \approx \frac{\lambda^2}{2}$

$\sigma (\omega) = \frac{3\lambda^2}{2\pi} \frac{1}{1 + 48\frac{\lambda^2}{P}}$

Valid for 2-level system


For multi-level systems, there are some subtleties w.r.t. light polarization, level structure, etc. (see Foot 7.6)

but more generally

\[
\sigma(\omega) = \frac{G}{g_y} \frac{\pi c^2}{w_0^2} A_2 \frac{1}{2\pi} \frac{\Gamma}{\gamma^2 + \frac{\Gamma^2}{4}}
\]
A bit more detail on $\langle e | F, \ell | g \rangle$, or, in our case,

$$\langle F', m'_F | F, \ell | F, m_F \rangle \neq \text{depends on initial state } | F, m_F \rangle, \text{ final state } | F', m'_F \rangle$$

Let's assume polarization denoted by $g$ and polarization $\ell$.

The number $g$

where $g = 0$ corresponds to $\pi$-transitions

and $g = \pm 1$ correspond to $\sigma_{\pm}$-transitions

$$\langle F', m'_F | r_g | F, m_F \rangle = A \cdot B \cdot C \cdot D \cdot E$$

$A = (-1)^{I + L' + S + J' + J + I - m'_F}$

$$B = \sqrt{(2J+1)(2J'+1)(2F+1)(2F'+1)}$$

$$C = \left\{ \begin{array}{c} \left\{ \begin{array}{c} L' \ J' \ S \ \{ J' \ F' \ I \} \ 0 \ L \ 1 \ \{ F \ J \ 1 \} \end{array} \right\} \text{ symbols} \\ \end{array} \right\}$$

$$D = \left( \begin{array}{c} F \\ F' \\ m_F \\ q - m'_F \end{array} \right) \text{ by symbol rules for } g$$

$$E = \langle \alpha' L' | r | \alpha L \rangle = \int_0^\infty r^2 R_{\alpha' L' \ell}^* R_{\alpha \ell} \, dr \text{ reduced matrix element}$$

By expanding $| F, m_F \rangle$ states in the $| m_L, m_s, m_r \rangle$ basis, one finds

Then the $| m_L, m_s, m_r \rangle$ basis can calculate for $\pi$-dargaon. Beyond that, determines from experiment (e.g. from $\pi$).
The selection rules

\[ m_F' = m_F + q \]
\[ \Delta F = 0, \pm 1 \] ("parity rule")
\[ \Delta F = 0, \pm 1 \]

\[ \Delta F = 0, \Delta m_F = 0 \] transitions

No transitions.

The results of the dipole matrix elements are generally presented in tables, charts, diagrams. [See Stock's documents for some examples]

Just be careful about conventions (minor signs, factors of 2, square roots, etc.)