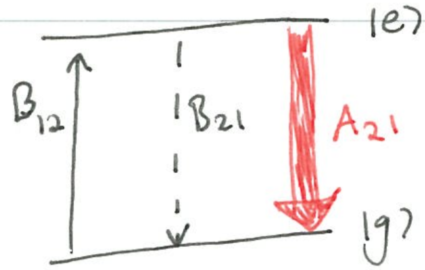
## What sets $\Gamma$ (spontaneous decay rate)?

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

For a simple 2-level system

we can have 3 processes occur (@ first order).




$B_{12}$ : (stimulated) absorption

$B_{21}$ : stimulated emission

$A_{21}$ : spontaneous emission

How are the rates of these 3 processes related?

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

$$\dot{N}_e = -A_{21} N_e = -N_e/\tau$$

$$\dot{N}_g = +A_{21} N_e$$

w/ applied radiation, having energy density $\rho(\omega)$ @ $\omega_{eg}$, we have:

$$\dot{N}_e = B_{12} N_g \rho(\omega_{eg}) - B_{21} N_e \rho(\omega_{eg}) - A_{21} N_e$$

$$\dot{N}_g = -\dot{N}_e$$

Einstein's idea - assume our 2-level system is in a thermal blackbody environment w/ temp. $T$.

2 expressions for equilibrium

* First, find $\dot{N}_g = \dot{N}_e = 0$ condition

w/ $$\rho(\omega) = \frac{\hbar\omega^3}{\pi c^3} \frac{1}{e^{\hbar\omega/KT} - 1}$$

$\Longrightarrow$ leads to condition $$\rho(\omega_{eg}) = \frac{A_{21}}{B_{21}} \frac{1}{\left(\frac{N_g}{N_e}\right)\left(\frac{B_{12}}{B_{21}}\right) - 1}$$

* Second, apply Boltzmann

$$\frac{N_e}{g_e} = \frac{N_g}{g_g} e^{-\hbar\omega_{eg}/KT}$$

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)

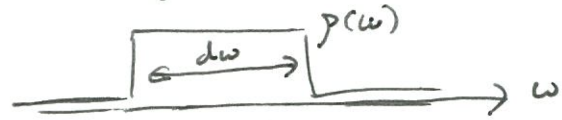
$$\text{w/ } \Omega = \frac{e E_0 \langle e | \vec{r} \cdot \hat{\varepsilon} | g \rangle}{\hbar}$$

let $D_{eg} = \langle e | \vec{r} | g \rangle$ (typically $\sim$ few $a_0$)

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

for random polarization

Assuming spectral function




$$\rho(\omega)\, d\omega = \frac{\varepsilon_0 E_0^2}{2}$$

Can relate excitation rate as

$$B_{12} = \frac{e^2}{\varepsilon_0 \hbar^2} \frac{\pi}{3} |D_{eg}|^2 = B_{21} \frac{g_e}{g_g}$$

$$A_{21} = \left(\frac{g_g}{g_e}\right) \frac{\pi e^2}{3 \varepsilon_0 \hbar^2} \frac{\hbar \omega^3}{\pi^2 c^3} |D_{eg}|^2 = \frac{g_g}{g_e} \frac{4 \alpha}{3 c^3} \omega^3 |D_{eg}|^2$$

$$A_{21} = \left(\frac{g_g}{g_e}\right) \frac{e^2 \omega^3}{3\pi \varepsilon_0 \hbar c^3} |D_{eg}|^2$$

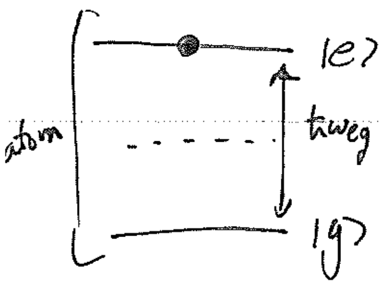
Key $\omega^3$ scaling

Key overlap integral, dipole matrix element

What sets the value of $\Gamma$?

Another argument, tied to dissipation [Metcalf / van der Straten on Wigner-Weisskopf theory]

@ $t=0$




w/ "environment" devoid of photons $\quad |\psi(t=0)\rangle = |e\rangle \otimes |vac\rangle$

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Let's assume that the atom can decay and emit a photon at freq. $\omega$ [note: $\omega$ does not have to equal $\omega_{eg}$] with polarization $\hat{\varepsilon}$ along some direction $\hat{k} = \frac{\vec{k}}{|\vec{k}|}$. Let's denote the photon state by $S = (\omega, \hat{k}, \hat{\varepsilon})$. The decay to a specific state $|g\rangle \otimes |1_s\rangle$ has a probability $c_{g1_s}(t)$ at time $t$.

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

$$|\psi(t)\rangle = \sum_S c_{g1s}\, e^{-i(\omega - \frac{\omega_{eg}}{2})t} |g;1_s\rangle + c_{e0}\, e^{-i\frac{\omega_{eg}}{2}t} |e,0\rangle$$

To describe how $c_{g1s}(t)$ grow 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 semiclassical coupling of the form

$$\dot{c}_{g1s} = -i\, c_{e0}\, \Omega_s^{*}\, e^{i(\omega-\omega_{eg})t} \qquad (1)$$

and

$$\dot{c}_{e0} = -i \sum_s c_{g1s}\, \Omega_s\, e^{-i(\omega-\omega_{eg})t} \qquad (2)$$

here, $\Omega_s$ is the vacuum Rabi frequency associated w/ zero point energy in the field.

Let $-\hbar\Omega_s = -\vec{d}\cdot\vec{E}_\omega$, w/ $\vec{d} = e\langle e|\hat{\vec{r}}|g\rangle$

and $\vec{E}_\omega = \sqrt{\dfrac{\hbar\omega}{2\varepsilon_0 V}}\,\hat{e}$

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

Solving for $c_{e0}(t)$ by integration and substitution gives

$$\dot{c}_{e0}(t) = -\sum_s |\Omega_s|^2 \int_0^t e^{-i(\omega-\omega_{eg})(t-t')}\, c_{e0}(t')\, dt'$$

This relates to an exponential decay, where rate will depend on $\Omega_s$ and how <u>many</u> modes we couple to.

Counting modes $\quad S = (\omega, \hat{k}, \hat{\epsilon}) \quad$ [sum $\rightarrow$ integral]

cube of volume $\quad V = L \times L \times L$

$$\vec{K}_\sigma = \frac{2\pi n_\sigma}{L} \quad \text{w/ } \sigma = x, y, z$$

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

$$\omega = cK$$

switching to $\omega$ and spherical coordinates, we get

$$dn = 2 \times \frac{V}{8\pi^3 c^3}\, \omega^2 \sin\theta \, d\omega \, d\theta \, d\phi$$

$\uparrow$

due to 2 polarization for every $\hat{k}$.

$$\dot{C}_{eo}(t) = -\int \frac{\hbar\omega}{2\varepsilon_0 \cancel{V}} \frac{\cancel{V}}{4\pi^3 c^3}\, \omega^2 \, d\omega \underbrace{\int_0^{2\pi}\!\!\int_0^{\pi} |e\langle e|\vec{r}\cdot\hat{\epsilon}|g\rangle|^2 \sin\theta \, d\theta \, d\phi}_{\frac{4\pi e^2 |\langle e|\vec{r}|g\rangle|^2}{3}} \int_0^t C_{eo}(t') e^{-i(\omega-\omega_{eg})(t-} d$$

$\leftarrow$ random polarization

$$\dot{C}_{eo}(t) = -\frac{e^2 |D_{eg}|^2}{6\pi^2 \varepsilon_0 \hbar c^3} \int_0^\infty \omega^3 d\omega \int_0^t C_{eo}(t') e^{-i(\omega-\omega_{eg})(t-t')} dt'$$

Some simple assumptions ($D_{eg}$ roughly independent of frequency near $\omega_{eg}$, etc.)

gives $\quad \dot{C}_{eo}(t) = -\frac{\Gamma}{2} C_{eo}(t) \quad$ w/ $\boxed{\Gamma = \frac{e^2 |D_{eg}|^2 \omega^3}{3\pi \varepsilon_0 \hbar c^3}}$

recall our Optical Bloch Eqn's (OBEs)

for excited state decay

start w/ coupled 2-level system in interaction picture w/ $\mathcal{H}_0 = \hbar\omega_0 \hat{\sigma}_z$

redefine $\tilde{c}_g = c_g e^{-i\delta t/2}$ $\quad \tilde{c}_e = e^{i\delta t/2} c_e$

w/ $\delta = \omega - \omega_0$ $\quad \tilde{\rho}_{gg} = \rho_{gg} \quad \tilde{\rho}_{ge} = e^{-i\delta t}\rho_{ge}$

$\tilde{\rho}_{ee} = \rho_{ee} \quad \tilde{\rho}_{eg} = e^{i\delta t}\rho_{eg}$

include loss → add

$\dot{c}_e = \ldots \; -\frac{\Gamma}{2} c_e$

$\dot{c}_g = \ldots \; +\frac{\Gamma}{2} c_g$ !

equivalent to

$T_2 = 2T_1$

$T_1 = 1/\Gamma$

$$\Rightarrow \begin{cases} \dot{\rho}_{gg} = \Gamma\rho_{ee} + \frac{i}{2}\left(\Omega^* \tilde{\rho}_{eg} - \Omega\tilde{\rho}_{ge}\right) \\ \dot{\rho}_{ee} = -\Gamma\rho_{ee} + \frac{i}{2}\left(\Omega\tilde{\rho}_{ge} - \Omega^*\tilde{\rho}_{eg}\right) \\ \dot{\tilde{\rho}}_{ge} = -\left(\frac{\Gamma}{2} + i\delta\right)\tilde{\rho}_{ge} + \frac{i}{2}\Omega^*\left(\rho_{ee} - \rho_{gg}\right) \\ \dot{\tilde{\rho}}_{eg} = -\left(\frac{\Gamma}{2} - i\delta\right)\tilde{\rho}_{eg} - \frac{i}{2}\Omega\left(\rho_{ee} - \rho_{gg}\right) \end{cases}$$

or

$$\dot{u} = \delta v - \frac{\Gamma}{2} u$$

$$\dot{v} = -\delta u + \Omega w - \frac{\Gamma}{2} v$$

$$\dot{w} = -\Omega v - \Gamma(w-1)$$

w/ $\mathcal{U} = u\hat{x} + v\hat{y} + w\hat{z}$

$$\begin{cases} u = \tilde{\rho}_{eg} + \tilde{\rho}_{ge} \\ v = i\left(\tilde{\rho}_{eg} - \tilde{\rho}_{ge}\right) \\ w = (\rho_{ee} - \rho_{gg}) \end{cases}$$

$\Omega, \Gamma$ processes are generally fast

Typically observe

"long-time" equilibrium conditions

set $\dot{u} = \dot{v} = \dot{w} = 0$

recall, $\Omega \sim \frac{e E_0 (a_0)}{\hbar}$

$\sim 2\pi \times 1$ MHz

for $1 \frac{mW}{cm^2}$

$\Gamma \sim \frac{4\alpha}{3c^2} \omega^3 |D_{eg}|^2 \sim 2\pi \times 10$ MHz

for $\lambda = 600$ nm,

$|D_{eg}| \sim 3 a_0$

$$\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \frac{1}{\delta^2 + \frac{\Omega^2}{2} + \frac{\Gamma^2}{4}} \begin{pmatrix} \Omega \delta \\ \Omega \Gamma / 2 \\ -\left(\delta^2 + \frac{\Gamma^2}{4}\right) \end{pmatrix}$$

recall $\rho_{ee} = \frac{1+w}{2}$

let $\boxed{S = \frac{2\Omega^2}{\Gamma^2} = \frac{I}{I_{sat}} \text{ saturation parameter}}$

$$\rho_{ee} = \frac{1}{2}\left[\frac{1 - \left(\delta^2 + \frac{\Gamma^2}{4}\right)}{\delta^2 + \frac{\Omega^2}{2} + \frac{\Gamma^2}{4}}\right] = \frac{1}{2} \frac{S}{1 + S + 4\left(\frac{\delta^2}{\Gamma^2}\right)}$$

if $I = \frac{\varepsilon_0 c |E_0|^2}{2}$ then $I_{sat} = \frac{hc\pi}{3\lambda^2 \tau}$

or $\frac{hc\pi}{3\lambda^2}\Gamma$

typically few $\frac{mW}{cm^2}$ for alkalis

rate of spontaneous emission $\Rightarrow \Gamma \rho_{ee} = R$

In strong-driving (saturation) limit ($\Omega \gg \Gamma$, $S \gg 1$) w/ $\delta = 0$, $R \to \Gamma/2$

$\rho_{ee} \to 1/2$

at long times, atoms spend at most half their time in the excited state

A typical observable, rate of spont. emission

How is this affected by properties of the light?

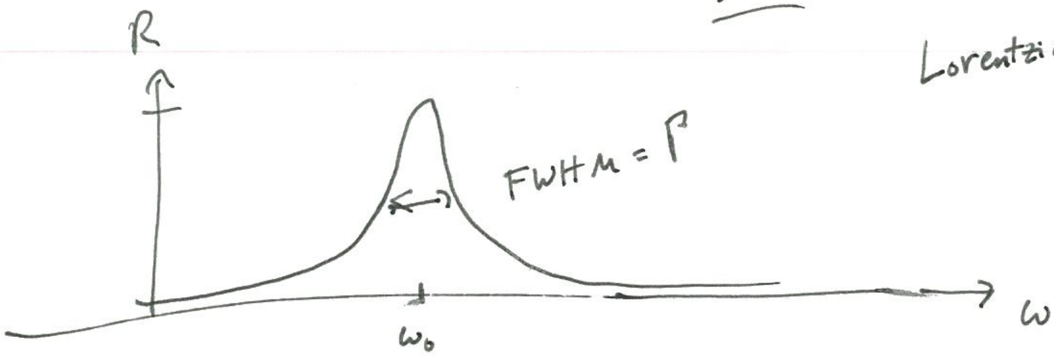
$$R = \frac{\Gamma}{2} \frac{s}{1 + s + \frac{4\delta^2}{\Gamma^2}} \quad w/ \quad s = \frac{2\Omega^2}{\Gamma^2}$$

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

low s

$s \ll 1$

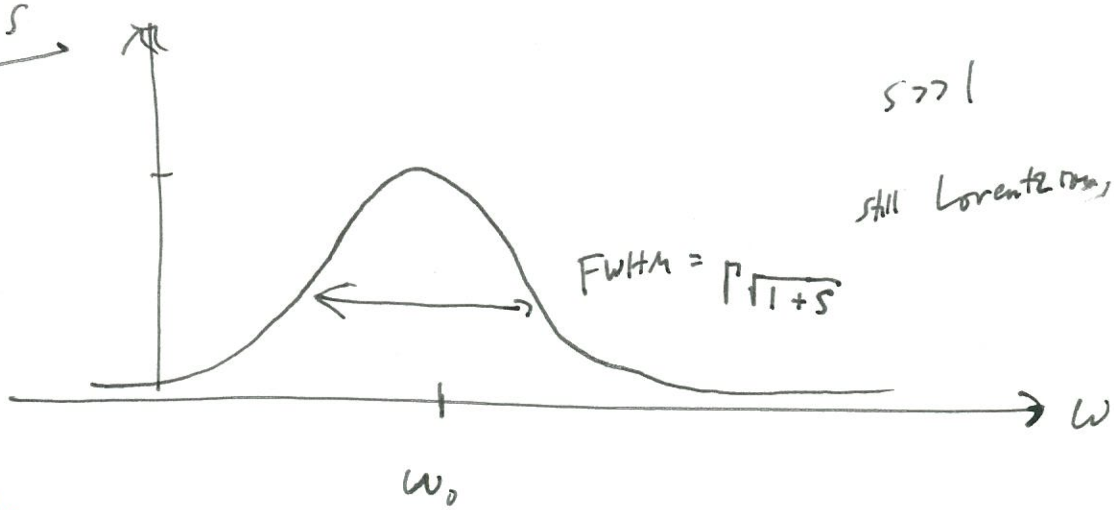
Lorentzian lineshape




large s

$s \gg 1$

still Lorentzian




Qualitatively

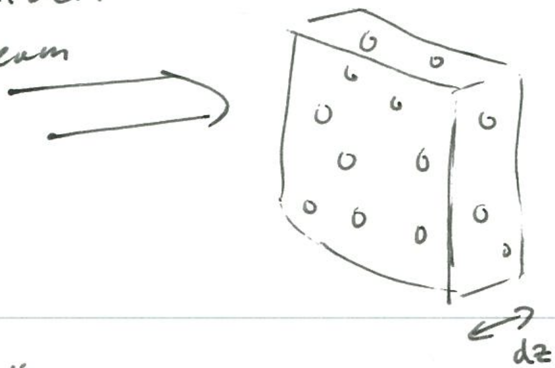
Gets broader w/ large s

Rate of excitation / fluorescence is saturated (by large pee) near resonance; less saturation for large $\delta$

## What about absorption?

Note: this treatment can break down for dense gases, where multiple scattering is important

incident beam



beam attenuation depends on # density of scatterers and prob. for absorption by each scatterer.

$$\frac{\Delta I}{I} = -n\,\sigma(\omega)\,\Delta z$$

depends on $\omega$

$n = \#$ density

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

$n\sigma\,dz \sim$ fraction of surface covered by atoms

in differential form

$$(1)\quad \frac{dI}{dz} = -n\,\sigma(\omega)\,I$$

w/ solution $I(\omega,z) = I(\omega,0)\,e^{-K(\omega)z}$

Beer's law

we know the scattered power per unit volume will be

$$\frac{\dot{E}}{V} = \frac{\dot{N}E_p}{V} = \hbar\omega R n$$

$$(2)\quad \longrightarrow \frac{dI}{dz} = -\hbar\omega R_n = -\frac{\hbar\omega\Gamma s}{2} \times \frac{1}{1+s+\left(\frac{2\delta}{\Gamma}\right)^2} \times n$$

using $I_{sat} = \frac{hc\pi}{3\lambda^2\tau} = \frac{hc\pi}{3\lambda^2}\Gamma$

we can combine (1) and (2) to get

$\delta = 0$

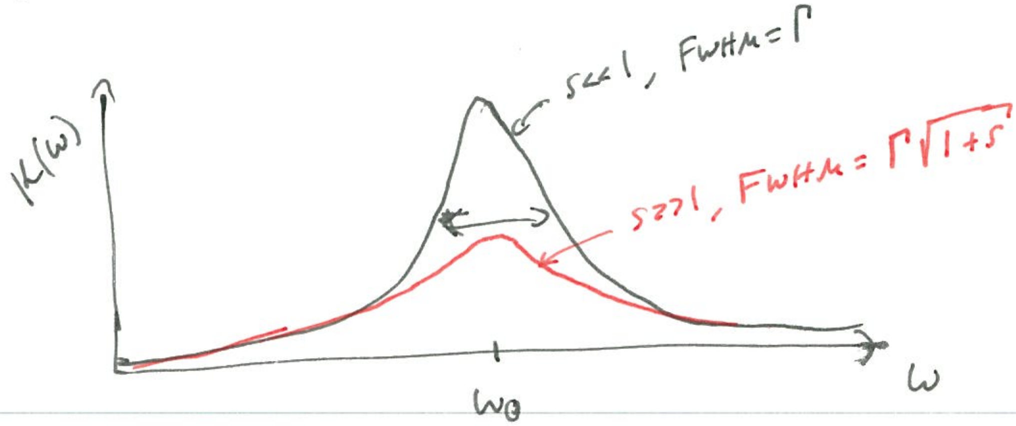
$$\sigma(\omega=\omega_{eg}) = \frac{3\lambda^2}{2\pi} \simeq \frac{\lambda^2}{2}$$

Valid for 2-level system

$$\text{or}\quad \sigma(\omega) = \frac{3\lambda^2}{2\pi}\,\frac{1}{1+4\delta^2/\Gamma^2}$$

more generally

# Lineshape for absorption coefficient




absorption coefficient reduced (saturates) on resonance, even though total fluorescence increases. This leads to power broadening.

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

but more generally

$$\sigma(\omega_0) = \frac{g_e}{g_g} \frac{\pi^2 c^2}{\omega_0^2} A_{21} \frac{1}{2\pi} \frac{\Gamma}{\delta^2 + \frac{\Gamma^2}{4}}$$

A bit more detail on $\langle e|\vec{r}\cdot\hat{\epsilon}|g\rangle$, or, in our case,

$\langle F', m_F' | \vec{r}\cdot\hat{\epsilon} | F, m_F\rangle$ ← depends on initial state $|F, m_F\rangle$, final state $|F', m_F'\rangle$ and polarization $\hat{\epsilon}$.

Let's assume polarization denoted by the number $\underline{q}$

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

and $q=\pm 1$ correspond to $\sigma_\pm$-transitions

By expanding $|F, m_F\rangle$ states in the $|m_J, m_I\rangle$ basis and then the $|m_L, m_S, m_I\rangle$ basis, one finds

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

w/ $A = (-1)^{1+L'+S+J+J'+I-m_F'}$

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

$$C = \begin{Bmatrix} L' & J' & S \\ J & L & 1 \end{Bmatrix}\begin{Bmatrix} J' & F' & I \\ F & J & 1 \end{Bmatrix}$$ 6-j symbols

$$D = \begin{pmatrix} F & 1 & F' \\ m_F & q & -m_F' \end{pmatrix}$$ 3-j symbol → [selection rules for $q$]

$$E = \langle \alpha' L' \| r \| \alpha L\rangle = \int_0^\infty r^2 R_{n'\ell'}\, r\, R_{n\ell}\, dr$$

← reduced matrix element

can calculate for hydrogen. Beyond that, determine from experiment (e.g. from $\Gamma$)

The selection rules [remember, $q$ is polarization relative to quantization axis]

$$m_F' = m_F + q$$

$$\Delta l = \pm 1 \quad (\text{"parity rule"})$$

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

no $\Delta F = 0$, $\Delta m_F = 0$ transitions

The results of these dipole matrix elements are generally presented in tables, charts, diagrams. [see Steck documents for some examples]

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