Absorption and emission rates are related to $g(\nu)$

which characterize the transition.

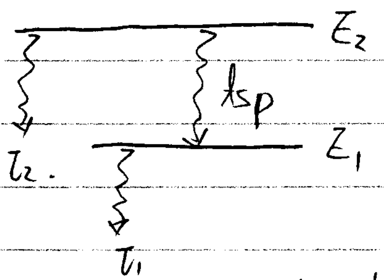
About $g(\nu)$: sources of broadening

* lifetime broadening:

$$\boxed{g(\nu) = \frac{\Delta\nu/2\pi}{(\nu-\nu_0)^2 + (\Delta\nu/2)^2}}$$

$$\boxed{\Delta\nu = \frac{1}{2\pi t_{sp}}}$$

t_{sp}: lifetime for single channel decay from E_2 to E_1



Account for multiple channel decay, which result in τ_1 & τ_2: the total radiative lifetime of E_1 & E_2

then

$\Delta\nu$, the frequency uncertainty of the transition between E_1 & E_2

has to be modified to

$$\boxed{\Delta\nu = \frac{1}{2\pi\tau}}$$

where τ : transition lifetime,

$\tau \leq t_{sp}$ and $\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2}$.

So peak cross-section:

$$\sigma_0 = S g(\nu_0)$$
$$= \frac{\lambda^2}{8\pi t_{sp}} \cdot \frac{2}{\pi \Delta\nu}$$
$$= \frac{\lambda^2}{4\pi^2 t_{sp}} \cdot 2\pi\tau$$
$$= \frac{\lambda^2}{2\pi} \cdot \frac{\tau}{t_{sp}}$$

Maxium possible cross section $\boxed{\sigma_{max} = \frac{\lambda^2}{2\pi}}$

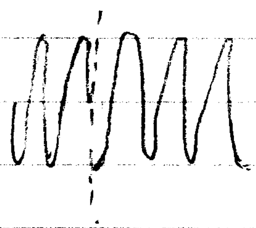
independent of properties of atom.

* another source of broadening: collisions.

two types: (i) inelastic, atom changes state
→ contribute to the lifetime of state.

so we can include it within τ_1 and τ_2.
i.e. now τ_1 τ_2 are the life time of E_1 & E_2
due to both radiative and non-radiative decay.

② elastic: atom doesn't change state, but phase of radiative field is disturbed as shown, and this will broaden the line shape.



To calculate, need to use statistical techniques from ch 10.

To make simple arguement:

on average, radiation amplitude decays as $e^{-f_{col} t}$

since after a collision, random phases average out.

For emission, argued that amplitude decayed as $e^{-t/2t_s}$

so expect f_{col} comes in like $\frac{1}{2t_s}$.

After accounting for this broadening mechanism, the lineshape function is still Lorentian,

but, now

$$\Delta\nu = \frac{1}{2\pi}\left(\frac{1}{\tau_1} + \frac{1}{\tau_2} + 2f_{col}\right)$$

In a gas, collisions are real collisions between particles

$f_{col} = N \sigma_{col} \bar{v}$ at 1 atm $f_{col} \sim 5\,GHz$

σ_{col} = collision cross section $\sim 10^{-14}\,cm^2$
for atoms & small molecules
N = particle density
$\bar{v}$ = mean spead.

Collisions are in a crystal too: $f_{col} \sim 100 - 1000\,GHz$
collisions with phonons
= perturbation due to lattice vibrations

Radiation & collisions are main forms of
homogeneous broadening:
mechanism that affect all atoms equally.

Also, inhomogenous broadening:
mechanism that affect different atoms differently

Example: Doppler broadening in a gas. have distribution
of speed $\bar{V}$.

$$P(\bar{V}) = \sqrt{\frac{M}{2\pi k_B T}}\, e^{-\frac{M\bar{v}^2}{2k_B T}}$$

T: temp
k_B: Boltzman const
M: mass

Frequency of light emitted by atom shifted by $\frac{\bar{V}}{\lambda}$

in lab frame Doppler shift $(\bar{V} \ll c)$

$$\nu_0 \to \nu_0' = \nu_0 + \frac{\bar{V}}{\lambda}$$

So individual atom with velocity $\bar{V}$ has

$$g_{\bar{V}}'(\nu) = \frac{\Delta\nu/2\pi}{[\nu - \underbrace{(\nu_0 + \frac{\bar{V}}{\lambda})}_{\nu_0'}]^2 + (\Delta\nu/2)^2}$$

peak at $\nu_0' = \nu_0 + \frac{\bar{V}}{\lambda}$

convert to probability for atom have ν_0':

$p(\bar{V})\,d\bar{V}$ = prob that atom has velocity $\bar{V}$
$p(\nu_0')\,d\nu_0'$ = prob. that atom has freq ν_0'

If $\nu_0' = \nu_0 + \frac{\bar{V}}{\lambda}$, then must have

$$p(\nu_0') = p(\bar{V})\frac{d\bar{V}}{d\nu_0'} = \lambda\, p[\bar{V} = \lambda(\nu_0' - \nu_0)]$$

$$= \sqrt{\frac{M\lambda^2}{2\pi k_B T}}\, e^{-\frac{M\lambda^2(\nu_0' - \nu_0)}{2kT}}$$

Consider all atoms, need to average over to get total line shape.

$$\bar{g}(\nu) = \int_{-\infty}^{\infty} g'_{\nu_0'}(\nu)\, p(\nu_0')\, d\nu_0'$$

can't do integral in general, but often have $\Delta\nu$ (with of g) $\ll \sqrt{\frac{kT}{M\lambda^2}}$ (with of $p(\nu_0')$)

$g'(\nu)$ peak at $\nu = \nu_0'$ looks like δ function

$$\delta\left[\nu - \underbrace{\left(\nu_0 + \frac{v}{\lambda}\right)}_{\nu_0'}\right]$$

so $\bar{g}(\nu) \approx p(\nu_0' = \nu) \underbrace{\int_{-\infty}^{\infty} \delta(\nu - \nu_0')\, d\nu_0'}_{=1}$

$$\bar{g}(\nu) = \sqrt{\frac{M\lambda^2}{2\pi kT}}\, e^{-\frac{M\lambda^2}{2kT}(\nu - \nu_0)^2}$$

Doppler line shape.

- Gaussian not Lorentzian

- FWHM $\overline{\Delta\nu} = \underbrace{(8 \ln 2)^{1/2}}_{2.35} \sqrt{\frac{kT}{M\lambda^2}}$ typical ~1GHz

- peak value $\bar{g}(\nu_0) = \sqrt{\frac{M\lambda^2}{2\pi kT}} = \frac{0.94}{\overline{\Delta\nu}}$

Other common type of inhomogeneous broadening:

lattic defects in crystal. each atom sees slightly different environment.

General approach.

Transition freq. (in Lab fram) depends on some external parameter β.

$$\nu_0' = f(\beta)$$

Need to know distribution function $\rho(\beta)$

Then $\rho(\nu_0') = \rho(\beta) \frac{d\beta}{d\nu_0'} = \rho(\beta) \frac{1}{df/d\beta|_{\beta = f^{-1}(\nu_0')}}$

and

$$\bar{g}(\nu) = \int g'(\nu)\, \rho(\nu_0')\, d\nu_0'$$

for $g'(\nu) = \frac{\Delta\nu/2\pi}{(\nu - \nu_0')^2 + (\Delta\nu/2)^2}$ $\Delta\nu$: homogeneous LW.