15: Spectral Line Broadening

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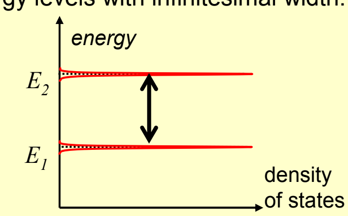
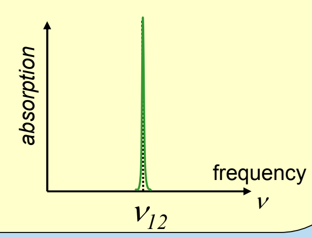
- Spectral lineshape and spontaneous emission
- Spectral lineshape and stimulated emission
- Effect on Einstein relations
- Homogeneous broadening
- Inhomogeneous broadening
- Homogeneous **and** inhomogeneous broadening
- Optical gain in broadened system
- *What you need to know!*

Energy Level Broadening

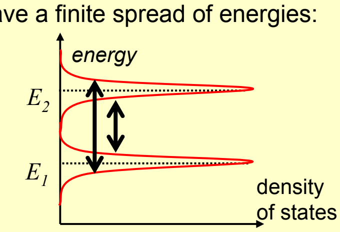
We previously considered atomic energy levels with infinitesimal width:



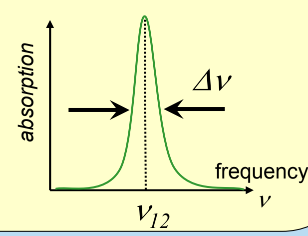
Leading to delta-function (single-frequency) lines:



Real atomic and molecular levels have a finite spread of energies:



Absorption lines have an appreciable width $\Delta\nu$:



What are the consequences for optical transitions, gain and lasing?

Spectral Lineshape and *Spontaneous* Emission

Einstein's coefficient A_{21} becomes $A_{21}(\nu)$, described by a *lineshape function*:

$$A_{21}'(\nu) = A_{21} g(\nu)$$

where $g(\nu)d\nu$ is the probability of spontaneous photon emission in the frequency range ν to $\nu + d\nu$

Therefore, including all frequencies, our rate equation for spontaneous emission becomes:

$$\frac{dN_2}{dt} = -N_2 \cdot \int_0^\infty A_{21}'(\nu) d\nu = -N_2 \cdot A_{21} \int_0^\infty g(\nu) d\nu = -N_2 \cdot A_{21}$$

normalised to unity

i.e. rate equation for spontaneous emission is unchanged by spectral broadening

Spectral Lineshape and *Stimulated* Emission

Einstein's coefficient B_{21} becomes $B_{21}(\nu)$, described by a *lineshape function*:

$$B_{21}'(\nu) = B_{21} g(\nu)$$

where $g(\nu)d\nu$ is the probability of spontaneous photon emission in the frequency range ν to $\nu + d\nu$

Therefore, including all frequencies, our rate equation for spontaneous emission becomes:

$$\frac{dN_2}{dt} = -N_2 \cdot \int_0^\infty B_{21}'(\nu)\rho(\nu) d\nu = -N_2 \cdot B_{21} \int_0^\infty g(\nu, \nu_0)\rho(\nu) d\nu$$

i.e. we have to account for the radiation field at different frequencies $\rho(\nu)$ interacting with the lineshape $g(\nu, \nu_0)$ centred on frequency ν_0.

Lineshape and stimulated emission (2)

There are two special cases of the radiation field $\rho(\nu)$

$$\frac{dN_2}{dt} = -N_2 \cdot \int_0^{\infty} B_{21}'(\nu)\rho(\nu)d\nu = -N_2 \cdot B_{21} \int_0^{\infty} g(\nu,\nu_0)\rho(\nu)d\nu$$

"white light"
(relevant to **black-body** radiation)

$\rho(\nu)$ is a constant over the spectral range of $g(\nu,\nu_0)$

$$\rho(\nu) = \rho(\nu_0)$$

$$\frac{dN_2}{dt} = -N_2 \cdot B_{21} \; \rho(\nu_0)$$

i.e. ***unchanged*** *compared to non-broadened 2-level system*

monochromatic light
(relevant to **lasers**)

$\rho(\nu)$ is non-zero only at a single frequency ν_1

$$\rho(\nu) = \rho_1 \delta(\nu - \nu_1)$$

$$\frac{dN_2}{dt} = -N_2 \cdot B_{21} \, g(\nu_0,\nu_1)\rho_1(\nu_0)$$

i.e. ***modified*** *by lineshape factor*

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What is effect of line broadening …?

… On Einstein relations?

Energy density of black body radiation varies slowly over the range of transition energies, hence:

$$\int_0^{\infty} g(\nu,\nu_0)\rho(\nu)d\nu \approx \rho(\nu_0)\int_0^{\infty} g(\nu,\nu_0)d\nu = \rho(\nu_0)$$

Therefore Einstein's relations are unchanged!

… On the gain?

To look at the effects on the gain, we need to distinguish between *homogeneous* and *inhomogeneous* broadening.

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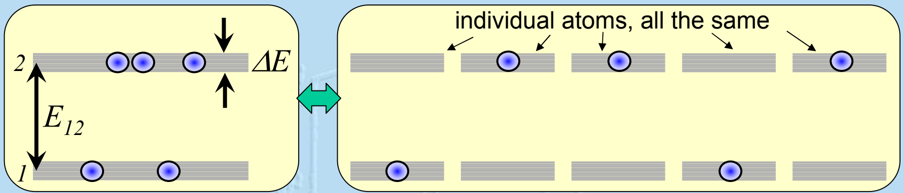
Homogeneous Line Broadening

All atoms in an ensemble are broadened in the *same* way by the *same* amount



Origins:

1. "Natural Broadening"
   Any transition which has a finite lifetime Δt has an energy uncertainty given by:

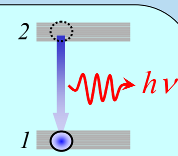
   $$\Delta E = \hbar / \Delta t$$

   and a spectral width:

   $$\Delta \nu = \Delta E / h = 1/(2\pi \Delta t)$$

2. In a crystal: scattering by phonons
3. In a gas: pressure broadening

Example:



The spectral broadening associated with spontaneous emission is:

$$\Delta \nu = \frac{1}{2\pi \Delta t_{spont}} = \frac{A_{21}}{2\pi}$$

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Lineshape Function for Natural Broadening

Consider an ensemble of atoms in an excited state which decays by spontaneous emission with lifetime τ. The irradiance will decay as:

$$I(t) = I_0 \exp(-t/\tau)$$

We can consider this (a bit handwaving?!) as arising from damped oscillators:

$$E(t) = E_0 \exp(-t/2\tau)\cos(\omega_0 t)$$

$$\therefore I(t) = \sum_i E_0^2 \exp(-t/\tau)\cos^2(\omega_0 t + \varepsilon_i) = \tfrac{E_0^2}{2}\exp(-t/\tau)\sum_i \{1 + \cos(2(\omega_0 t + \varepsilon_i))\}$$

Then we can find the electric field in the frequency domain using a Fourier transform:

$$E(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} E(t)\exp(-i\omega t)dt = \frac{E_0}{4\pi}\left[\frac{1}{\omega_0 - \omega + \frac{i}{2\tau}} - \frac{1}{\omega_0 + \omega - \frac{i}{2\tau}}\right]$$

The irradiance is given by the magnitude:

$$I(\omega) \propto |E(\omega)|^2 \propto \frac{1}{(\omega - \omega_0)^2 + \left(\frac{1}{2\tau}\right)^2}$$

or in terms of frequency ν:

$$I(\nu) \propto \frac{1}{(\nu - \nu_0)^2 + \left(\frac{1}{4\pi\tau}\right)^2}$$

This is a ***Lorentzian*** centred on ν_0 with width determined by τ.

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Lorentzian Lineshape for Homogeneous Broadening

The spectral width of the lineshape function is described by $\Delta\nu$, the Full Width at Half Maximum (FWHM):

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

and the irradiance can be re-written:

$$I(\nu) \propto \frac{1}{(\nu-\nu_0)^2 + (\Delta\nu/2)^2}$$

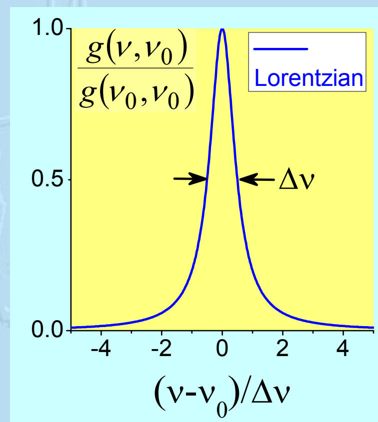
This lineshape function $g(\nu,\nu_0)$ is therefore this Lorentzian, normalised to unity area:

$$g(\nu,\nu_0) = \frac{2/(\pi\Delta\nu)}{1+[2(\nu-\nu_0)/\Delta\nu]^2}$$

The value of g at resonance is approximately the inverse linewidth:

$$g(\nu_0,\nu_0) = \frac{2}{\pi}\left(\frac{1}{\Delta\nu}\right) = 0.64\left(\frac{1}{\Delta\nu}\right)$$

$$g(\nu_0,\nu_0) \approx \left(\frac{1}{\Delta\nu}\right)$$



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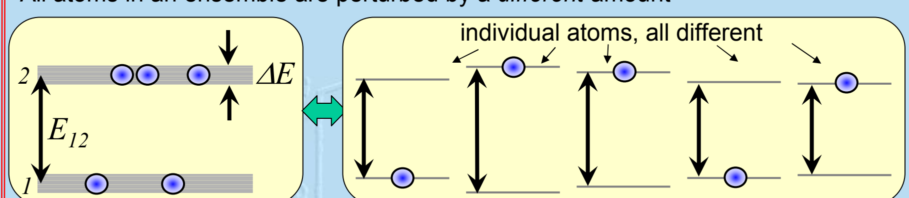
Inhomogeneous Line Broadening

All atoms in an ensemble are perturbed by a *different* amount

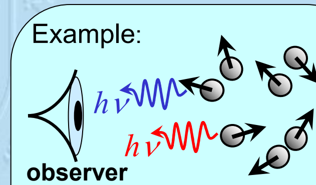


Origins:

1. Doppler broadening
2. Environmental variations:
   1. Composition or doping variation
   2. Variation of orientation with respect to the matrix
   3. Impurities
   4. Lattice imperfections

…anything that makes life different in one part of the sample from that in another …

Example:



The Doppler broadening depends on the distribution of velocities

$$\Delta\nu = \frac{\nu_0}{c}\Delta v$$

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Lineshape Function for Doppler Broadening

In atom with component of velocity v_x towards the observer has a shifted frequency:

$$\nu = \nu_0 + \frac{v_x}{c}\nu_0$$

The velocities are distributed according to the Maxwell-Boltzman distribution for particles of mass M at temperature T:

$$f(v_x)dv_x = \sqrt{\frac{M}{2\pi kT}}\exp\left(-\frac{Mv_x^2}{2kT}\right)dv_x$$

The distribution of Doppler-shifted frequencies is therefore:

$$g(\nu,\nu_0)d\nu = f(v_x)\frac{dv_x}{d\nu}d\nu = f(v_x)\frac{c}{\nu_0}d\nu$$

$$= \frac{c}{\nu_0}\sqrt{\frac{M}{2\pi kT}}\exp\left(-\frac{M}{2kT}\left(\frac{c}{\nu_0}\right)^2(\nu-\nu_0)^2\right)d\nu$$

This is a ***Gaussian*** centred on ν_0 with width determined by M, T and ν_0.

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Gaussian Lineshape for Inhomogeneous Broadening

The FWHM Gaussian linewidth for Doppler broadening is:

$$\Delta\nu = 2\nu_0\sqrt{\frac{2kT\ln 2}{Mc^2}}$$

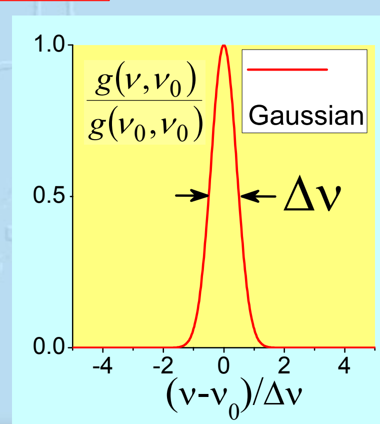
and the normalised lineshape can be re-written:

$$g(\nu,\nu_0) = \frac{2}{\Delta\nu}\sqrt{\frac{\ln 2}{\pi}}\exp\left(\left(-2(\nu-\nu_0)/\Delta\nu\right)^2\ln 2\right)$$

The value of g at resonance is again approximately the inverse linewidth:

$$g(\nu_0,\nu_0) = 2\sqrt{\frac{\ln 2}{\pi}}\left(\frac{1}{\Delta\nu}\right) = 0.939\left(\frac{1}{\Delta\nu}\right)$$

$$g(\nu_0,\nu_0) \approx \left(\frac{1}{\Delta\nu}\right)$$



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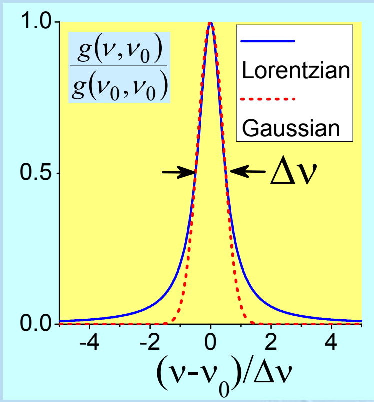
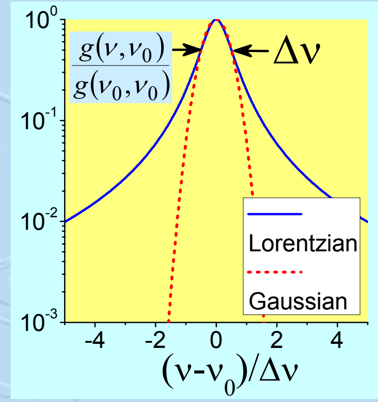
Comparison of Lorentzian and Gaussian Lineshapes





Lorentzian (homo-): $g(\nu,\nu_0)=\frac{2/(\pi\Delta\nu)}{1+[2(\nu-\nu_0)/\Delta\nu]^2}$ $g(\nu_0,\nu_0)=\frac{2}{\pi}\left(\frac{1}{\Delta\nu}\right)\approx\left(\frac{1}{\Delta\nu}\right)$

Gaussian (inhomo-): $g(\nu,\nu_0)=\frac{2}{\Delta\nu}\sqrt{\frac{\ln 2}{\pi}}\exp\left\{\left[-2\frac{(\nu-\nu_0)}{\Delta\nu}\right]^2\ln 2\right\}$ $g(\nu,\nu_0)=2\sqrt{\frac{\ln 2}{\pi}}\left(\frac{1}{\Delta\nu}\right)\approx\left(\frac{1}{\Delta\nu}\right)$

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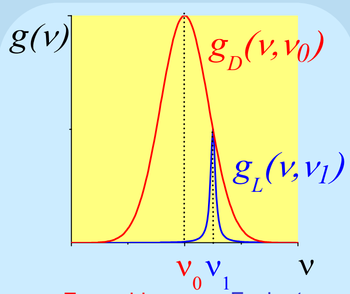
'Real' systems: homogeneous & inhomogeneous broadening



Ensemble described by inhomogeneous term (e.g. Doppler)

Each atom described by homogeneous term (e.g. lifetime)

Consider atoms with centre frequencies between ν_1 and $\nu_1+d\nu_1$ with homogeneous lineshape $g_L(\nu,\nu_1)$. There are $Ng_D(\nu_1,\nu_0)\,d\nu_1$ such atoms where $g_D(\nu_1,\nu_0)$ is the inhomogeneous lineshape. Their gain is therefore:

$$d\gamma=\left(N_2-\frac{g_2}{g_1}N_1\right)\frac{c^2A_{21}}{8\pi\nu^2}g_D(\nu_1,\nu_0)g_L(\nu,\nu_1)d\nu_1$$

$$\therefore\gamma(\nu,\nu_0)=\left(N_2-\frac{g_2}{g_1}N_1\right)\frac{c^2A_{21}}{8\pi\nu^2}g(\nu,\nu_0)$$

where $g(\nu,\nu_0)=\int_{-\infty}^{\infty}g_D(\nu_1,\nu_0)g_L(\nu,\nu_1)d\nu_1$

is just the convolution of g_D and g_L.

If homogeneous linewidth is small, $g(\nu,\nu_0)\rightarrow g_D(\nu,\nu_0)$

If inhomogeneous linewidth is small, $g(\nu,\nu_0)\rightarrow g_L(\nu,\nu_0)$

If g_D is Gaussian and g_L is Lorentzian, then g is a 'normalised Voigt profile'

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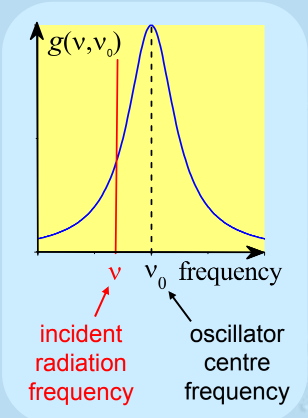
Optical gain in broadened system



The optical gain at frequency ν (within the frequency range of the broadened oscillator) is :

$$\gamma(\nu,\nu_0) = \left(N_2 - \frac{g_2}{g_1}N_1\right)\frac{c^2 A_{21}}{8\pi\nu^2}g(\nu,\nu_0)$$

$$= \sigma_0(\nu,\nu_0)\left(N_2 - \frac{g_2}{g_1}N_1\right)$$

The maximum value of the gain cross-section occurs when the incident radiation is at the oscillator centre frequency ($\nu_1 = \nu_0$):

$$\sigma_0 = \frac{c^2 A_{21}}{8\pi\nu_0^2}g(\nu_0,\nu_0) \approx \frac{c^2 A_{21}}{8\pi\nu_0^2}\frac{1}{\Delta\nu}$$

$$\sigma_0 \propto \frac{A_{21}}{\Delta\nu} = \frac{\text{spontaneous transition rate}}{\text{linewidth}}$$

the broader the transition, the smaller the optical gain

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What U need 2 know: Line broadening 15

- 'Real' atomic transitions are broadened by a lineshape function $g(\nu)\, d\nu$
- The Einstein relations are *unchanged* as a consequence
- The laser gain is modified by a lineshape function, which is a convolution of homogeneous and inhomogeneous terms
- In homogeneous broadening, all atoms are broadened in the same way (e.g. lifetime broadening)
- In inhomogeneous (e.g. Doppler) broadening, each atom has its centre frequency shifted by a different amount, and the ensemble is broadened
- Homogeneous broadening usually results in a *Lorentzian* lineshape
- Inhomogeneous broadening usually results in a *Gaussian* lineshape
- For *both* homogeneous and inhomogeneous broadening, the value of $g(\nu_0)$ at the centre frequency ν_0 is *approximately* the reciprocal of the linewidth $\Delta\nu$
- Hence the optical gain is inversely proportional to the linewidth

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