

# Topic 2: Radiation and Materials Interaction

## 2.1 Introduction

The electrons in all materials have discrete energy levels, and in particular we have,

1. **Atomic Energy Levels:** electrons have widely spaced discrete energies between shells and closely spaced level within shells.
2. **Molecular Energy Levels:** Closely and widely spaced levels due to vibrational, bending and rotational modes of the molecule.
3. **Band in Solids:** Very closely spaced within band, large spaces between bands.

This result in a typical material having many hundred of possible energy levels. However in most of laser physics we need only consider a much simplified system with **two** energy level these being the *upper* and *lower* laser level between which the laser action occurs. Other levels in the system do not contribute.

## 2.2 Two Level System

Consider two (excited) states  $E_1$  and  $E_2$ , above a ground state  $E_0$  as shown in figure 1.

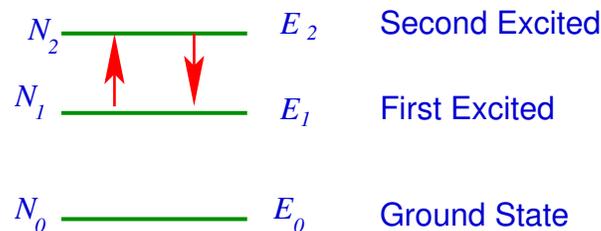


Figure 1: Simple two level system containing two excited states

The energy between the two states is  $\Delta E$ , and when an electron in state  $E_2$  drops to  $E_1$  it will emit a photon of frequency  $\nu$  where we have that,

$$\Delta E = E_2 - E_1 = h\nu$$

where  $h$  is Plank's constant. We know that the energy levels in any systems are not *infinitely* well defined which gives rise to a range of transitions energies  $\Delta E$ , and thus a range of emitted photon frequencies since

$$\Delta E = h\nu$$

as shown in figure 2. Then if we define the probability that the emitted photon will have frequency  $\nu \rightarrow \nu + \delta\nu$  to be  $g(\nu)$  where

$$\int_0^{\infty} g(\nu) d\nu = 1$$

Then since the intensity of the transition is proportional to the number of photons with a particular frequency, then  $g(\nu)$  is just the normalised (spontaneous) line shape of the transition from  $E_2 \rightarrow E_1$ . In fact absorption, spontaneous emission and stimulated emission are **all** characterised by the *same* probability distribution; assume this, the proof is very complex.

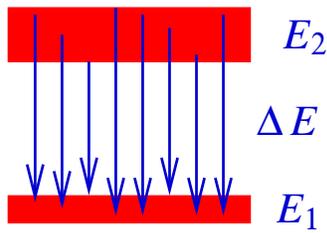


Figure 2:

## 2.3 Finite Lifetimes

If the emitting upper state has lifetime  $\tau$ , then from the *Uncertainty Principal* we get a spread of energies in the upper state given by

$$\delta E_2 \tau \approx h$$

so a  $\tau$  become shorter, then the energy range become larger, and we get a larger spread of transitions, and hence a wider spectral line.

The shape of the line is most easily derived from a classical argument. Start with  $N_2$  atoms in excited state  $E_2$  and transition lifetime of  $E_2 \rightarrow E_1$  being  $\tau$ . The emitted intensity against time will drop exponentially with time constant  $\tau$ , so being

$$I(t) = I_0 \exp\left(-\frac{t}{\tau}\right)$$

so if the frequency of the transition is  $\nu_0$  the amplitude against time is given by

$$e(t) = e_0 \exp\left(-\frac{t}{2\tau}\right) \cos(2\pi\nu_0 t)$$

which is just the expression for a damped harmonic oscillator. We have that the transition probability  $g(\nu)$  is just the normalised frequency spectrum, which is the modulus squared of the Fourier Transform of  $e(t)$ , the amplitude against time. This gives, after some work!, (see workshop question 2.1) that

$$g(\nu) = \frac{\Delta\nu}{2\pi \left[ (\nu - \nu_0)^2 + \left(\frac{\Delta\nu}{2}\right)^2 \right]} \quad \text{where} \quad \Delta\nu = \frac{1}{2\pi\tau}$$

which is a Lorentzian. This is plotted in figure 3, which  $\nu = 1000$  and  $\Delta\nu = 50, 100 \& 140$ .

The peak height is  $g(\nu_0) = \frac{2}{\pi\Delta\nu}$ , so the half-height is at,

$$g(\nu_h) = \frac{1}{\pi\Delta\nu} \quad \text{when} \quad \nu_h = \nu_0 \pm \frac{\Delta\nu}{2}$$

so the *full width at half height* of a Lorentzian is just  $\Delta\nu$ . If we take  $\Delta\nu$  to be the line-width, then noting noting that

$$\Delta\nu = \frac{1}{2\pi\tau} \quad \text{and} \quad \Delta\nu = \frac{\delta E_2}{h}$$

we get (classically) that

$$\delta E_2 \tau = \frac{h}{2\pi}$$

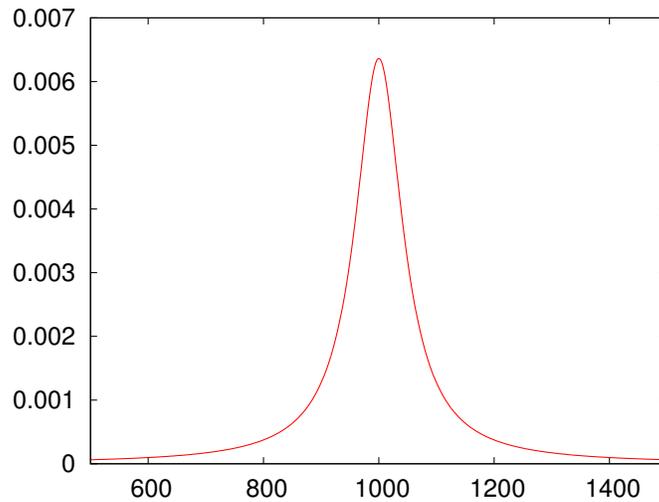


Figure 3: A Lorentzian line-shape with  $\nu_0 = 1000$ , with  $\Delta\nu = 50, 100$  &  $140$ .

which is back to the *Uncertainty Principal*, but from a totally classical argument!

When the both upper  $E_2$  and lower  $E_1$  states have a finite lifetime, being  $\tau_2$  and  $\tau_1$ , then there is an uncertainty associated with  $h$  both levels, the total line-width becomes,

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

This gives the minimum spectral line-width, or *natural line-width* of the transition between two levels with finite lifetime.

## 2.4 Pressure Broadening

When there are elastic collisions between atoms in a gas, or between atoms and phonons in a crystal, this effectively shortens the *lifetime* of each state, and hence further broadens the spectral line. In this case the line broadens to,

$$\Delta\nu = \frac{1}{2\pi} \left( \frac{1}{\tau_2} + \frac{1}{\tau_1} + \frac{1}{\tau_{c,2}} + \frac{1}{\tau_{c,1}} \right)$$

where  $\tau_{c,2}$  and  $\tau_{c,1}$  and the mean time between collisions for the upper  $E_2$  and lower  $E_1$  state respectively. In gases the collision rate is proportional to pressure (atomic density) and is usually called *pressure broadening* of the spectral line.

*Aside:* High output spectral lamps require high atomic density (pressure), which results is wide spectral lines. For example high pressure mercury lamps as almost “white light”.

## 2.5 Doppler Broadening

If an atom in a gas with velocity component  $v_z$  in the observation direction, emits of photon of frequency  $\nu_0$ , the observer frequency is

$$\nu = \nu_0 + \frac{v_z}{c} \nu_0 \quad \text{where } c \text{ is velocity of light}$$

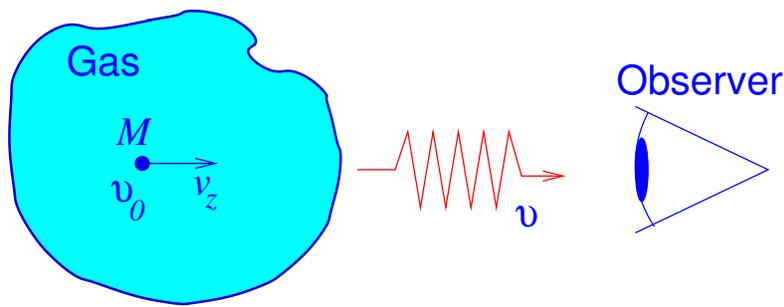


Figure 4: Doppler Broadening

so frequency is Doppler Shifted. We also know from *Statistical Mechanics*, that probability of an atom of mass  $M$  having velocity  $\mathbf{v} \rightarrow \mathbf{v} + d\mathbf{v}$  in gas at temperature  $T$  is given by,

$$P(\mathbf{v}) d^3\mathbf{v} = \left( \frac{M}{2\pi kT} \right)^{\frac{3}{2}} \exp \left( -\frac{M}{2kT} (v_x^2 + v_y^2 + v_z^2) \right)$$

which is just the *Maxwell velocity distribution* normalised so that

$$\int \int \int P(\mathbf{v}) dv_x dv_y dv_z = 1$$

which is Gaussian in shape.

Now if we assume that the lifetime effects, discussed above are small, then a photon traveling in the  $z$ -directions having frequencies  $\nu \rightarrow \nu + d\nu$  must arise from atoms traveling in the  $z$ -direction with velocities  $v_z \rightarrow v_z + dv_z$  being irrespective of their  $v_x$  and  $v_y$  values. Therefore the probability of photon having frequency  $\nu \rightarrow \nu + d\nu$  is found by substituting for  $v_z$  and integrating over all  $v_x$  and  $v_y$ , giving

$$g(\nu) d\nu = \left( \frac{M}{2\pi kT} \right)^{\frac{3}{2}} \int \int \exp \left( -\frac{M}{2kT} (v_x^2 + v_y^2) \right) dv_x dv_y \exp \left( -\frac{M}{2\pi kT} v_z^2 \right) dv_z$$

Then noting that

$$v_z = c \left[ \frac{\nu - \nu_0}{\nu_0} \right] \quad \text{so} \quad dv_z = \frac{c}{\nu_0} d\nu$$

we can then use the standard integrals expression for Gaussians, giving that,

$$g(\nu) = \frac{c}{\nu_0} \left( \frac{M}{2\pi kT} \right)^{\frac{1}{2}} \exp \left( -\frac{M}{2kT} \left( \frac{c}{\nu_0} \right)^2 (\nu - \nu_0)^2 \right)$$

which is a Gaussian about  $\nu_0$ , which has been normalised so that

$$\int_0^{\infty} g(\nu) d\nu = 1$$

This can be written as

$$g(\nu) = \frac{1}{2\sigma\sqrt{\pi}} \exp \left( -\left( \frac{\nu - \nu_0}{2\sigma} \right)^2 \right) \quad \text{where} \quad \sigma = \sqrt{\left( \frac{kT}{2Mc^2} \right)} \nu_0$$

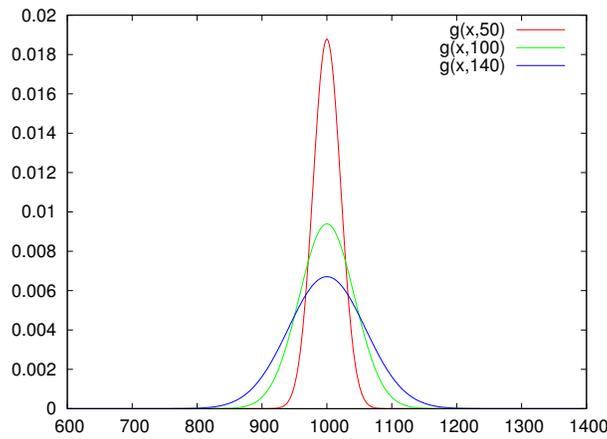


Figure 5: Gaussian centered on 1000, with  $\Delta v_D = 50, 100 \& 140$

which is plotted in figure 5 for  $v_0 = 100$  and  $\Delta v_D = 50, 100 \& 140$ .

We know that for a Gaussian the *full width at half height* is given by

$$\Delta v_D = 4\sigma\sqrt{\ln 2}$$

so after a bit of re-arrangement, gives that the Doppler Broadened line-width is given by

$$\Delta v_D = 2v_0\sqrt{\frac{2kT \ln 2}{Mc^2}}$$

which is proportional to the square root of  $T$ . Thus *hot* gases have wider spectral lines than *cool* gases, as would be expected.

## 2.6 Homogeneous and Inhomogeneous Broadening

*Natural* and *Pressure* broadening apply equally to all atoms (or molecules) so allowing them to be treated as being identical and indistinguishable. This effect is known as **Homogeneous Broadening** and results in the Lorentzian line-shape.

In Doppler broadening, the atoms are *identified* by their velocity in a particular direction, and so become distinguishable. This is typical of **Inhomogeneous Broadening** and when a large number of atoms are considered results in a Gaussian line-shape.

In many systems one type dominates, and the line-shape is either Lorentzian or Gaussian. If however **both** are of similar size then the line-shape is a convolution of the two with the width being approximately given by

$$\Delta v_T \approx \Delta v + \Delta v_D$$

with the detail of the line-shape being given by the relative values of  $\Delta v$  and  $\Delta v_D$ .

As well as Doppler effects in gases, if atoms (or molecules) are distinguishable by location for example as interstitial depends in a crystal, then each atom may have a slightly different natural frequency  $v_0$  (due to perturbations of the energy levels). This again results in **inhomogeneous** broadening with a *Gaussian* line-shape; this is actually the most common effect in lasers, for example

- $\text{Nd}^{3+}$  ions in  $\text{CaWO}_4$  lattice (YAG)
- $\text{Cr}^{3+}$  ions in  $\text{Al}_2\text{O}_3$  (Ruby).
- $\text{Ti}^{2+}$  ions in Sapphire (Ti-Sapphire)

This effect can result in line-width of many nm, and is the basis of tunable solid state LASERs (more on this later)

Some materials have a vast number of very closely packed energy levels allowing a huge number (effective continuum) of transitions. Most common are:

1. Organic Dyes: Each energy level multiply split by vibrational and rotational modes of the molecule. Natural line-width of each energy level overlap giving an effective continuum (over several hundred nm with some dyes).
2. LED: Large number of closely packed levels on conduction band (electron in  $n$ -type, holes in  $p$ -type). So large range of electron-hole combinations possible.

In most cases the spectral transitions in atoms (or molecules) are **not** narrow and generally widen as atomic density **and** temperature increase.

In a LASER we are going to select a very small spectral range to *feedback* which will result in a output with is very much spectrally narrower than the underlying material. The underlying broadening scheme make very major differences to the laser output and mode of operation, and as we will see later *homogeneous* and *inhomogeneous* media result in very different operating conditions.

## 2.7 Absorption and Decay Processes

Let us first consider the two level system in some (semi-classical) detail. Consider a **two** level system in presence of radiation spectrum  $\rho(\nu)$  as shown in figure 6. Define  $N_i$  as the number of states per unit volume of material in energy state  $E_i$ .

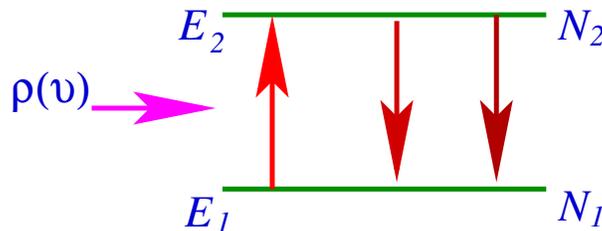


Figure 6: Energy diagram of two level system in the presence of radiation.

In the presence of radiation, we have **three** possible transition between these levels, these being:  
**Spontaneous Decay:** from  $E_2 \rightarrow E_1$ . This depends on population density  $N_2$  of the upper state *only*. Thus the rate of change of  $N_2$  is simply given by,

$$\frac{dN_2}{dt} = A_{2,1} N_2$$

where  $A_{1,2}$  is called the *Einstein “A” Coefficient*. Clearly

$$A_{2,1} = \frac{1}{\tau_{sp}}$$

where  $\tau_{sp}$  is the decay time for the  $E_2 \rightarrow E_1$  transmission, and if  $\rho(\nu) = 0$ , we simply get

$$N_2(t) = N_2(0) \exp(-A_{2,1}t)$$

exponential decay; this is the assumption used for *natural line-widths*. If the  $E_2 \rightarrow E_1$  is the only allowed decay path from  $E_2$ , then  $\tau_{sp}$  is also the life time of the  $E_2$  state. This is the most common transition, for example spectral lamps, but in lasers, is the one we will want to *minimise*.

**Absorption:** from  $E_1 \rightarrow E_2$ . This depends on population density  $N_1$  of the lower state only and  $\rho(\nu)$ , given by so the rate of change of  $N_1$  is given by

$$\frac{dN_1}{dt} = B_{1,2} N_1 \rho(\nu)$$

where  $B_{1,2}$  is called the *Einstein “B” Coefficient* for the  $E_1 \rightarrow E_2$  transmission, and  $\rho(\nu)$  gives the number of photons incident.

**Stimulated Emission:** from  $E_2 \rightarrow E_1$ . This depends on population density  $N_2$  the upper state and  $\rho(\nu)$ , so the rate of change of  $N_2$  is given by,

$$\frac{dN_2}{dt} = B_{2,1} N_2 \rho(\nu)$$

where  $B_{2,1}$  is called the *Einstein “B” Coefficient* for the  $E_2 \rightarrow E_1$  transmission. This is the one that is normally *ignored*, usually being a very small effect, this is however what we need for laser action!

Most situations we only consider *Spontaneous Decay* (atomic spectra, line-widths etc), and *Absorption* (Fraunhofer Lines); but LASERS depend on the *Stimulated Emission* term.

## 2.8 Thermal Equilibrium

To investigate the relation between the  $A$  and  $B$  coefficients, lets initially consider the system in thermal equilibrium and isolated from other energy level. For a two state system we have that a fixed number of atoms being  $N_1 + N_2$ , so we must have that,

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

so from above we must have that,

$$B_{1,2} N_1 \rho(\nu) = B_{2,1} N_2 \rho(\nu) + A_{2,1} N_2$$

Now if system in *Thermal Equilibrium*, then the population of  $N_1$  and  $N_2$  are related by *Boltzmann statistics*, so

$$N_2 = N_1 \exp\left(-\frac{\Delta E}{kT}\right) = N_1 \exp\left(-\frac{h\nu}{kT}\right)$$

where  $\nu$  is the photon frequency of the transition. If, however, energy level  $E_1$  has degeneracy  $g_1$ , and  $E_2$  degeneracy  $g_2$ , the *Boltzmann relation* includes these degeneracies and becomes,

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} \exp\left(-\frac{h\nu}{kT}\right)$$

Now if we substitute for  $N_1$  and cancel terms we get that,

$$\rho(\nu) \left[ \frac{g_1}{g_2} B_{1,2} \exp\left(\frac{h\nu}{kT}\right) - B_{2,1} \right] - A_{2,1} = 0$$

so in terms of the radiation spectrum,  $\rho(\nu)$ , we have that,

$$\rho(\nu) = \frac{A_{2,1}}{\frac{g_1}{g_2} B_{1,2} \exp\left(\frac{h\nu}{kT}\right) - B_{2,1}}$$

Since we have assumed the system to be *thermal equilibrium*, then  $\rho(\nu)$  must be given by the *Plank Blackbody* relation of

$$\rho(\nu) = \frac{8\pi\mu^3 h\nu^3}{c^3} \left[ \frac{1}{\left(\exp\left(\frac{h\nu}{kT}\right) - 1\right)} \right]$$

so we can equate these two expressions for  $\rho(\nu)$ .

This expression *must* be equally valid for all all  $T$ , so immediately giving that

$$B_{2,1} = \frac{g_1}{g_2} B_{1,2}$$

If we assume state  $sE_1$  and  $E_2$  gave the same degeneracy, that  $g_1 = g_2$  (this is true in many laser media, for example in Ruby), then we can write

$$B_{2,1} = B_{1,2} = B \quad \text{and also} \quad A_{2,1} = A$$

then (after some work), we can get a relation between  $A$  and  $B$  given by

$$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3}$$

which gives the interaction of radiation, associated with the  $B$  coefficient, in terms of the  $A$  coefficient which is associated with the lifetime of the excited state.

In lasers we are interested in the *Spontaneous Emission*, which we identify as being  $B\rho(\nu)$ , while the *Spontaneous Emission* is identified with  $A$ , so we can define

$$R = \frac{A}{B\rho(\nu)} = \exp\left(\frac{h\nu}{kT}\right) - 1$$

as the ratio of *Spontaneous Emission* to *Stimulated Emission*.

**Optical Wavelengths:** Take  $\lambda = 600\text{nm}$ , and  $T = 300\text{K}$ .

$$\nu = 5 \times 10^{14} \quad \Rightarrow \quad R \approx 10^{36}$$

So at optical wavelengths *Spontaneous Emission* is totally dominant, as in almost all cases, the *Stimulated Emission* is totally ignored, this is a bit of a problem for LASERS which operate by *Stimulated Emission*!

To get  $R \approx 1$  require  $\lambda \approx 60 \mu\text{m}$ , in the Microwave regions. Hence the MASER<sup>1</sup> was developed  $\approx 20$  years earlier than the LASER.

The *trick* is that the LASER does **not** operate in *thermal equilibrium*. We have to arrange a *population inversion* with  $N_2 > N_1$  which is *impossible* in a system in thermal equilibrium.

The LASER is **not obvious**, perhaps this is why it was not developed until 1960, while the underlying atomic theory, in the form of the relation between the  $A$  and  $B$  coefficients, was developed by Einstein in 1917.

## 2.9 Add Line-shape

To make these expressions more useful, we have to add in the effect of the line-widths, characterised by  $g(\nu)$  which is a probability density. Thus the probability of a *Stimulated Emission* between two *real* laser levels becomes,

$$B_{2,1} \rho(\nu) g(\nu) d\nu \quad \text{in region } \nu \rightarrow \nu + d\nu$$

Take a very narrow spectral region (as is found in LASERS), and define the transition probability from state  $E_2$  to  $E_1$  as being,

$$W_{2,1}(\nu) = \int_{\nu}^{\nu+d\nu} B_{2,1} \rho(\nu) g(\nu) d\nu$$

If we can then assume that  $g(\nu) \approx \text{Const}$  over the range  $\nu \rightarrow \nu + d\nu$ , which is a good assumption, and noting that,

$$B_{2,1} = \frac{A_{2,1} c^3}{8\pi h \nu^3}$$

we get that

$$W_{2,1}(\nu) = \frac{A_{2,1} c^3}{8\pi h \nu^3} g(\nu) \int_{\nu}^{\nu+d\nu} \rho(\nu) d\nu$$

We also notice that  $\rho(\nu)$  is just the intensity (normalised by  $c$  the speed of light), so define *intensity profile*, as

$$I(\nu) = c \rho(\nu)$$

Again for narrow spectral line (true in LASER), so

$$\int_{\nu}^{\nu+d\nu} \rho(\nu) d\nu \rightarrow \frac{I}{c}$$

so by substitution we get that

$$W_{2,1}(\nu) = \frac{A_{2,1} c^2 I(\nu)}{8\pi h \nu^3} g(\nu)$$

which gives the probability of *stimulated emission* probability from state  $E_2 \rightarrow E_1$  in terms of *measurable* quantities of the laser media, these being,

1.  $A_{2,1}$  is the spontaneous transition rate (the state lifetime).
2.  $g(\nu)$  is the spectral line-shape (including broadening).

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<sup>1</sup>Microwave Amplification by Stimulated Electro-magnetic Radiation

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3.  $I(\nu)$  is the intensity of light in the medium.

4.  $\nu$  is the frequency of the light.

Note the  $\nu^3$  on the lower line, so the shorter the wavelength the smaller the transition rate.

In our analysis we have assumed a medium with refractive index of unity, if we have refractive index  $n$ , which is a constant throughout the analysis, we get (see Yariv),

$$W_{2,1}(\nu) = \frac{A_{2,1} c^2 I(\nu)}{8\pi n^2 h \nu^3} g(\nu)$$

which we will need for solid state LASERS.

This gets us to the first fundamental equation for laser operation, which we shall go on to develop in further sections.

## 2.10 Summary

In this section we have detailed the semi-classical two level system, and have

1. derived the expression for a line-spread due to finite lifetimes of states,
2. considered Doppler state broadening, and derived an expression for its associated line-spread,
3. outlined the difference between homogeneous and inhomogeneous broadening,
4. derived the relation between the  $A$  and  $B$  coefficients in thermal equilibrium,
5. derived an expression for *stimulated emission* in terms of measurable quantities,
6. added in the effect of line widths, to derive the main fundamental expression for laser action.

We have also identified, that if a laser is to work by *stimulated emission*, then it cannot work in thermal equilibrium, the effect is  $\approx 10^{36}$  too small, and we have to use some *trick* to form a *population inversion*.

# Workshop Questions



## 2.1 Lorentzian Lineshape

Calculate the *Power spectrum* (modulus squared of Fourier Transform) of a damped harmonic oscillator of the form

$$a(t) = a_0 \exp\left(-\frac{\alpha t}{2}\right) \cos(2\pi\nu_0 t)$$

and show that it approximates to a Lorentzian for frequencies close to  $\nu_0$ .

## 2.2 Line width of Spectral Line

What is the natural frequency width of a spectral line if the upper and lower states have mean lifetimes of 120 nsecs and 40 nsecs respectively. If the transition energy is 1.845 eV what is the mean wavelength and width of the spectral line in nm.

## 2.3 Doppler in CO<sub>2</sub> and Cadmium

Calculate the Doppler width of the CO<sub>2</sub> LASER line at 10.6  $\mu\text{m}$  at 400 K and compare it with the Cadmium ion LASER (325 nm) at the same temperature.



## 2.4 The Sodium Doublet

The sodium double consists of two lines at 589.6nm and 589.0nm. At what temperature to these two lines merge to become one. Comment on you answer.



## 2.5 Why wavenumber

Many spectroscopy books (both old and modern) frequently use the non-SI unit of *wavenumber* when describing spectral lines. This is defined as

$$\kappa = \frac{1}{\lambda}$$

and is usually quoted in  $\text{cm}^{-1}$ . Suggest reason(s) why this *old* non-SI is still used rather than the more obvious  $\lambda$ , or frequency  $\nu$  ?

## 2.6 The B Coefficient in ruby

Estimate the value of the Einstein *B* coefficient for absorption of resonance radiation at 694 nm by ruby given that the lifetime of the upper (<sup>2</sup>E) state is 5 msecs. For ruby  $g_1 = g_2$ .

State carefully the units of *B*.