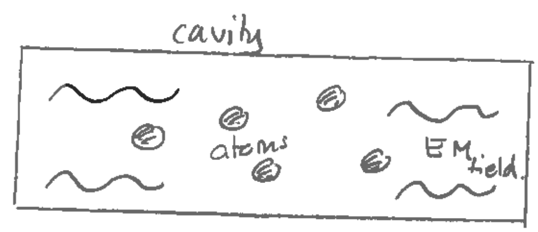
Absorption and Emission by Atoms.

We have seen that atomic, molecular and other systems have the property that, when their energy is measured, the result is one of a discrete (as opposed to continuous) set of possibilities. Quantum theory then provides a framework for understanding how such systems interact with surrounding electromagnetic fields.

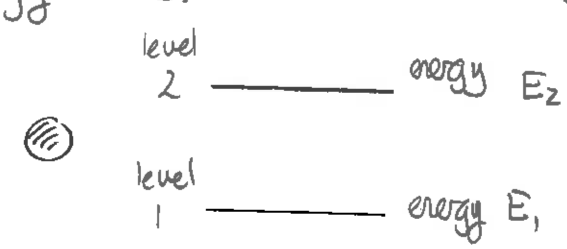
We now consider a simple model of such a system that interacts with an electromagnetic field. The model will eventually show how stimulated emission can arise and how this can produce laser light.

The model consists of a fixed number of two-level atoms in a cavity, which is host to an electromagnetic field.

The atoms are all identical and are simplified to the extent that

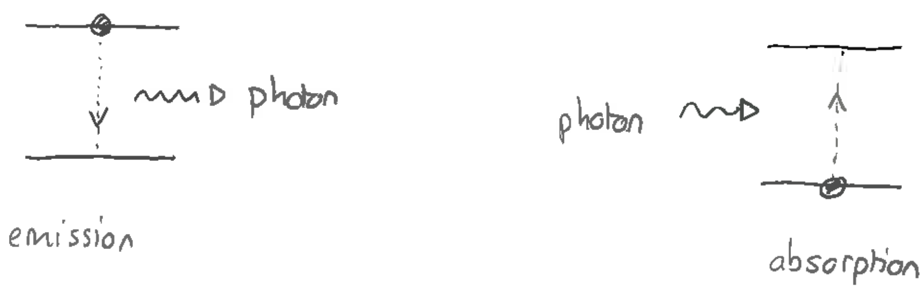


Each atom has exactly two energy levels.



It suffices to consider situations where each atom is either in energy level 1 or level 2, although many other quantum states are possible.

The exact quantum theory description of how the atom interacts with the electromagnetic field is complicated and we consider a simpler model where the atom absorbs or emits a single photon and undergoes a transition between the energy states:



In either case the frequency of the photon is related to the atomic energy levels via

$$\boxed{hf = E_2 - E_1 \qquad \text{or} \qquad f = (E_2 - E_1)/h}$$

As is typical for quantum physics situations, either absorption or emission is non-deterministic and we can only describe the probabilities with which these processes occur. This means that we need to consider a large collection of identical atoms that interact with the electromagnetic field

Ensemble of atoms interacting with a field

Suppose that many identical atoms inhabit the same cavity that hosts an electromagnetic field. We can describe the state of the atoms by the following variables:

N = total number of atoms

N_1 = number of atoms in state 1

N_2 = " " " " " 2

"populations"

Since N is fixed and

$$\boxed{N = N_1 + N_2}$$

it will suffice to describe the state of atoms via either N_1 or N_2.

Our ultimate aim will be to predict N_2 as a function of time and to use this to determine equilibrium values for N_2. We shall do this via two strategies:

Strategy 1

Develop differential equations for $N_2(t)$ and $N_1(t)$

↓

Solve differential equations and find equilibrium values of $N_2(t)$ and $N_1(t)$

Strategy 2

Assume that the field and the atoms are in thermal equilibrium at a fixed temperature

↓

Use statistical physics to determine thermal equilibrium populations

Presumably the two strategies should yield the same results. We when equate them in this way we will see a surprising result regarding the interactions between atoms and field.

Prior to this we need a description of the state of the field. It may appear that simply describing the number of photons would suffice. However, in quantum physics photons associated with different modes are to be counted independently

For cavities with more than one spatial dimension, there are many distinct modes with distinct wavevectors but the same frequency. We would

have to describe the number of photons assigned to each wavevector. But if the frequencies associated with these are the same then their interactions with the atoms, with respect to probability of emission + absorption, will be the same. Since all the photons in modes with the same frequency have the same energy, a better description of the state of the electromagnetic field would use the energy of the field, or alternatively the energy density of the field. To this end we describe the field via:

> The <u>spectral energy density</u> of the electromagnetic field is:
>
> $u(f)$
>
> which has the meaning that the energy per unit volume for all modes with frequencies $f \to f+df$ is
>
> $u(f)\,df$

Equilibrium thermodynamics of the field and atoms

Classical statistical physics gives:

> If the available energy states for a system are ϵ_i $\quad i=1,2,\ldots$
> then the probability that the system is in state i is
>
> $$\text{prob}(i) = \frac{e^{-\epsilon_i/k_BT}}{Z}$$
>
> where $Z = \sum_i e^{-\epsilon_i/k_BT}$ and $k_B =$ Boltzmann's const.

Then in this case

$$N_i = N \, prob(i)$$

$$\Rightarrow \frac{N_2}{N_1} = \frac{prob(2)}{prob(1)} = \frac{e^{-E_2/k_BT}}{e^{-E_1/k_BT}}$$

$$\Rightarrow \frac{N_2}{N_1} = e^{-(E_2-E_1)/k_BT}$$

and using $E_2 - E_1 = hf$ we get that classical statistical physics predicts:

$$\frac{N_2}{N_1} = e^{-hf/k_BT} \qquad \text{or} \qquad \frac{N_1}{N_2} = e^{hf/k_BT}$$

In general, when the energy levels are degenerate, this requires modification, but we will consider a simple non-degenerate model here. Now consider the state of the electromagnetic field. We show that

In statistical equilibrium the spectral energy density has form:

$$u(f) = \frac{8\pi hf^3}{c^3} \frac{1}{e^{hf/k_BT} - 1}$$

Proof: For photons in a single mode, the grand canonical partition function is

$$Z_G = \sum_{n=0}^{\infty} e^{-\epsilon n \beta} \qquad \beta = 1/k_BT$$

and the average energy $= \bar{\epsilon} = -\frac{1}{Z_G}\frac{\partial Z_G}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z_G$

Then

$$Z_G = \frac{1}{1-e^{-\epsilon\beta}}$$

Then $\ln Z_G = -\ln(1-e^{-\epsilon\beta})$

$$\Rightarrow \frac{\partial \ln Z_G}{\partial \beta} = -\frac{\epsilon e^{-\epsilon\beta}}{1-e^{-\epsilon\beta}} \Rightarrow \bar{\epsilon} = \frac{\epsilon e^{-\epsilon\beta}}{1-e^{-\epsilon\beta}}$$

$\Rightarrow$ for a single mode $\bar{\epsilon} = \epsilon \dfrac{1}{e^{\epsilon\beta}-1}$

and here $\epsilon = hf$ gives that, for a single mode

$$\bar{\epsilon} = hf \frac{1}{e^{hf/k_BT}-1}$$

However, there are many modes with the same frequency. To get the average energy we need to multiply $\bar{\epsilon}$ by the number of modes. We therefore need to count the number of modes. We consider a cubic cavity with sides L. Then the modes are described by wavevector $\vec{k} = (k_x, k_y, k_z)$. For waves with nodes at the sides of the cube $k_x = \frac{n_x \pi}{L}$, $k_y = \frac{n_y \pi}{L}$, ...

Then the set of all modes is described by n_x, n_y, n_z. The number of nodes in region

$$n_x \to n_x + dn_x$$
$$n_y \to n_y + dn_y$$
$$n_z \to n_z + dn_z$$

is $dn_x dn_y dn_z = \dfrac{L^3}{\pi^3} dk_x dk_y dk_z$

Passing to spherical co-ordinates for $\vec{k} = (k_x, k_y, k_z)$, i.e, k, θ, ϕ we get that the number of modes in

$$k \to k + dk$$
$$\theta \to \theta + d\theta$$
$$\phi \to \phi + d\phi$$

is $\dfrac{L^3}{\pi^3} k^2 \sin\theta \, dk \, d\theta \, d\phi$

Now $\omega = kv$ implies that all modes with the same k contribute the same frequency + energy regardless of θ, ϕ. Integrating over all θ, ϕ and changing $2\pi f = kv \Rightarrow k = \frac{2\pi}{v} f$ gives:

number of modes $f \to f+df$ is

$$\frac{L^3}{\pi^3} \left(\frac{2\pi}{v} f\right)^2 \left(\frac{2\pi}{v}\right) df \; 4\pi$$

$$= \pi L^3 \frac{8 \times 4 f^2}{v^3} df$$

This has overcounted since we only require positive k_x, k_y, k_z. Thus we get

$$\frac{4\pi L^3 f^2}{v^3} df$$

Now, there are two polarization states. Thus the number of modes is:

$$\frac{8\pi f^2 df}{c^3} V$$

where V is the volume of the cube, and we assume that the speed of light is c. It follows that the total energy in the volume is:

$$\frac{8\pi f^2}{c^3} \frac{hf}{e^{hf/k_B T} - 1} df \, V$$

This gives the energy density as $\frac{8\pi h f^3}{c^3} \frac{1}{e^{hf/k_B T} - 1} df$ and this immediately gives the correct energy density. $\blacksquare$

These results imply that

$$\boxed{\text{In thermal equilibrium:} \quad u(f) = \frac{8\pi h f^3}{c^3} \frac{1}{N_1/N_2 - 1}}$$

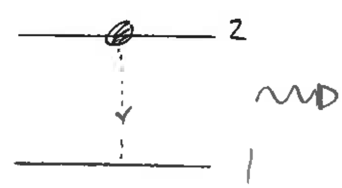
Clearly as N_1 decreases, $u(f)$ increases as this means that there is less scope for absorption and more scope for emission.

Rate Equations

In the alternative approach we consider three possible interactions

1) spontaneous emission

An atom in level 2 spontaneously drops to level 1



We assume that the probability with which this occurs in time Δt is

$$A_{21} \Delta t$$

where A_{21} is the Einstein coefficient for spontaneous emission from 2 to 1.

2) absorption

An atom in level 1 absorbs a photon and makes a transition to level 2. Probability with which this occurs in time Δt is

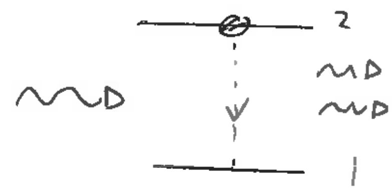
$$B_{12} \Delta t$$

where B_{12} the Einstein coefficent for absorption from 1 to 2.

3) stimulated emission

A photon interacts with an atom in state 2 causing emission of another photon and a transition to state 1. Again probability with which this occurs is

$$B_{21} \Delta t$$



Suppose that only spontaneous emission could occur. Then if the population of level 2 at time t were $N_2(t)$ then

$$N_2(t+\Delta t) = N_2(t) - A_{21} \Delta t \, N_2(t)$$

$$\Rightarrow \quad \frac{N_2(t+\Delta t) - N_2(t)}{\Delta t} = -A_{21} N_2(t)$$

$$\Rightarrow \quad \frac{dN_2}{dt} = -A_{21} N_2$$

This is an example of a rate equation and it has solution

$$N_2(t) = N_2(0) e^{-A_{21} t}$$

Now suppose all three processes are possible. Then:

$$\boxed{\begin{aligned} \frac{dN_2}{dt} &= -A_{21} N_2(t) + B_{12} u(f) N_1(t) - B_{21} u(f) N_2(t). \\ \frac{dN_1}{dt} &= A_{21} N_2(t) - B_{12} u(f) N_1(t) + B_{21} u(f) N_2(t) \end{aligned}}$$

and these are the rate equations for the populations.

In equilibrium $\frac{dN_2}{dt} = 0$ and this implies:

$$-A_{21} N_2 + B_{12} u(f) N_1 - B_{21} u(f) N_2 = 0$$

Thus

$$u(f)\left[B_{12} N_1 - B_{21} N_2\right] = A_{21} N_2$$

$$\Rightarrow u(f) = \frac{A_{21} N_2}{B_{12} N_1 - B_{21} N_2}$$

$$= \frac{A_{21}}{B_{12} N_1/N_2 - B_{21}}$$

$$= \frac{A_{21}}{B_{12}} \frac{1}{N_1/N_2 - B_{21}/B_{12}}$$

We can now compare the the statistical physics prediction. As T varies so does N_1/N_2. Thus for

$$\frac{8\pi h f^3}{c^3} \frac{1}{N_1/N_2 - 1} = \frac{A_{21}}{B_{12}} \frac{1}{N_1/N_2 - B_{21}/B_{12}}$$

to be true for all temperatures requires

$$\boxed{\frac{A_{21}}{B_{12}} = \frac{8\pi h f^3}{c^3} \quad \text{and} \quad B_{21} = B_{12}}$$

This implies that:

All three processes must exist. The probability rates for stimulated emission + absorption must be equal.!

Detailed quantum physics treatments corroborate these.