Lasers

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Contents

1 Introduction

LASER means **Light Amplification by Stimulated Emission of Radiation**. To understand the mechanism of Laser, one has to understand the concept of Energy levels (which will be studied later in Quantum Field theory).

1.1 Energy Level

An energy level is a specific, quantized state that an e^- can occupy in an atom or molecule, each with a fixed energy value. We will be studying about these energy levels in depth when we will be learning Quantum Physics.

What does an atom getting excited mean? An atom getting excited means that the atom has gained some energy (relative to its ground state). When an electron of the atom get excited, it gains energy and as an electron is part of an atom, so the atom too does gain energy. From whatever we know till now, when a photon is absorbed by an atom, it is more accurate to say that the electron has been excited. But, in this chapter, we will often keep atom as our point of reference. So, whenever we say that an atom has been excited, we refer to excitation of the outermost valence shell electron. Refer to Born-Oppenheimer approximation for a better idea on how nucleus of an atom is not affected when the photon is absorbed by the atom.

> If an electron has been excited, then the atom too gets excited but if an atom has been excited, there are many possibilities. But, in this chapter, we will be only considering the excitation of the outermost valence shell electron as the only possibility.

1.2 Energy Gap

Usually for an **isolated gaseous atom**, there are many energy levels in discrete which the electron can occupy. But, in the case of solids, due to tightly packed atoms and their orbital overlap, the discrete energy levels become very close and appear to be continuous. Such continuous energy levels are called as energy bands and the e^- can take any energy value between the lowest and highest value of energy band. The concept of energy bands will be discussed again in Band Theory of Solids in depth.

1.3 Classical Representation of Atom

In classical view (an extended version of Newtonian mechanics), these energy levels are related with the orbits of the e^- revolving around the nucleus (See figure 1).

Electron at E_2

Electron at E_1

Nucleus

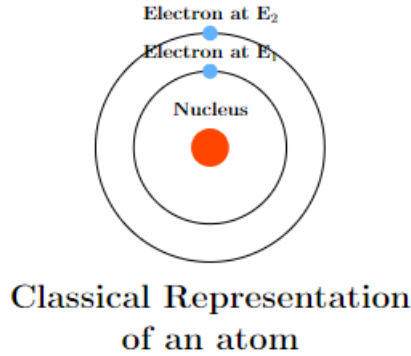**Classical Representation of an atom**

Figure 1: Classical Representation of an Atom

This idea is very outdated and is wrong as we move towards the concept of Quantum Mechanics. The atom is often represented like this in some books to keep things simple. In the quantum mechanical model of the atom, we consider electrons to be in the orbitals corresponding to their energy levels.

1.4 Energy Level Diagrams

To explain phenomena related to interaction between radiation and matter, we need a good diagrammatic representation of an atom. As stated earlier, we are not interested in outdated classical representation of atom anymore in favour of the quantum mechanical model.

Now, if we follow the quantum mechanical model, representing orbitals in an atom is highly complicated, making it even more challenging to use those diagrams to explain certain phenomena. We have discussed earlier that in this chapter we are going to equate energy states of an atom with the energy state of its outermost valence electron, i.e. when an electron excites from E_1 to E_2, the atom too excites from E_1 to E_2. So, instead of using diagrams of electrons, orbitals or orbits, we will be using the diagram of energy levels (see figure 2) to explain several phenomena.
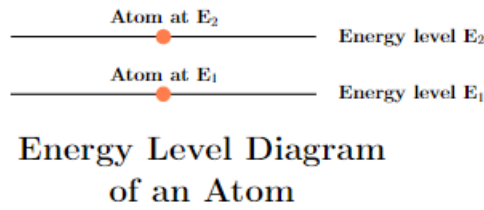
Figure 2: Energy level diagram of an Atom

This energy level diagram helps use to visualise in which energy state the atom (or its outermost valence shell e^-) is in without violating any idea of quantum mechanical model of an atom. Compare figure 2 with figure 1.

1.5 References

- Read Basavaraju's book on Engineering Physics for fundamental ideas (Chapter 5 Lasers)

- Watch this YT video for a complete animated video of the whole mechanism of LASER. The only con of this video will be its attempt of using the classical representation of atom in it.

- See this Reddit post for question on energy levels.

This page has to be updated once we complete studying Quantum Physics and its mechanics.

2 Types of Interactions

Working of laser depends on the three different ways of interaction of radiation and matter. In this chapter, there will only be an introduction to the interactions and will study them later in depth in Quantum Mechanics. **Note** that these interactions happen only in isolated atoms with discrete E levels.

2.1 Stimulated Absorption

This interaction is also called as **Induced Absorption** in some books (like in Basavaraju's) while in some others, it is called as **Stimulated Absorption**.
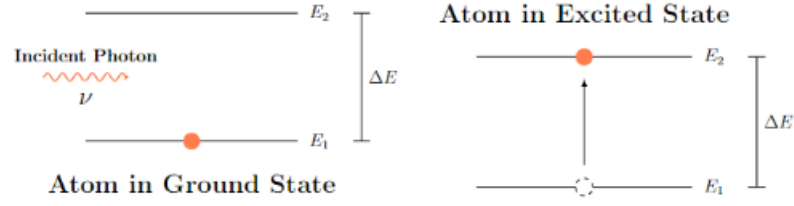
Figure 3: Stimulated Absorption

Here (and for the other 2 interactions too), assume E_1 is the ground state and E_2 is some excited state of that atom.

$$\Delta E = E_2 - E_1 \tag{1}$$

Note although E_1 will be greater than E_2 in magnitude but their values are in negative thus making the ΔE positive.

Here, the photon is absorbed by the atom to excite itself from the ground state to an excited state. This is only possible if the energy of photon is same as the energy different between two levels. So, by **Planck's formula**.

$$\Delta E = h\nu \tag{2}$$
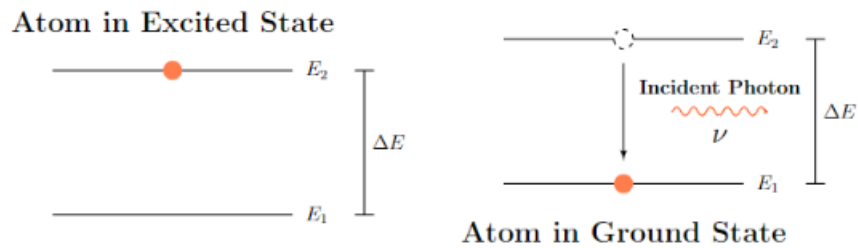
2.2 Spontaneous Emission

Figure 4: Spontaneous Emission

Any atom in an excited state is unstable and tends to de-excite to the ground state without any external aid (thus spontaneous). During this process, it emits an photon of an energy equal to the energy difference. **Note** that, there is an universal tendency for any system to be in the lowest energy state to keep itself stable.

Photons emitted by two atoms excited under (and are in) identical conditions undergoing spontaneous emission, **will not have any phase relationship** (i.e. in any direction and can have phase differences). So, photons emitted under this process are incoherent (i.e. no phase relationship). Such incoherent emissions can be seen in Thermoionic emission in bulb, candle flame, etc.
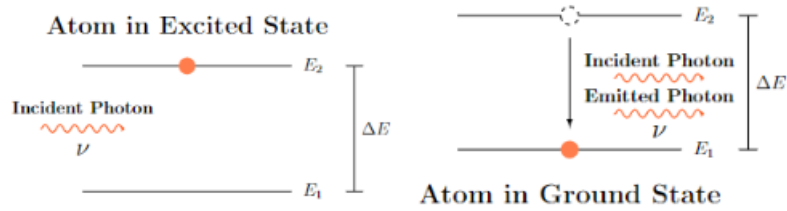
2.3 Stimulated Emission

Figure 5: Stimulated Emission

Although, atoms can get de-excited without any external aid as seen in Spontaneous emission, they can also get de-excited by an incident photon of an energy equal to the energy difference between the excited levels. When such de-excitation happens, the atom emits another photon which will be in phase (i.e. coherent) with the incident photon. This process is also referred to as "negative absorption".

3 Population distribution of Atoms in Excited states

In a system, let n_i be the number density (i.e. number of units per unit volume) of atoms existing in the energy state i. To keep things more simple in understanding the lasing process, we will use the energy level diagrams to show the distribution of atoms of system in the excited states (see figure 6). Also, by "population", we mean the "number" of atoms.
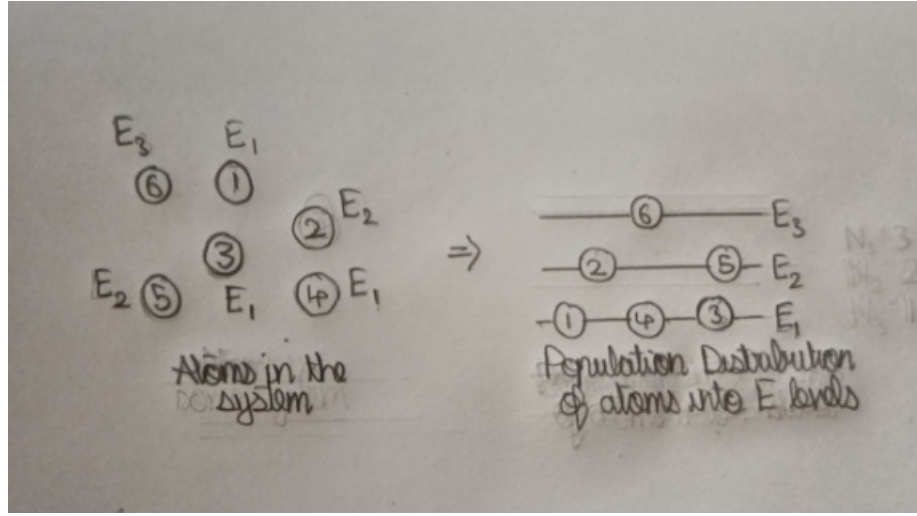
Figure 6: Population distribution of atoms in the system

Note that population distribution is only for identical atoms. In real systems, the number of atoms exceed the number of energy levels possible in that system. (??)

3.1 Rate of change of Population Density

Then, dn_i/dt will be the rate at which the number density of atoms exciting or de-exciting (depending on the sign of the derivative) from/to an energy state i.

Let's consider a system having energy states E_1, E_2, ..., E_i. Let it have a total population density (of atoms) n,

$$n_1 + n_2 + ... + n_i = n \tag{3}$$

We can differentiate this equation (w.r.t t) to get a relation between the rate of atoms exciting and de-exciting in each energy state,

$$\frac{dn_1}{dt} + \frac{dn_2}{dt} + ... + \frac{dn_i}{dt} = \frac{dn}{dt}$$

In a fixed system, we can assume n to be constant, which makes dn/dt to be 0,

$$\frac{dn_1}{dt} + \frac{dn_2}{dt} + ... + \frac{dn_i}{dt} = 0$$

In transition of atoms, involving only two states, the rates of other states

will become zero,

$$\frac{dn_1}{dt} + \frac{dn_2}{dt} = 0$$

$$\Rightarrow \frac{dn_2}{dt} = -\frac{dn_1}{dt} \tag{4}$$

3.2 Thermodynamic Equilibrium

At Thermodynamic Equilibrium, the net energy exchanged will be 0 (energy exchange will happen but the sum will be 0). Excitation and de-excitation of atoms are energy exchanges too as they involve absorbing and emitting radiation (energy), so at Thermodynamic Equilibrium, the net change in the number of excited atoms will be 0 too.

This means, for any state i at Thermodynamic Equilibrium,

$$\frac{dn_i}{dt} = 0 \tag{5}$$

3.3 Boltzmann Factor

At Thermodynamic Equilibrium, energy states having large population densities can be related with each other by the Boltzmann factor,

$$\frac{n_2}{n_1} = e^{-\frac{E_2 - E_1}{kT}} \tag{6}$$

This formula is built on approximation of the theoretical data and works only for large n values.

The derivation of this equation is given in this paper.

3.4 Non Thermodynamic Equilibrium Conditions

We know in energy level scheme, $E_2 > E_1$. By substituting this inequality in Boltzmann's equation in (6), we get $n_2 < n_1$. If we place the system at a very huge temperature (i.e. $T \to \infty$ but in equilibrium), then from equation (6), we get $n_2 \to n_1$.

As Boltzmann's equation is only valid at Thermodynamic Equilibrium, we can say n_2 is always lesser than or equal to n_1 (i.e $n_2 \leq n_1$) under Thermodynamic Equilibrium. In short, n_2 can never be greater than n_1 under Thermodynamic Equilibrium conditions.

$$n_2 \leq n_1 \text{ (under Thermodynamic Equilibrium)}$$

So, to make $n_2 > n_1$, we have to feed energy in other ways to the system resulting in non equilibrium conditions which is essential for Lasing process (will be discussed later).

4 Einstein's Coefficients

The formation of atomic spectral lines is due to the three different interactions of radiation and matter which was proposed by Einstein in 1916. In his studies, he assumed matter is in Thermodynamic Equilibrium (see 3.2) with Black Body radiation.

Each of these processes (interactions) proposed by Einstein are associated with an Einstein coefficient. Einstein considered the case of isotropic radiation of frequency ν (i.e. having same frequency in all directions the radiation is propagating at) and spectral energy density $\rho(\nu)$.

Read more about this in Wikipedia.

4.1 Spectral Energy Density

Let radiation of continous spectrum of frequencies be incident on the system. Let $\rho(\nu)d\nu$ be the energy incident per unit volume (i.e. energy density) of the radiations having frequencies between ν and $\nu + d\nu$ in the spectrum. Here, $\rho(\nu)$ is called as spectral energy density (having dimensions of $E/A\nu$) which is the energy density per frequency of radiations having frequencies between ν and $\nu + d\nu$.

Also, in some books (like in Basavaraju's), this has been represented by U_γ where the frequency is represented by γ. **Note** that, this parameter is independent of direction of radiation as we have assumed isotropic frequencies.

According to **Planck's law**, the spectral energy density is given as,

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\frac{h\nu}{kT}} - 1} \tag{7}$$

We will study about this law later in Quantum Physics.

4.2 Description of Einstein's coefficients

Let's consider two energy levels E_1 (ground state) and E_2 (some excited state) where n_1 and n_2 are the respective population densities of atoms in

those energy states. Now, let's see how the three kinds of interactions of radiation and matter are described by the Einstein's coefficients,

4.2.1 Stimulated Absorption

In this process, the atoms excite from E_1 to E_2 due to the incident radiation of frequency ν. To measure the rate of this process (and for the others too), we will consider E_1 (ground state) and its population density n_1 as reference, i.e.,

Rate of stimulated = Rate at which atoms are undergoing stimulated
absorption   absorption from E_1 to E_2
$$= (\frac{dn_1}{dt})_{st.a.}$$

And, from experiments, we know,

$$\text{Rate of stimulated absorption} \propto -n_1 \rho(\nu)$$
$$(\frac{dn_1}{dt})_{st.a.} \propto -n_1 \rho(\nu)$$

As atoms excite from E_1 to E_2, it results in decrease in n_1 (and increase in n_2) which explains the negative sign. The rate of stimulated absorption will be more if there are more atoms in the ground state E_1 to get excited to E_2 so the rate depends on n_1. This points out the fact that the rate of stimulated absorption will decrease as more and more atoms in E_1 get excited. Also, as this process is initiated by the energy of the incident radiation, it also depends on the spectral energy density of it.

The proportional constant for the equation is the Einstein coefficient B_{12} $[m^3 J^{-1} s^{-2}]$ where 12 indicates the direction of process (i.e. E_1 to E_2) and B indicates the process is stimulated (induced). After plugging the Einstein coefficient in the proportional equation, we get,

$$(\frac{dn_1}{dt})_{st.a.} = -B_{12} n_1 \rho(\nu) \tag{8}$$

To find the rate at which the atoms are getting excited to E_2 by stimulated absorption, we can substitute the above rate in the equation (4),

$$(\frac{dn_2}{dt})_{st.a.} = -(\frac{dn_1}{dt})_{st.a.} = B_{12} n_1 \rho(\nu)$$

4.2.2 Spontaneous Emission

In this process, the atoms de-excite from E_2 to E_1 spontaneously (i.e. without any external aid). Like we did for stimulated absorption, we are going to consider E_1 (ground state) as our reference to find rate of this emission.

Rate of spontaneous = Rate at which atoms are undergoing spontaneous
emission   emission from E_2 to E_1

$$= (\frac{dn_1}{dt})_{sp.e.}$$

And, from experiments, we know,

$$\text{Rate of spontaneous emission} \propto n_2$$

$$(\frac{dn_1}{dt})_{sp.e.} \propto n_2$$

As atoms de-excite from E_2 to E_1, there will be an increase in n_1 (and decrease in n_2) which explains why it has no negative sign. The rate of spontaneous emission will be more if there are more excited atoms in E_2 (i.e. n_2) to get de-excited spontaneously, so the rate depends on n_2. As this process is independent of any external aid (i.e. no incident radiation like in stimulated absorption), the rate is independent of spectral energy density.

The proportional constant for the equation is the Einstein coefficient A_{21} $[s^{-1}]$ where 21 indicates the direction of process (i.e. E_2 to E_1) and A indicates the process is spontaneous. After plugging the Einstein coefficient in the proportional equation, we get,

$$(\frac{dn_1}{dt})_{sp.e.} = A_{21}n_2 \tag{9}$$

We can get the rate of this emission keeping E_2 as our reference by applying equation (4) like we did earlier in stimulated absorption.

4.2.3 Stimulated Emission

In this process, the atoms de-excite from E_2 to E_1 due to incident of radiation of frequency ν. Taking E_1 (ground state) as our reference like we did earlier.

Rate of stimulated = Rate at which atoms are undergoing stimulated
emission   emission from E_2 to E_1

$$= (\frac{dn_1}{dt})_{st.e.}$$

And, from experiments, we know,

$$\text{Rate of stimulated emission} \propto n_2 \rho(\nu)$$

$$(\frac{dn_1}{dt})_{st.e.} \propto n_2 \rho(\nu)$$

Like in spontaneous emission, the atoms get de-excited from E_2 to E_1 making the rate dependent on the population density in excited state (i.e. n_2) and has a positive sign (due to the increase in n_1). Unlike in spontaneous emission, here the emission takes place because of the incident radiation, so the rate here depends on the spectral energy density of the incident radiation (like in stimulated absorption).

The proportional constant for the equation is the Einstein coefficient B_{21} $[m^3 J^{-1} s^{-2}]$ where 21 indicates the direction of process (i.e. E_2 to E_1) and B indicates the process is stimulated. After plugging the Einstein coefficient in the proportional equation, we get,

$$(\frac{dn_1}{dt})_{sp.e.} = B_{21} n_2 \rho(\nu) \tag{10}$$

Again, we can get the rate of this emission keeping E_2 as our reference by applying equation (4) like we did earlier in stimulated absorption.

4.3 Probability aspect of Einstein Coefficients

4.3.1 Stimulated absorption-only system

Let's take a system where atoms only undergo stimulated absorption (no stimulated emission or spontaneous emission) from its E_1 state to E_2 state when an radiation of frequency ν is incident on it.

In that system, let $P(t)$ be the probability of an atom to undergo stimulated absorption from E_1 to E_2 at time t and let $P^c(t)$ be the probability of an atom to remain in the same E_1 state at time t (i.e. not undergoing any transition),

$$P(t) + P^c(t) = 1 \tag{11}$$

As more and more atoms in E_1 undergo stimulated absorption to E_2, the population density n_1 decreases which means an atom in E_1 state has more chances (i.e. probability) to absorb the incident radiation and get excited to E_2. One can imagine it like this: if the supplies are fixed and the number of people in the crowd is decreasing, then it becomes more probable for each person in the crowd to obtain a supply. This explains

why is the probability of an atom getting excited or not is a function of time t (i.e. dependent on time t).

We can define the probability of an atom to remain in the same state (i.e. $P^c(t)$) as,

Probability of an atom to = Ratio of population density of atoms
remain in the state   in that state at t=t to the population
population density at t=0

$$\Rightarrow P^c(t) = \frac{n_1(t)}{n_1(0)} \tag{12}$$

Here, $n_1(t)$ is the population density at E_1 state at time t.

Since we assumed there is only stimulated absorption taking place in the system, the change in population density of atoms in E_1 is only due to stimulated absorption,

$$\frac{dn_1}{dt} = (\frac{dn_1}{dt})_{st.a.}$$

Now, we can plug equation (8) into it,

$$\frac{dn_1}{dt} = -B_{12}n_1\rho(\nu)$$

After rearranging the terms, we can integrate the equation on the LHS from $n_1(0)$ to $n_1(t)$ and on the RHS from 0 to t, where $n_1(t)$ is the population density n_1 at time t,

$$\Rightarrow \frac{dn_1}{n_1} = -B_{12}\rho(\nu)dt$$

$$\Rightarrow \int_{n_1(0)}^{n_1(t)} \frac{dn_1}{n_1} = \int_0^t -B_{12}\rho(\nu)dt$$

$$\Rightarrow ln(\frac{n_1(t)}{n_0(0)}) = -B_{12}\rho(\nu)(t-0)$$

$$\Rightarrow \frac{n_1(t)}{n_1(0)} = e^{-B_{12}\rho(\nu)t} \tag{13}$$

Now, we can substitute the equation (12) into it,

$$P^c(t) = e^{-B_{12}\rho(\nu)t}$$

Using equation (11), we can find the value of $P(t)$,

$$P(t) = 1 - P^c(t)$$
$$\Rightarrow P(t) = 1 - e^{-B_{12}\rho(\nu)t} \tag{14}$$

Thus, we have arrived at the equation for the probability of an atom undergoing stimulated absorption . **Note** that this has been derived under the assumption that no other interactions (such as stimulated emission or spontaneous emission) are taking place. In reality (e.g., in the lasing process), all three interactions (i.e. stimulated absorption, stimulated emission, and spontaneous emission) take place, so in such cases, we cannot apply this equation.

Interactions like stimulated absorption usually occur almost instantly, so we can consider $t \to 0$. To simplify our equation further, we can use the limit $t \to 0$, for which we will divide our equation with t first,

$$\Rightarrow \frac{P(t)}{t} = \frac{1 - e^{-B_{12}\rho(\nu)t}}{t}$$

Now, apply limits only on the RHS of the equation,

$$\Rightarrow \frac{P(t)}{t} = \lim_{t \to 0} \frac{1 - e^{-B_{12}\rho(\nu)t}}{t}$$
$$\Rightarrow \frac{P(t)}{t} = B_{12}\rho(\nu)$$
$$\Rightarrow P(t) = B_{12}\rho(\nu)t \tag{15}$$

Usually, when applying limits, we have to apply it on both sides not just on one side of the equation. However, in this case, we were trying to simplify by approximation. **Note** that if t is significant enough, this equation fails because of the approximation, so in such cases, we have to use equation (14).

Time Saving Result

Exponential functions of form like in equation (14) are very common in Physics. They can be simplified by approximation if $x \to 0$ by applying limits on the RHS.

$$y = 1 - e^{kx}$$
$$\Rightarrow y \approx -kx \quad \because x \to 0$$

By rearranging the terms in equation (15), we can arrive at,

$$B_{12} = \frac{P(t)}{\rho(\nu)t}$$

Thus, we can define B_{12} as the probability per unit time per unit energy density of the radiation field per unit frequency that an atom in E_1 absorb the incident radiation (of suitable energy) and get excited to E_2 in a system where no other interactions (processes) are taking place in a small interval of time.

A lot of books or articles (like Wikipedia), refers Einstein coefficients as "probability" and by "probability", this is what they mean. Truly speaking, Einstein coefficients are more of rate constants (which we can see even in the differential equations) than probability. As the value of einstein coefficient increases, the rate increases and as the rate increases, more atoms excite from E_1 to E_2 so there are more chances for an atom in E_1 to undergo stimulated absorption thus affecting the value of probability. So, even in a system where all kind of interactions takes place, the einstein coefficient is related to probability but not linearly proportional as derived above under several assumptions.

4.3.2 Stimulated emission-only system

Let's take a system where only atoms undergo stimulated emission from E_2 to E_1 when a radiation of frequency ν is incident on it.

In this system, let $P(t)$ be the probability of an atom to undergo stimulated emission from E_2 to E_1 at time t and let $P^c(t)$ be the probability of an atom to remain in the same E_2 state at time t (i.e. not undergoing any transition).

Unlike in absorption, where atoms move from E_1 to E_2, in emission, atoms move from E_2 to E_1, so we will be using dn_2/dt and n_2 to obtain probability equation,

$$P^c(t) = \frac{n_2(t)}{n_2(0)}$$

$P^c(t)$ represents the probability of atoms that did not undergo the process. In the absorption process, $P^c(t)$ refers to the atoms in the state E_1 that did not undergo absorption. Conversely, in the emission process, $P^c(t)$ refers to the atoms in the state E_2 that did not undergo emission. Therefore, we use n_2 instead of n_1 to determine $P^c(t)$ in the emission process.

Since we assumed there is only stimulated emission taking place in the system, the change in population density of atoms in E_2 is only due to stimulated emission,

$$\frac{dn_2}{dt} = (\frac{dn_2}{dt})_{st.e.}$$

Here, we are finding the value of dn_2/dt instead of dn_1/dt because we are interested in the value of the fraction $n_2(t)/n_2(0)$.

As we are familiar with the math and the procedure, we can skip steps,

$$\frac{dn_2}{dt} = -B_{21}n_2\rho(\nu)$$
$$\Rightarrow \frac{n_2(t)}{n_2(0)} = e^{-B_{21}\rho(\nu)t} \quad \because \text{Integrating both sides}$$
$$\Rightarrow P^c(t) = e^{-B_{21}\rho(\nu)t}$$
$$\Rightarrow P(t) = 1 - e^{-B_{21}\rho(\nu)t} \quad \because P(t) = 1 - P^c(t)$$
$$\Rightarrow P(t) \approx B_{21}\rho(\nu)t \quad \because t \to 0$$

Now, by rearranging the terms, we arrive at,

$$B_{21} = \frac{P(t)}{\rho(\nu)t}$$

Thus, we can define B_{21} as the probability per unit time per unit energy density of the radiation field per unit frequency that an atom in E_2 gets stimulated by the incident radiation (of suitable energy) and get de-excited to E_1 emitting a radiation of an equal energy in a system where no other interactions (processes) are taking place in a small interval of time.

4.3.3 Spontaneous emission-only system

Let's take a system where only atoms undergo spontaneous emission from E_2 to E_1. In this system, let $P(t)$ be the probability of an atom to undergo spontaneous emission from E_2 to E_1 at time t and let $P^c(t)$ be the probability of an atom to remain in the same E_2 state at time t (i.e. not undergoing any transition).

Since spontaneous emission is a type of emission process similar to stimulated emission, with the key difference being that spontaneous emission does not require incident radiation to be stimulated and is thus independent of the spectral energy density of the incident radiation, we can modify the equation for the probability of stimulated emission by removing $\rho(\nu)$

and changing the Einstein coefficient B_{21} to A_{21}. This modification yields the probability of spontaneous emission.

$$\frac{dn_2}{dt} = -A_{21}n_2)$$

$$\Rightarrow \frac{n_2(t)}{n_2(0)} = e^{-A_{21}t} \quad \because \text{Integrating both sides}$$

$$\Rightarrow P^c(t) = e^{-A_{21}t}$$

$$\Rightarrow P(t) = 1 - e^{-A_{21}t} \quad \because P(t) = 1 - P^c(t)$$

$$\Rightarrow P(t) \approx A_{21}t \quad \because t \to 0$$

Now, by rearranging the terms, we arrive at,

$$A_{21} = \frac{P(t)}{t}$$

Thus, we can define A_{21} as the probability per unit time per unit energy density of the radiation field per unit frequency that an atom in E_2 gets de-excited to E_1 emitting a radiation (of a suitable energy) in a system where no other interactions (processes) are taking place in a small interval of time.

4.4   Relation between the Einstein Coefficients

Let's consider system having two energy levels (like we did earlier) i.e., E_1 (ground state) and E_2 (excited state). If radiation with energy equal to ΔE between the energy states, then, all the three kind of interactions between radiation and matter will happen. So, at any point of time t,

Rate of change in = Rate at which atoms − Rate at which atoms
no. of atoms in E_i are excited from E_i are de-excited to E_i

$$\Rightarrow \frac{dn_i}{dt} = (\frac{dn_i}{dt})_{st.a.} - ((\frac{dn_i}{dt})_{sp.e.} + (\frac{dn_i}{dt})_{st.e.})$$

As we have considered, E_1 (ground state) to be our reference for rate equations, we will take $i = 1$ and plug-in the equations (8), (9), (10) in the above one,

$$\Rightarrow \frac{dn_1}{dt} = (\frac{dn_1}{dt})_{st.a.} - ((\frac{dn_1}{dt})_{sp.e.} + (\frac{dn_1}{dt})_{st.e.})$$

$$\Rightarrow \frac{dn_1}{dt} = B_{12}n_1\rho(\nu) - (A_{21}n_2 + B_{21}n_2\rho(\nu)) \tag{16}$$

Now, we can consider Thermodynamic Equilibrium which will make $dn_1/dt = 0$ by using the equation (5),

$$\Rightarrow 0 = B_{12}n_1\rho(\nu) - (A_{21}n_2 + B_{21}n_2\rho(\nu))$$
$$\Rightarrow B_{12}n_1\rho(\nu) = A_{21}n_2 + B_{21}n_2\rho(\nu) \tag{17}$$

Thus, we have arrived at an relationship between the Einstein's coefficients at Thermodynamic Equilibrium. Considering $dn_1/dt = 0$ under equilibrium conditions is called as **Detailed Balancing**.

Also, we can further manipulate the equation to get the spectral energy density of the radiation,

$$\Rightarrow \rho(\nu) = \frac{A_{21}n_2}{B_{12}n_1 - B_{21}n_2}$$
$$\Rightarrow \rho(\nu) = \frac{A_{21}}{B_{21}} \frac{1}{\frac{B_{12}n_1}{B_{21}n_2} - 1}$$

As we have already assumed Thermodynamic Equilibrium, we can substitute the Boltzmann factor of equation (6) here,

$$\Rightarrow \rho(\nu) = \frac{A_{21}}{B_{21}} \frac{1}{\frac{B_{12}}{B_{21}}e^{-\frac{E_1 - E_2}{kT}} - 1}$$

We are more interested with the frequency of incident radiation involved in the interaction (also spectral energy density is a function of that frequency), so we can substitute equation (2) here,

$$\Rightarrow \rho(\nu) = \frac{A_{21}}{B_{21}} \frac{1}{\frac{B_{12}}{B_{21}}e^{\frac{hf}{kT}} - 1} \tag{18}$$

Now, compare this equation with Planck's law in equation (7), we get,

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3} \tag{19}$$
$$B_{12} = B_{21} \tag{20}$$

Note that these relations are valid only under Thermodynamic Equilibrium conditions.

Now, B_{12} and B_{21} are same (independent of directions), we can drop the subscript notation for the coefficients when discussing equilibrium conditions, i.e., A is the Einstein coefficient for spontaneous process and B

is the Einstein coefficient for stimulated process. With this, we can make equation (13) look more simple,

$$\rho(\nu) = \frac{A}{B} \frac{1}{e^{\frac{hf}{kT}} - 1}$$

From (15), we can deduce that the probability of an atom in E_1 undergoing stimulated absorption is same as the probability of an atom in E_2 undergoing stimulated emission in equilibrium conditions. To put it simply, there is an equal probability for an atom to undergo stimulated emission or absorption by the incident radiation irrespective of its energy state under equilibrium conditions.

From (14), we can get this proportional equation,

$$\frac{A_{21}}{B_{21}} \propto \nu^3$$

Here, we can deduce that for atomic transitions involving radiations of lower frequencies, stimulated emissions are more probable ($A_{21} << B_{21}$) and for atomic transitions involving radiations of higher frequencies, spontaneous emissions are more probable ($A_{21} >> B_{21}$). Now, substituting (2) in that proportional equation gives us,

$$\frac{A_{21}}{B_{21}} \propto (\Delta E)^3 \quad \because \nu = \frac{\Delta E}{h} \tag{21}$$

From this, we can deduce that (same logic as earlier) if the energy difference between the energy levels is too low, it is more probable for the atom to undergo stimulated emission ($A_{21} << B_{21}$) and if the energy difference is too high, it is more probable for the atom to undergo spontaneous emission ($A_{21} >> B_{21}$).

This makes sense because, the instability of an excited atom increases with energy (i.e. ΔE) absorbed by it to get excited. The instability of an atom makes the atom to de-excite faster without any external aid to make itself stable which makes it probable for spontaneous emission to occur.

To understand how high is considered high and how low is considered low, we can modify Planck's law in equation (7) by substituting equation

(14) into it,

$$\rho(\nu) = \frac{A_{21}}{B_{21}} \frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

$$\Rightarrow \rho(\nu)\frac{B_{21}}{A_{21}} = \frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

$$\Rightarrow \frac{1}{\rho(\nu)}\frac{A_{21}}{B_{21}} = e^{\frac{h\nu}{kT}} - 1 \tag{22}$$

From equation (17), we can get the idea of high and low,

1) If $\Delta E = h\nu >> kT$,

$$e^{\frac{h\nu}{kT}} >> 1$$

$$\Rightarrow e^{\frac{h\nu}{kT}} - 1 >> 1$$

$$\Rightarrow \frac{1}{\rho(\nu)}\frac{A_{21}}{B_{21}} >> 1$$

$$\Rightarrow A_{21} >> B_{21}$$

Spontaneous emission becomes more probable than stimulated emission.

2) If $\Delta E = h\nu << kT$,

$$e^{\frac{h\nu}{kT}} << 1$$

$$\Rightarrow e^{\frac{h\nu}{kT}} - 1 << 1$$

$$\Rightarrow A_{21} << B_{21}$$

Stimulated emission becomes more probable than spontaneous emission.

Note that if A_{21} and B_{21} becomes comparable, we cannot say which will be more probable as it will depend on the complete probability equation (and several factors) which we will be discussing after Quantum Physics.

5   Production of Lasers