

$$\begin{aligned} \therefore AA^* \int_0^a \frac{1 - \cos\left(2\frac{\pi x}{a}\right)}{2} dx &= 1 \\ AA^* \left[\int_0^a dx - \int_0^a \cos\left(\frac{2\pi x}{a}\right) dx \right] &= 2 \\ AA^* \left[x - \frac{a}{2\pi} \left(\frac{\sin 2\pi x}{a} \right) \right]_0^a &= 2 \\ AA^* [a - 0 + 0] &= 2 \quad \text{or} \quad AA^* = \frac{2}{a} \end{aligned}$$

But $AA^* = |A|^2$ Hence $|A|^2 = \frac{2}{a}$,

Assuming A to be real, we get $A = \sqrt{2/a}$

Therefore, normalized wave function is

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$

1.15 ENERGY LEVELS

In the previous section, we learnt that light energy cannot take arbitrary values but must be multiples of photon energy $h\nu$. It was similarly established that the electrons in an atom cannot have arbitrary amounts of energy but they take only discrete energies. This is a consequence of the Bohr's postulate of permitted orbits. In each of the permitted (stationary) orbits, the electron has a specific amount of energy and cannot possess any other energy value. The energy of electron at a very large distance from the nucleus is purely kinetic energy and it is assigned a positive value. As the distance between nucleus and electron decreases, the kinetic energy decreases. When the electron is just about to come under the influence of nucleus, its energy becomes zero. When the electron becomes bound to the nucleus and orbits round it, electron energy is potential in nature and treated as a negative quantity. Among the infinite number of mechanically possible orbits, only a certain set of orbits are actually permissible for electron due to quantum restrictions. These permitted orbits are characterized by allowed energy values. We therefore say that electron in an atom can occupy only certain energy levels. The energy levels are schematically represented by horizontal lines drawn to an energy scale. For example, electron orbits and the corresponding energy levels of the hydrogen atom are shown in Fig.1.7. The atom is in its lowest possible energy level when the electron is in

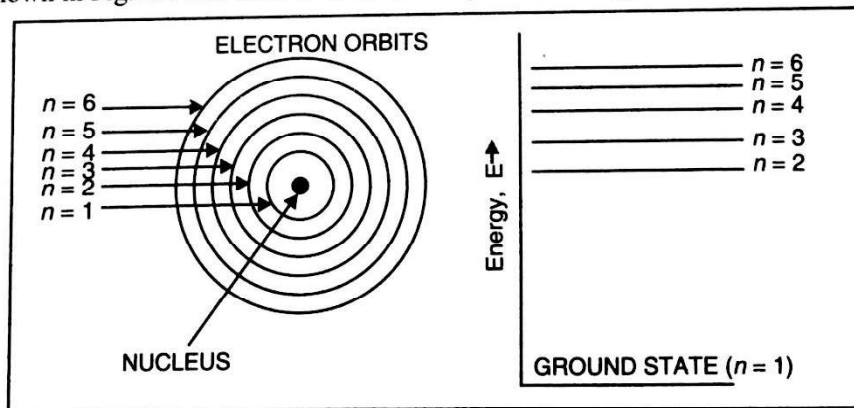


Fig. 1.7. Electron orbits and the corresponding energy levels of the hydrogen atom

the innermost orbit, closest to the nucleus. Then, the atom is said to be in the *ground state*. An electron in this ground state is stable and moves in this orbit continuously without emitting energy. If an electron in ground state absorbs energy in some way, it will go to a higher energy level and the atom is said to be *excited*. The passing of an electron from one energy level to another level within the atom occurs in a jump which is called a *quantum transition*. The electron transitions may be induced by a variety of ways. Interaction with light photons is one of the means of supplying energy to orbital electrons which causes upward electron transitions and sends the atom into its excited state.

1.16 POPULATION

The atoms of each chemical element have their own characteristic system of energy levels. The energy difference between the successive energy levels of an atom is of the order of 1 eV to 5 eV. The energy levels are common to all the atoms in a system which is composed of identical atoms. We can therefore say that a certain number of atoms occupy a certain energy state. The number of atoms per unit volume that occupy a given energy state is called the *population* of that energy state. The population N of an energy level E depends on the temperature T . Thus,

$$\boxed{N = e^{-E/kT}} \quad \text{Boltzmann's equation} \quad \dots(1.41)$$

where k is known as the Boltzmann constant.

In a material, atoms are distributed differently in different energy states. The atoms normally tend to be at their lowest possible energy level which need not be the ground state. At temperatures above 0 K, the atoms always have some thermal energy and therefore, they are distributed among the available energy levels according to their energy.

1.17 THERMAL EQUILIBRIUM

At thermal equilibrium, the number of atoms (population) at each energy level decreases with the increase of energy level, as shown in Fig. 1.8.

If we, in particular, consider two energy levels E_1 and E_2 as in Fig. 1.9, their population can be computed with the help of Boltzmann equation (1.41). Thus,

$$\text{and} \quad N_1 = e^{-E_1/kT} \quad \dots(1.42)$$

$$N_2 = e^{-E_2/kT} \quad \dots(1.43)$$

The ratio of the population in these two states, N_2/N_1 , is called the *relative population*. It is given by

$$\frac{N_2}{N_1} = \frac{e^{-E_2/kT}}{e^{-E_1/kT}}$$

or

$$\boxed{\frac{N_2}{N_1} = e^{-(E_2 - E_1)/kT}} \quad \dots(1.44)$$

It follows from the above that

$$\boxed{N_2 = N_1 e^{-\Delta E/kT}} \quad \dots(1.45)$$

where

$$\Delta E = (E_2 - E_1)$$

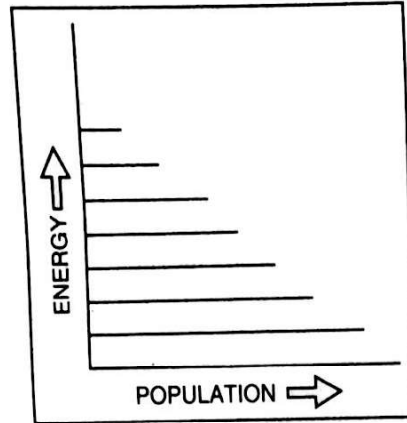


Fig. 1.8. Relative populations of energy levels as a function of energy above the ground state at thermal equilibrium.

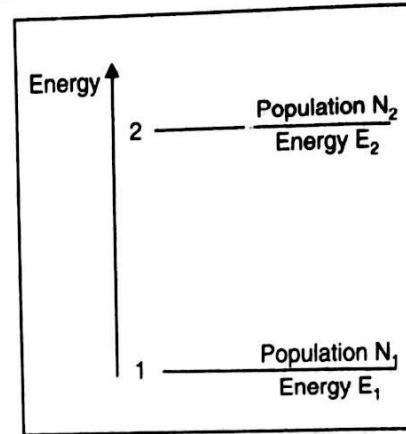


Fig. 1.9. Two energy level system.

The plot of the equation (1.45) is known as *Boltzmann distribution*.

Eq. (1.44) suggests that the relative population N_2/N_1 is dependent on two factors: (i) the energy difference ($E_2 - E_1$) and (ii) the temperature T . For the sake of estimation, let us assume hydrogen gas to be a monoatomic gas and find out the atomic population at room temperature at the first excited level. Here $E_1 = -13.6$ eV, $E_2 = -3.39$ eV and $T = 300$ K. Thus,

$$\begin{aligned}
 +\Delta E &= +(E_2 - E_1) = +[(-3.39) - (-13.6)] \text{ eV} = +10.21 \text{ eV} \\
 kT &= (8.6 \times 10^{-5} \text{ eV/K}) (300 \text{ K}) = 0.025 \text{ eV} \\
 \frac{N_2}{N_1} &= e^{\frac{-10.21 \text{ eV}}{0.025 \text{ eV}}} = e^{-408.4} \approx 0
 \end{aligned}$$

It means that at room temperature all atoms are in the ground state. If temperature is raised, say to 6000K

$$\frac{N_2}{N_1} = e^{\frac{-10.21}{0.516}} = e^{-19.79} = 2.5 \times 10^{-9}$$

We thus find that in a material at thermal equilibrium, more atoms are in the lower energy state than in the higher energy state. We call such a distribution of atoms as *normal distribution*. Thermal collisions, on one hand, make some atoms jump into higher energy state but, on the other hand, bring some atoms down to lower energy state. On the whole, the Boltzmann distribution will be maintained.

There is an important implication of Eq. (1.44) that we should understand. The fraction of excited atoms would be large, if the energy levels are close or the temperature is very high. In the limiting case $E_2 - E_1 = 0$, we find that

$$\frac{N_2}{N_1} = e^0 = 1$$

$$\therefore N_2 = N_1$$

Similarly, when $T \rightarrow \infty$,

$$\frac{N_2}{N_1} = e^0 = 1$$

$$\therefore N_2 = N_1$$

Therefore, as long as the material is in thermal equilibrium, the population of the higher state cannot exceed the population of the lower state. This is a very important conclusion to be borne in mind.

Example 1.25. Find the relative population of the two states in a ruby laser that produces a light beam of wavelength 6943 \AA at 300 K and 500 K .

Solution : The population ratio is given by

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

$$E_2 - E_1 = h\nu = \frac{hc}{\lambda} = \frac{12400}{\lambda} \text{ eV}$$

$$\therefore E_2 - E_1 = \frac{12400}{\lambda} \text{ eV} = 1.79 \text{ eV}$$

$$(a) \therefore \frac{N_2}{N_1} = \exp \left[\frac{-1.79 \text{ eV}}{(8.61 \times 10^{-5} \text{ eV/K}) \times 300 \text{ K}} \right] = e^{-69.3}$$

$$= 8 \times 10^{-31}$$

$$(b) \left[\frac{N_2}{N_1} \right]_{500\text{K}} = \exp \left[\frac{-1.79 \text{ eV}}{(8.61 \times 10^{-5} \text{ eV/K}) \times 300 \text{ K}} \right] = e^{-69.3}$$

$$= e^{-41.58}$$

$$= 8.7 \times 10^{-19}$$

Example 1.26. Find the ratio of population of the two states in a He-Ne laser that produces light of wavelength 6328 \AA at 27° C .

Solution :
$$\frac{N_2}{N_1} = e^{-(E_2 - E_1)/kT}$$

$$\therefore E_2 - E_1 = \frac{12400}{6328} \text{ eV} = 1.96 \text{ eV}$$

$$\therefore \frac{N_2}{N_1} = \exp \left[\frac{-1.96 \text{ eV}}{(8.61 \times 10^{-5} \text{ eV/K}) \times 300 \text{ K}} \right] = e^{-75.88}$$

$$= 1.1 \times 10^{-33}$$

Example 1.27. Find the ratio of population of two energy states of the Ruby laser, the transition between which is responsible for the emission of photon of wavelength $\lambda = 6928 \text{ \AA}$. Assume the ambient temperature is 18 K . (GBTU, 2010)

Solution : Given $\lambda = 6928 \text{ \AA} = 6928 \times 10^{-10} \text{ m}$
 $T = 18 \text{ K}$

$$E_2 - E_1 = h\nu = \frac{hc}{\lambda}$$

$$= 6.6 \times 10^{-34} \times 3 \times 10^8 / 6928 \times 10^{-10}$$

$$= 0.0028 \times 10^{-16} \text{ J.}$$

The ratio of population of two energy states is given by

$$\frac{N_2}{N_1} = e^{-\left(\frac{h\nu}{kT}\right)}$$

$$= e^{-\left(\frac{0.0028 \times 10^{-16}}{1.38 \times 10^{-23} \times 18}\right)} = e^{-(0.0001127 \times 10^7)} = e^{-1127} \cong 0 \text{ (approx.)}$$

Example 1.28. The ratio of population of two energy levels out of which upper one corresponds to a metastable states is 1.059×10^{-30} . Find the wavelength of light emitted at temperature $T = 330 \text{ K}$. (GBTU, 2010)

Solution : Given :

$$\frac{N_2}{N_1} = e^{\left(\frac{-hv}{kT}\right)} = 1.059 \times 10^{-30}$$

$$T = 330 \text{ K}$$

$$h = 6.6 \times 10^{-34} \text{ J sec.}$$

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

\therefore Frequency,

$$\nu = -\log_e \left[\frac{N_2}{N_1} \right] \frac{kT}{h} = -\log_e (1.059 \times 10^{-30}) \times \frac{kT}{h}$$

$$\lambda = \frac{c}{\nu} = 3 \times 10^8 / \nu$$

$$\lambda = \frac{-3 \times 10^8 \times 1.38 \times 10^{-23} \times 6.6 \times 10^{-34}}{\log_e (1.059 \times 10^{-30}) \times 1.38 \times 10^{-23} \times 330}$$

$$= 1.1 \times 10^{-7} \text{ m}$$

1.18 ABSORPTION AND EMISSION OF LIGHT

In an atom, an electron in the ground state is stable and moves continuously in that orbit without radiating energy. When the electron receives an amount of energy equal to the difference of energy of the ground state and one of the excited states (*i.e.* outer orbits), it absorbs energy and jumps to the excited state. There are a variety of ways in which the energy may be supplied to the electron. One way is to illuminate the material with light of appropriate frequency $\nu = (E_2 - E_1)/h$. The photons of energy $h\nu = (E_2 - E_1)$ induce electron transitions from the energy level E_1 to the level E_2 , as shown in Fig.1.10.

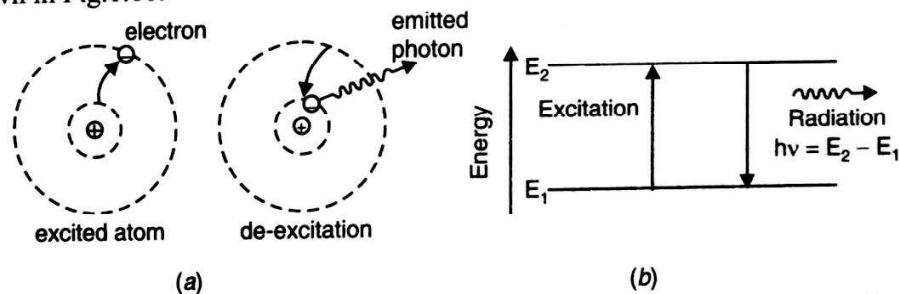


Fig. 1.10 (a) Absorbing energy, electron jumps from an inner orbit to an outer orbit. When the electron returns to the inner orbit, it emits the same energy in the form of a photon. (b) energy level representation of excitation and de-excitation of the atom

However, the electron cannot stay in the outer orbit (excited state) for a longer time. The Coulomb attraction due to the positive nucleus pulls the electron back to the initial inner orbit and the electron returns to the ground state. The excited electron has excess energy equal to $(E_2 - E_1)$ and it has to get rid of this energy in order to come to the lower energy level. The only mechanism through which the electron can lose its excess energy is through the emission of a photon. Therefore, the excited electron emits a photon of energy $h\nu = (E_2 - E_1)$ and returns to the ground state. This is the visualization of emission of light according to Bohr's quantum theory.

When we see light from any source, we actually "see" electrons jumping from excited states to lower states. This type of emission of light which occurs on its own is known as *spontaneous emission* and is responsible for the light coming from candles, electric bulbs, fire, stars, sun etc. conventional sources of light.

1.19 EINSTEIN'S PREDICTION

Einstein predicted in 1917 that there must be a second emission process to establish thermodynamic equilibrium. For example, if we illuminate a material with light of suitable frequency, the atoms in it absorb light and go to higher energy state.

The excited atoms tend to return randomly to the lower energy state. As the ground state population is very large, more and more atoms are excited under the action of incident light and it is likely that a stage may be reached where all atoms are excited. This violates thermal equilibrium condition. Therefore, Einstein suggested that there could be an additional emission mechanism, by which the excited atoms can make downward transitions. He predicted that the photons in the light field induce the excited atoms to fall to lower energy state and give up their excess energy in the form of photons. He called this second type of emission as *stimulated emission*.

1.20 THE THREE PROCESSES

When radiation is incident on a medium, three quantum mechanical process may occur:

- (a) The photons of the incident radiation are absorbed by the atoms in the medium and the atoms go into excited states. This process is called absorption.
- (b) The excited atoms return to the ground state on their own accord and emit the energy difference in the form of photons. This process is called spontaneous emission.
- (c) The excited atoms get de-excited by the incident photons and they fall to the ground state emitting the extra energy in the form of photons. This process is called stimulated emission.

The process of absorption causes loss of photons. In the process of spontaneous emission light is emitted in all directions. This process dominates in all conventional and natural light sources.

In the process of simulated emission, photons are multiplied and their characteristics are related to each other. Hence, amplification of light takes place. This process is made to dominate in the laser light source.

Let us consider a medium consisting of identical atoms capable of being excited from the energy level 1 to the energy level 2 by absorption of photons. Let the levels be denoted by E_1 and E_2 and their populations be N_1 and N_2 respectively. Let the atoms be in thermal equilibrium. In the equilibrium condition, the number of atomic transitions upward must be equal to the number of downward transitions. Thus no net photons are generated or lost. However, when the atoms are subjected to an external light of frequency ν , the following three processes occur in the medium.

(a) Absorption

An atom residing in the lower energy level E_1 may absorb the incident photon and jump to the excited state E_2 as depicted in Fig. 1.11. This transition is known as *induced* or *stimulated absorption* or simply as *absorption*. Corresponding to each absorption transition, one photon disappears from the incident light field and one atom adds to the population at the excited energy level E_2 . This process may be represented as



where A denotes an atom in the lower state and A^* an excited atom.

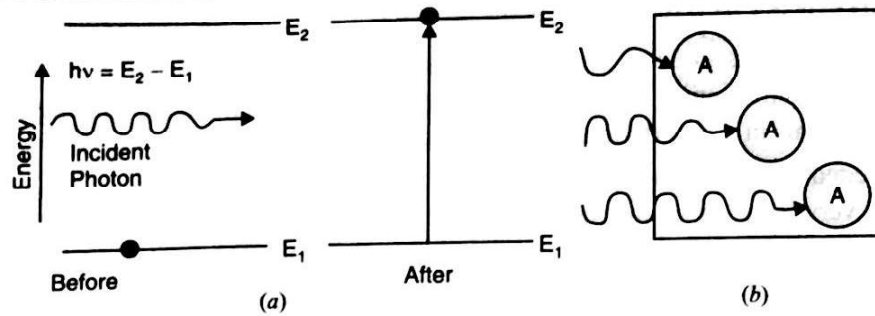


Fig. 1.11 Absorption process (a) Induced absorption (b) Material absorbs photons.

The number of atoms per unit volume that makes upward transitions from the lower level to the upper level per second is called the *rate of absorption transition*. It is represented by

$$R_{abs} = \frac{-dN_1}{dt}$$

where $-(dN_1/dt)$ stands for the rate of decrease of population at the lower level E_1 . The rate of absorption transition can also be represented by the rate of the increase of population at the upper level E_2 . Thus,

$$R_{abs} = \frac{dN_2}{dt}$$

$$\therefore R_{abs} = \frac{-dN_1}{dt} = \frac{dN_2}{dt} \quad \dots(1.47)$$

The number of absorption transitions occurring in the material at any instant will be proportional to the population in the lower level and the number of photons per unit volume in the incident beam. The rate of absorption may be expressed conveniently as

$$R_{abs} = B_{12} \rho(\nu) N_1 \quad \dots(1.48)$$

where B_{12} is a constant of proportionality, and $\rho(\nu)$ is the energy density of incident light. B_{12} is known as the *Einstein coefficient for induced absorption* and it indicates the probability of an induced transition from level $1 \rightarrow 2$.

At thermal equilibrium, the population in the lower energy state is far larger than that in the higher energy state. Therefore, as light propagates through the medium, it gets absorbed.

(b) Spontaneous Emission

An excited atom can stay at the excited level for an average lifetime τ_{sp} . If it is not stimulated by any other agent during its short lifetime, the excited atom undergoes a transition to the lower energy level on its own. During the transition, it gives up the excess energy in the form of a photon, as shown in Fig. 1.12. This process in which an excited atom emits a photon all by itself and without any external impetus is known as *spontaneous emission*.

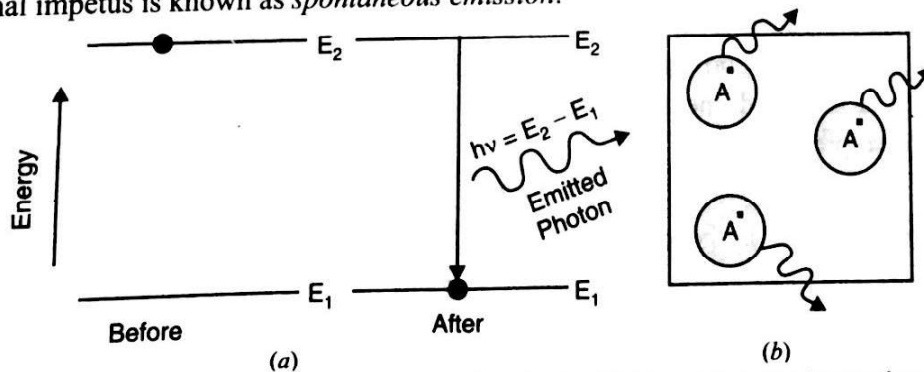


Fig. 1.12. Spontaneous emission process (a) emission (b) Material emits photons haphazardly.

The process is represented as,



The rate of spontaneous transitions, R_{sp} , is given by,

$$R_{sp} = \frac{-dN_2}{dt} = \frac{N_2}{\tau_{sp}} \quad \dots(1.50)$$

The number of photons generated will be proportional to the population of the excited level only and may be expressed as follows :

$$R_{sp} = A_{21}N_2 \quad \dots(1.51)$$

where A_{21} is known as the *Einstein coefficient for spontaneous emission* and is a function of frequency and properties of the material. It indicates the probability of a spontaneous transition from level $2 \rightarrow 1$. It is to be noted from eq.(1.51) that the process of spontaneous emission is independent of the light energy.

A comparison of equations (1.50) and (1.51) establishes that

$$A_{21} = 1/\tau_{sp} \quad \dots(1.52)$$

Thus, the reciprocal of the coefficient A_{21} is the time for the spontaneous transition τ_{sp} and represents the *lifetime of the spontaneous emission* also. It is the average time for which the excited atom would remain in the upper level before undergoing spontaneous transition.

It follows from quantum mechanical considerations that spontaneous transitions take place from a given state only to states lying lower in energy. Therefore, spontaneous transitions cannot occur from level E_1 to level E_2 . The rate of spontaneous transitions from E_1 to E_2 is zero.

$$\therefore A_{12} = 0 \quad \dots(1.53)$$

Important Features :

1. The process of spontaneous emission is not amenable for control from outside.
2. It is essentially probabilistic in nature.

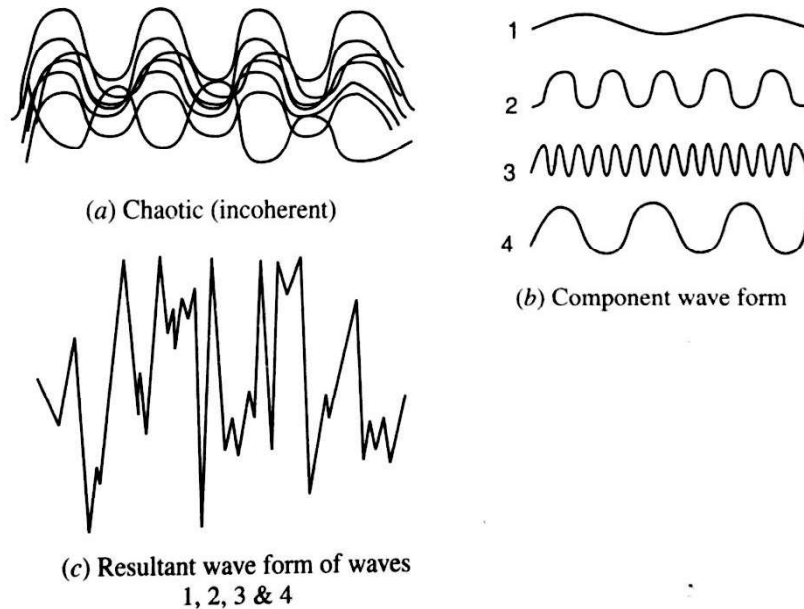


Fig. 1.13. Incoherent radiation (a) Incoherent waves, (b) component wave form (c) Resultant wave.

3. The instant of transition, direction of propagation, the initial phase and the plane of polarization of each photon are all random. They are different for different photons emitted by various atoms. Thus, an atom can radiate into any of the 4π steradians with any sense of polarization.
4. The light is not monochromatic because of various line broadening processes.
5. Because of lack of directionality, the light spreads in all directions around the source. The light intensity goes on decreasing rapidly with distance from the source.
6. The light is incoherent. It results from a superposition of wavetrains of random phases as depicted in Fig. 1.13. The net intensity due to superposition of incoherent waves is proportional to the number of radiating atoms. Thus,

$$I_{Total} = NI \quad \dots(1.54)$$

where I is the intensity of light emitted by one atom.

The process of spontaneous emission dominates in conventional light sources.

If only the two processes, namely absorption and spontaneous emission exist, then under the equilibrium condition,

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

$$B_{12} \rho(\nu) N_1 = A_{21} N_2$$

or

$$\rho(\nu) = \frac{A_{21} N_2}{B_{12} N_1}$$

\therefore

$$\rho(\nu) = \frac{A_{21}}{B_{12}} e^{-h\nu/kT}$$

The above equation does not correspond to Planck's equation for radiation in thermal equilibrium. Planck's equation was confirmed experimentally and derived theoretically.

From the equations (1.51) and (1.48), we understand that the probability of a spontaneous transition is determined only by the population at the higher energy level whereas the probability of an absorption transition is determined by two factors, namely, (i) the population at the lower energy level and (ii) the density of light energy. If absorption and spontaneous emission were the only processes operative, obviously the number of atoms absorbing radiation per second would be more than the number of atoms emitting light per second. Eventually, we may end up with a non-equilibrium condition where almost all the atoms are excited. But this is not observed in practice. It means that equilibrium is maintained. In order to account for the existence of the state of equilibrium between light and matter, Einstein concluded that *if a photon can stimulate an atom to move from a lower energy state N_1 to higher energy state N_2 by means of absorption, then a photon should also be able to stimulate an atom from the same upper state N_2 to the lower state N_1 .* This alternative mechanism of photon emission depends on the photon density present and is called stimulated emission.

(c) Stimulated Emission

An atom in the excited state need not "wait" for spontaneous emission to occur. If a photon with appropriate energy ($h\nu = E_2 - E_1$) interacts with the excited atom, it can trigger the atom to undergo transition to the lower level and to emit another photon, as shown in Fig.1.14.