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Chapter 4

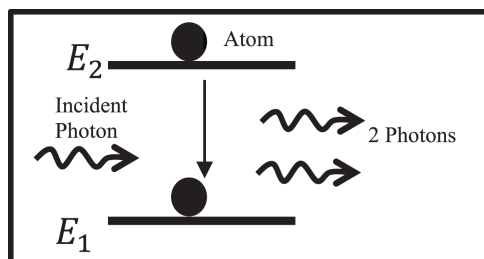# Spontaneous and stimulated emission

The full form of the acronym **laser** is '*light amplification by stimulated emission of radiation*'. Historically, the term 'radiation' referred to the 'quantum' of energy emitted by a hot body. The radiation density when plotted against the wavelength had its maximum shifted to shorter wavelengths at higher temperatures. The theoretical model based on Wein's law was unable to explain this in the ultraviolet region. Planck explained this 'ultraviolet catastrophe' by suggesting an empirical formula known as 'Planck's radiation law', which stated that the number of radiation emitters in an energy state is given by the Boltzmann distribution at room temperature. The relationship between spontaneous and stimulated emission was given by Einstein in his famous paper of 1917. The diagram shows how an incident photon stimulates an atom in the excited state to emit a photon of the same frequency. You will learn in this chapter why and how the amplification of EM radiation was achieved in the microwave region (in the form of the *maser*) before the *laser* came into existence.

Learning objectives
Describe the temperature dependence of radiation density;
Identify the Boltzmann distribution;

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Write down the rate equations for a two-level system;
Differentiate between spontaneous and stimulated emission rates;
Describe Einstein's *A* and *B* coefficients;
Relate Planck's law of radiation to the radiation density in a two-level system;
Understand the concept of the lifetime of an excited state;
Illustrate the frequency dependence of the ratio of stimulated and spontaneous emission.

4.1 Thermal radiation and Planck's law

4.1.1 Radiation density in a cavity

According to the first law of thermodynamics, a hot body tries to be in thermal equilibrium with its surroundings. Heat is radiated in the forms of temperature and EM radiation. Generally, black-body radiation is the EM radiation emitted by a body in thermodynamic equilibrium with its surroundings. For example, mosquitoes and other insects are able to sense the heat of the human body. IR-based temperature sensors are used in monitoring fever as well as in night-vision equipment. Stars with different temperatures appear in various colors. For example, Betelgeuse in the constellation of Orion is a red star with a temperature of about 3500 °C, while Rigel is blue (10 000 °C). Apart from the Sun, fire was also the source of heat and light that was directly accessible to humans on earth. Edison's incandescent filament bulb is a source of photons from the visible (light) region to the IR region (heat).

♣ If you have ever come across a bonfire or a furnace in a laboratory, you may be able to identify the different colors of fire, predominantly red (burning coals) to yellow (flames). Occasionally, part of the flame can be bluish as well—suggesting higher temperatures.

4.1.2 Density of modes in a closed container

We consider a cubic box with perfectly reflecting walls in 3D (figure 4.1). In such a cavity, a standing wave can be formed if the width (L) of the cube is an integral number of half wavelengths ($\lambda/2$) of the radiation present. For the wave vector k, this can be expressed as $\lambda/2 \equiv q\pi/k$, with $q = 1, 2, 3,\ldots$. The corresponding frequency (ν_q) is $\frac{qc}{2L}$. The components of wave vector along the three axes are given by $k_x = \frac{q_x\pi}{L}$, $k_y = \frac{q_y\pi}{L}$, and $k_x = \frac{q_z\pi}{L}$. Each mode characterized by the integers (q_x, q_y, and q_z) is represented by a point in k-space.

The frequency ν and the wave vector k satisfy the resonance condition $k^2 = k_x^2 + k_y^2 + k_z^2 = \left(\frac{2\pi\nu}{c}\right)^2$. Here, the surface of the constant frequency ν is a sphere of radius k. The number of modes (N) within the frequency range is equal to the number of points within the radius k. N can be large, but it can be approximated by the volume of one portion of the cube in the positive quadrant of a sphere of radius q ($=k\pi/L$) as $\frac{1}{8}\left(\frac{4}{3}\pi q^3\right)$. For two states of polarization, it is multiplied by a factor of two. Therefore, the number of available modes in terms of ν can be given by
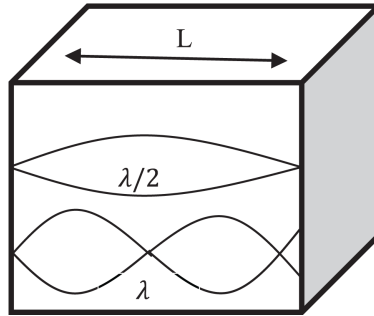
Figure 4.1. Cubic box of length L with perfectly reflecting walls called a cavity, which can contain integral multiples of half wavelengths ($\lambda/2$).

$$N = 2 \times \frac{1}{8}\left(\frac{4}{3}\pi q^3\right) \equiv \frac{8\pi\nu^3}{3c^3}L^3.$$

Here, L^3 is the volume (V) of the cavity. Differentiating this expression gives the number of modes per unit frequency interval

$$\frac{\mathrm{d}N}{\mathrm{d}\nu} = \left(\frac{8\pi\nu^2}{c^3}\right)V. \tag{4.1}$$

The number of modes per unit frequency bandwidth per unit volume $\left(\frac{8\pi\nu^2}{c^3}\right)$ is known as the Jeans number. It is also known as the number of oscillators or the 'density of modes'.

Exercise 4.1. Find the mode density for a 1D cavity.

    Solution: Let the length of the 1D cavity be L in the x direction. We have $L = \frac{\lambda_x}{2}; \frac{2\lambda_x}{2}; \frac{3\lambda_x}{2};$ so that for any number n,

$\frac{n\lambda_x}{2} = L; \lambda = \frac{2L}{n}$

$\nu_n = \frac{c}{2L}n, \left(\nu_{n+1} - \nu_n \equiv \partial\nu = \frac{c}{2L}\right).$

The mode density in a length L for two polarizations

$$g(\nu)\mathrm{d}\nu = \frac{2}{L}\left(\frac{(\nu + \mathrm{d}\nu - \nu)}{\partial\nu}\right) = \frac{4\mathrm{d}\nu}{c}$$

4.1.3 Wein's displacement law

The black-body radiation intensity $I(T)$ emitted from an opening in the cavity of a black body of temperature T is given by an empirical relation obtained by Stefan (in 1879), and later theoretically derived by Boltzmann (in 1884). According to this law, the total radiation intensity (W m^{-2}) emitted by a body is proportional to the fourth power of T, as follows:

$$I(T) = \sigma T^4$$

where $\sigma = 5.68 \times 10^{-8}$ W m^{-2} K^{-4} is known as the Stefan–Boltzmann constant. This formula also includes another constant known as emissivity ($\epsilon_M(\nu)$), a quantity specific to the material. The value of $\epsilon_M(\nu)$ ranges from zero to one. Here, for a perfect black body, its value is taken to be one.

Classically, the average energy per mode is k_BT. Here, k_B is the Boltzmann constant. The energy density of radiation per unit volume within a frequency range between ν and $\nu + d\nu$ is given by the Rayleigh–Jeans (RJ) law, as described below. From equation (4.1), the RJ law gives the energy density per unit frequency $\rho(\nu)$ as k_BT multiplied by the number of modes per unit frequency interval per unit volume as

$$\rho(\nu) = \left(\frac{8\pi\nu^2}{c^3}\right)k_BT, \tag{4.2}$$

where the emitted radiation intensity is expressed as a function of frequency and temperature $I(\nu, T)$, as follows:

$$I(\nu, T) = \int \rho(\nu)d\nu.$$

As shown in figure 4.2, the experimentally obtained values of $I(\nu,T)$ show a peak wavelength that follows the classic Wein's displacement law given by

$$\lambda_{\max}T = 2.8978 \times 10^{-3}\,\text{m K}.$$

The $I(\nu, T)$ spectra obtained for a black body at three temperatures are shown in figure 4.2. The maximum of the curves ($\lambda_{\max}$) shifts to lower wavelengths (higher frequencies) as the temperature of the body is increased. This reveals the fact that
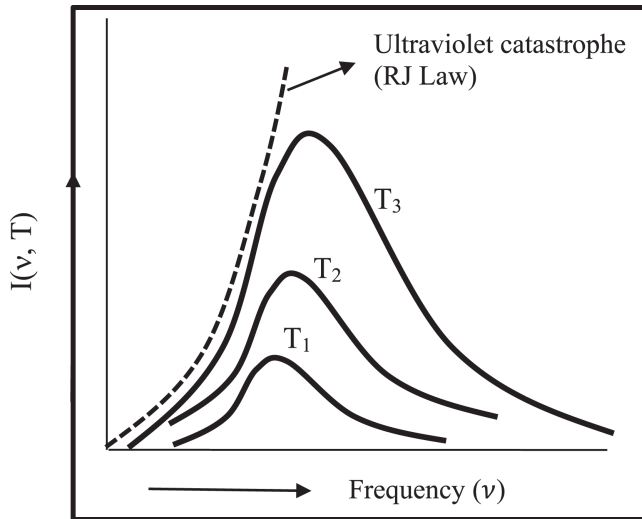

Figure 4.2. Plot of radiation intensity $I(\nu,T)$ versus frequency (ν) for a body at three temperatures $T_1 < T_2 < T_3$. The dashed line shows the theoretical prediction obtained via the RJ law.

cold objects emit at longer wavelengths (or lower frequencies). Hot objects emit many more frequencies with a shift of the peak to shorter wavelengths.

The attempts to explain these results using classical theories were unsuccessful. Figure 4.2 also shows the curve of $I(\nu, T)$ predicted by the RJ law (equation (4.2)). One can see that it agrees with the experimental values at lower frequencies, but deviates drastically from the experimental values at higher frequencies or in the UV region. This deviation was popularly known as the 'ultraviolet catastrophe' and was later explained by Planck (♠ see section 4.3).

Exercise 4.2. An optoelectronics engineer in the department of climate protection has to design a device for *animal detection* to be used in the forest at night. What typical wavelength (λ_{max}) of radiation should be considered for the components of the device?

Solution: The body temperatures of animals range between 37 °C and 41 °C. For example, for humans, the typical body temperature is above 35 °C (or 308 K). Using Wein's law, we can obtain the wavelength, as follows:

$$\lambda_{max} = 2.8978 \times \frac{10^{-3} \quad \text{m K}}{308 \text{K}} = 9.40 \times 10^{-6} \quad \text{m.}$$

Therefore, the device must have sensitivity in the IR region.

4.2 Boltzmann statistics

As described in chapter 2, in an atomic or molecular system, there are infinite set of discrete energy levels. The population (N_j) of an energy level with energy E_j in thermal equilibrium is given by Boltzmann statistics, as follows:

$$N_j = \frac{g_j N_0 e^{-E_j/k_B T}}{\sum_i g_i e^{-E_j/k_B T}}. \tag{4.3}$$

Here, $\sum_i g_i e^{-E_j/k_B T}$ is known as the partition function (z). Equation (4.3) shows that when E_j increases, N_j decreases, as shown in figure 4.3. Here, g_i and g_j are the degeneracies, or the statistical weights of the two states. For high-density materials such as solids, the energy levels may be continuously distributed or separated—depending upon the state of the matter. The probability per unit energy $g(E)$ of finding a fraction of atoms excited to energy level E is given by

$$g(E) = \frac{1}{KT} e^{-E/k_B T}.$$

The distribution of the population (N) in a state at temperature T is given by the Boltzmann distribution:
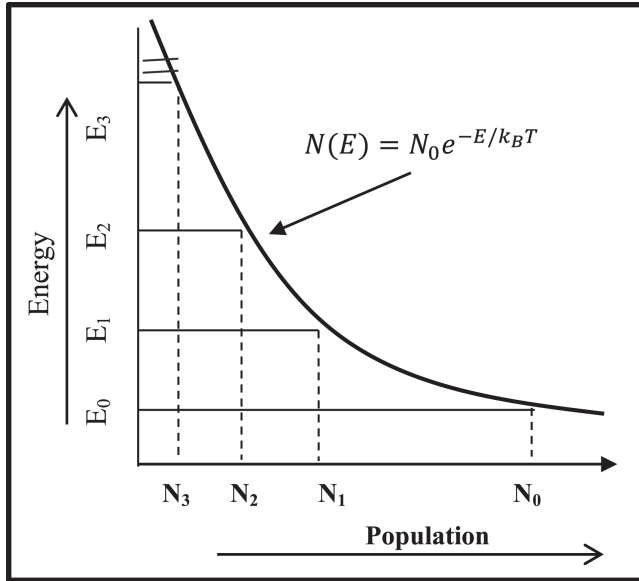
Figure 4.3. Boltzmann distribution of the population. The dashed lines correspond to the populations (N_0, N_1, N_2, and N_3) for indicated energy states ($E_0 < E_1 < E_2 < E_3$).

$$N(E) = N_0 e^{-E/k_\mathrm{B}T} \tag{4.4}$$

Here, N_0 is the population in the ground state and k_B is the Boltzmann constant ($= 1.3806488 \times 10^{-23}$ J K^{-1}). The higher particle states are also populated, depending on the temperature, as shown in figure 4.3.

We can write the ratio of the populations in two levels, 1 and 2, with energies E_1 and E_2 such that $\Delta E = E_2 - E_1$, as follows:

$$\frac{N_1}{N_2} = \frac{g_1}{g_2} e^{\Delta E/k_\mathrm{B}T}. \tag{4.5}$$

Exercise 4.3. Find the population of first thermally excited level for a visible wavelength (600 nm) at room temperature.

Solution: We must convert the wavelength (in nm) to energy (eV) (♠ see exercise 2.1). For 600 nm, $E = 2.268$ eV, the population is given by equation (4.4). Let the populations in the ground and excited states be N_0 and N_1, respectively. Using equation (4.5),

$$\frac{N_0}{N_1} = \exp(\Delta E/k_\mathrm{B}T)$$

$$\frac{N_0}{N_1} = \exp\left[\frac{2.268 \times (1.6 \times 10^{-19})}{\{(1.3\,806\,488 \times 10^{-23}) \times 300\}}\right]$$

$$= e^{87.6}$$

$$= 1.1 \times 10^{38}.$$

This shows that $N_0 \sim 10^{38} N_1$. At room temperature, the thermally populated value of the first excited state is smaller by a factor of 10^{-38} than that of the ground state. The ground-state population is dominant in this case.

Exercise 4.4. The wavelength of a ruby laser is 694.3 nm. What are the ratios of the populations in the ground (N_0) and excited states (N_1) corresponding to this wavelength at 300 K and 600 K?

Solution: We again use equation (4.5), $\frac{N_0}{N_1} = \exp(\Delta E/k_B T)$.

For the temperature of 300 K, the value of the ratio

$$\frac{N_1}{N_0} = \exp\left[-\left(\frac{hc}{\lambda K_B T}\right)\right]$$

$= \exp\left[-, \frac{6.64 \times 10^{-34}\ \text{Js} \times 3 \times 10^8 \text{ms}^{-1}}{694.3 \times 10^{-9}\,\text{m} \times 1.38 \times 10^{-23}\,\text{JK}^{-1} \times 300\,\text{K}}\right] = \exp[-69.27] = 8.26 \times 10^{-31}$. Similarly, at the higher temperature of 600 K, the ratio $\frac{N_1}{N_0}$ is $\exp[-34.63] = 9 \times 10^{-16}$. It can be estimated that at higher temperatures it will be easier to obtain population inversion (i.e. $N_1 > N_0$).

4.3 Planck's law of radiation

Apart from the ultraviolet catastrophe described in section 4.1.3, another problem with classical theory is that it predicts the total energy[1] density to be infinite, since all frequencies are possible. Physically, an infinite-energy EM field is not possible. In the year 1900, Planck described the spectral distribution of thermal radiation by introducing the idea of a quantum of energy E at a given transition frequency ν between two levels E_2 and E_1:

$$E = h\nu.$$

Here, h is known as Planck's constant ($h = 6.62 \times 10^{-34}$ Js). The empirical function proposed by Planck for the radiation density within the frequency interval $d\nu$ is as follows:

$$\rho(\nu)d\nu = \frac{8\pi h \nu^3}{c^3}\left(\frac{1}{e^{h\nu/k_B T} - 1}\right)d\nu. \tag{4.6}$$

The factor $1/(e^{h\nu/k_B T} - 1)$ was reintroduced for the ideal Bose gas by Einstein in the form of Bose–Einstein statistics for identical and indistinguishable particles (called bosons, with integral spins) for a number density $\rho(E)$ at an energy E as

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[1] The total power per unit area $I = \int_0^\infty I(\nu,\ T)d\nu$ diverges to ∞ when all frequencies are allowed.

$$\rho(E) = \frac{1}{(e^{(E-\mu)/k_{\mathrm{B}}T} - 1)}. \tag{4.7}$$

Here, μ is known as the chemical potential for identical particles, and for photons, $\mu = 0$. Planck's law fits the experimental results shown in figure 4.2 quite well.

♣ Fermions, i.e. particles such as electrons (whose spin is multiples of 1/2) follow the Fermi–Dirac statistics given by $\rho(E) = \frac{1}{\left(e^{(E-\mu)/k_{\mathrm{B}}T} + 1\right)}$.

Exercise 4.5. (a) Show that for long wavelengths, Planck's law reduces to the RJ law.
(b) What happens at shorter wavelengths?
Solution: (a) The exponential function in Planck's formula (equation (4.6)) can be expanded using a Taylor series for $f(x) = e^x$ i.e. $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$.

For longer wavelengths, or low frequencies, i.e. for small x (ignoring the higher terms in the expansion), $e^x = 1 + x$.

Therefore, for $h\nu k_{\mathrm{B}}T$, we have

$$\frac{1}{(e^{h\nu/k_{\mathrm{B}}T} - 1)} \cong \frac{k_{\mathrm{B}}T}{h\nu}.$$

Thus, at low frequencies, Planck's formula becomes $\rho(\nu)\mathrm{d}\nu = \left(\frac{8\pi\nu^2}{c^3}\right)k_{\mathrm{B}}T\mathrm{d}\nu$, which is the RJ law (equation (4.2)).

(b) For shorter wavelengths or higher frequencies, Planck's law behaves as Wein's law. This is the case because, for $h\nu kT$, we can rewrite equation (4.7) as

$$\rho(\nu)\mathrm{d}\nu \quad = \frac{8\pi h\nu^3}{c^3}e^{-\frac{h\nu}{k_{\mathrm{B}}T}}\mathrm{d}\nu.$$

The radiation intensity follows an exponential behavior, as shown in figure 4.2. This equation can be written in terms of wavelength as

$$E_\lambda \quad = \frac{8\pi hc}{\lambda^5}e^{-\frac{hc}{\lambda k_{\mathrm{B}}T}}.$$

To find the maxima, we can differentiate this expression with respect to λ and equate $\frac{\mathrm{d}E_\lambda}{\mathrm{d}\lambda}$ to zero. This is left as an exercise; it yields Wein's displacement law, $\lambda T = $ constant.

4.4 Einstein's A and B coefficients

4.4.1 Stimulated absorption coefficient

With reference to the Boltzmann distribution (figure 4.3), the exited states cannot have higher populations than the ground state. Nevertheless, there are ways in which the populations of the upper energy states can be made larger than that of the ground state. For example, on absorption of a photon by an atom, the thermal
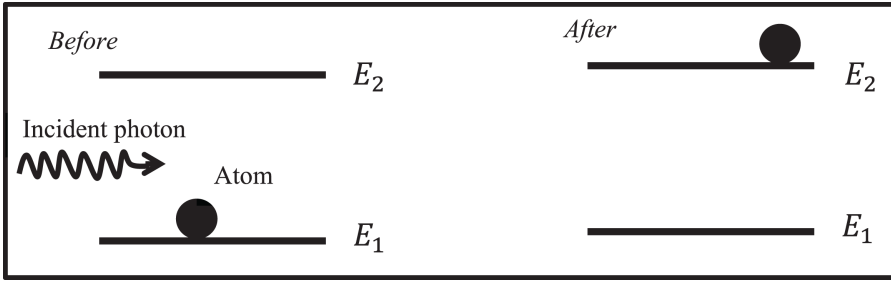
Figure 4.4. Process of absorption in an atomic system with two energy levels (E_1 and E_2): an atom before (*left*) and after (*right*) interacting with an incident photon.

equilibrium is disturbed. In 1917, Einstein combined Planck's law and the Boltzmann statistics and further developed the idea of light absorption and emission. To obtain the correct energy density of radiation, one must include a *stimulated emission probability* in dealing with the interaction of radiation with matter.

As shown in figures 4.4–4.6, consider the two energy levels of an atomic system E_1 and E_2 with populations of atoms denoted by N_1 and N_2, respectively. An atom can be placed in its higher level E_2 on absorption of a photon. The absorption of a photon is in addition to the thermal population, and hence it is also referred to as 'stimulated absorption'. This is due to the fact that EM radiation is required to stimulate the electrons to produce the short-lived entity—the excited state denoted by E_2 in figure 4.4.

The rate of change of the population in the lower state due to absorption is proportional to the population in the state E_1 and the incident photon density $\rho(\nu)$:

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} \propto \rho(\nu)N_1.$$

The rate of change of N_1 can be rewritten by introducing a rate constant B_{12}, known as the *Einstein's B coefficient* of stimulated absorption, as follows:

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = B_{12}\rho(\nu)N_1. \tag{4.8}$$

4.4.2 Spontaneous emission

Consider figure 4.5, in which the atom is now in the higher state E_2. As $E_2 > E_1$, the atom decays to the lower state E_1 by emitting a photon of frequency ν. This process is known as *spontaneous emission*.

In the condensed phase, the emission following optical excitation is also known as fluorescence or photoluminescence[2]. Overall, the population decay of the state E_2 in terms of another constant of proportionality known as the rate coefficient of spontaneous emission (A_{21}), is written as

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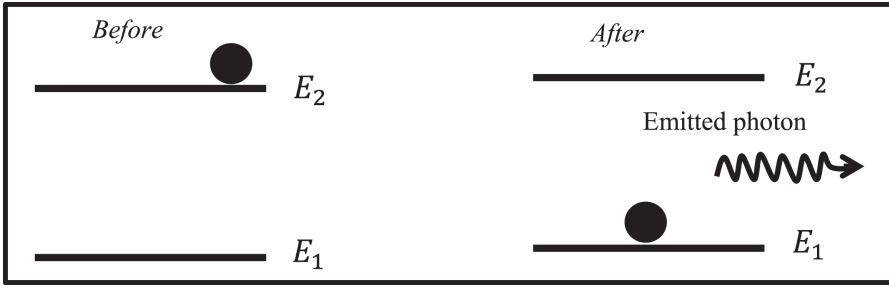[2] ♣To distinguish it from other types of emissions, see appendix A.

Figure 4.5. Schematic of the process of spontaneous emission in an atomic system with two energy levels (E_1 and E_2): an atom before (*left*) and after (*right*) spontaneously emitting a photon.

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = -A_{21}N_2. \tag{4.9}$$

The negative sign in this equation expresses the decrease of the population over time. Here, A_{21} is also known as *Einstein's A coefficient* and has units of s^{-1}. The photons in the spontaneous emission process are emitted in random directions with arbitrary polarization and within a broad range of frequencies for allowed transitions.

The solution of differential equation (4.9) is a first-order decay that is well known in physics:

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

Here, N_2^0 is the population of the upper state at $t = 0$. The time in which the population falls to $1/e$ of its initial value is known as the *lifetime* of the spontaneous emission (τ_0). It is the inverse of the decay rate $\left(= \frac{1}{A_{21}}\right)$ and is similar to that described in chapter 2 (♠ see section 2.9.7.8). For most molecules and semiconductors, τ_0 is of the order of nanoseconds (10^{-9} s). For several other laser materials, such as rare-earth ions (e.g. Cr^{+3} and Nd^{+3}), the lifetimes are found to be of the order of milliseconds (10^{-3} s).

4.4.3 Coefficient of stimulated emission

The excited state can be populated by the absorption of a photon as well as by thermal excitation. The phenomenon of stimulated absorption (from a lower state) suggests that a process that is the reverse of stimulated emission should exist for the excited state.

Let us consider a situation in which an atom is in the higher state E_2 and a photon of same frequency ν is incident on the system, as shown in figure 4.6. There is a finite probability that the incident photon will stimulate the atom to resonantly undergo a transition to the lower state E_1 by emitting another photon. If this happens, then the two emitted photons will possess properties analogous to each other. This means that light consisting of these photons has one frequency (the property of
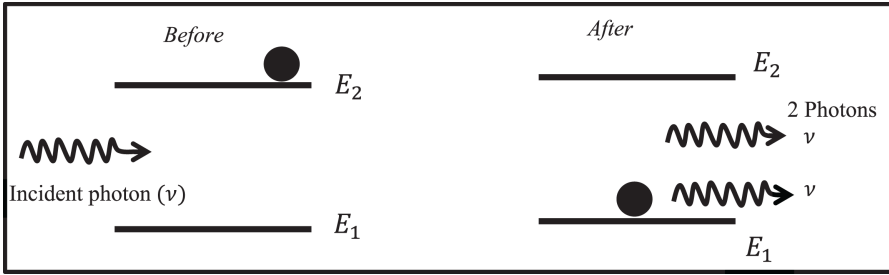
Figure 4.6. Schematic diagram of the process of stimulated emission in an atom when a photon of the same frequency (ν) is incident on it, showing the situations before (*left*) and after (*right*) the photon strikes the system.

monochromaticity) and is in phase (the property of *coherence*). These properties are not associated with spontaneously emitted photons.

Let us also consider the coefficient of spontaneous emission (A_{21}), which is independent of the external field. It is a statistical function of space and time and there is no phase relationship in the light emitted by the atoms. The fluorescence lifetime of the excited state (τ_0, ♠ see equation (2.13)) is an experimentally measurable quantity. On the other hand, the depletion of E_2 by B_{21} is given by its dependence on external factors. In this case, the rate of change of population of the upper state due to absorption is proportional to the population in the state E_1 and the incident photon density $\rho(\nu)$. It is given by

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} \propto \rho(\nu)N_2.$$

By introducing the rate coefficient of stimulated emission B_{21}, we can write this as

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = -B_{21}\rho(\nu)N_2. \tag{4.10}$$

The unit of energy density (ρ_ν) per unit frequency interval is J s m^{-3}. Therefore, comparing the units of A_{21} and $B_{21}\rho(\nu)$, the unit of Einstein's B coefficient is m^3 J^{-1} s^{-2}.

4.4.4 Rate equation analysis

The rates of stimulated absorption ($B_{12}\rho(\nu)N_1$), spontaneous emission ($A_{21}N_2$), and stimulated emission ($B_{21}\rho(\nu)N_2$) of a two-state system are indicated in figure 4.7. We now have sufficient information to work on the rate equations for a two-level system, as follows.

Using equations (4.8)–(4.10), we can write the rates of change of the populations of states E_2 and E_1 as

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = -B_{21}\rho(\nu)N_2 - A_{21}N_2$$
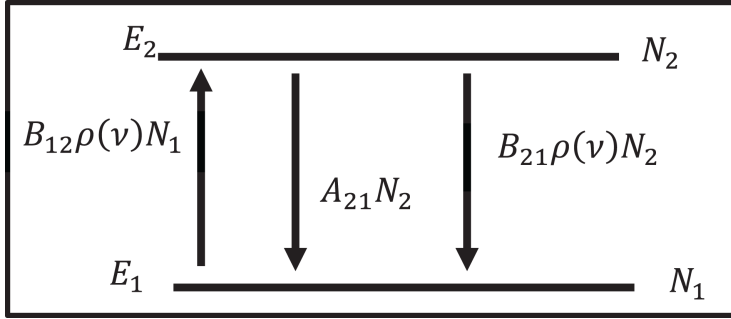
and

Figure 4.7. Two-level system used for analysis of the rate equation. $B_{12}\rho(\nu)N_1$, $A_{21}N_2$, and $B_{21}\rho(\nu)N_2$ are the rates of stimulated absorption, spontaneous emission, and stimulated emission, respectively.

$$\frac{dN_1}{dt} = B_{12}\rho(\nu)N_1,$$

respectively.

At equilibrium, the rate of increase of the upper state (E_2) via induced absorption is equal to its decay to the lower state (E_1) via the sum of the spontaneous and stimulated emission rates, as follows

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

Dividing this by $B_{21}\rho(\nu)N_2$ gives

$$\frac{A_{21}}{B_{21}\rho(\nu)} = \frac{B_{12}N_1}{B_{21}N_2} - 1.$$

From the Boltzmann distribution, substituting the value of N_1/N_2 from equation (4.5), we get

$$\frac{A_{21}}{B_{21}\rho(\nu)} = \frac{B_{12}}{B_{21}}\frac{g_1}{g_2}e^{\left(\frac{\Delta E}{k_B T}\right)} - 1. \tag{4.11}$$

This can be rewritten as

$$\rho(\nu) = \left(\frac{A_{21}}{B_{21}}\right)\bigg/\left(\frac{B_{12}}{B_{21}}\frac{g_1}{g_2}e^{\left(\frac{\Delta E}{k_B T}\right)} - 1\right). \tag{4.12}$$

By comparing this to the energy density of radiation at frequency ν in a cavity using Planck's law (equation (4.6)), we obtain

$$\left(\frac{A_{21}}{B_{21}}\right) = \frac{8\pi h\nu^3}{c^3} \tag{4.13}$$

and

$$\frac{B_{12}}{B_{21}}\frac{g_1}{g_2} = 1.$$

We assume here that either the split of the energy states is the same or that there is no split. Therefore, for the same degeneracies, i.e. $\frac{g_1}{g_2} = 1$, we obtain $B_{12} = B_{21}$. This indicates that the probabilities of absorption and stimulated emission for the transitions between the two states are equal. This is an important message, as it suggests that materials characterized by strong absorption coefficients can be expected to have strong emission coefficients, which is to say that they can be excellent laser materials. For example, organic dyes (such as rhodamine 6G) have strong absorption in the visible region and are excellent stimulated emitters. Two profound consequences of Einstein's coefficients are highlighted on rewriting the equations, as shown in the following subsections.

4.4.4.1 Relation between spontaneous and stimulated emission

From the relation given in equation (4.13), the lifetime of the upper level ($\tau_0 = 1/A_{21}$) can be related to the stimulated emission, as follows:

$$B_{21} = \frac{c^3}{8\pi h \nu^3 \tau_0}. \tag{4.14}$$

Therefore, if a material can be characterized by a spontaneous rate (by estimating the value of τ_0), the stimulated rate can be found from equation (4.14). Notice that in terms of wavelength, equation (4.14) can be written as $B_{21} = \frac{\lambda^3}{8\pi h \tau_0}$.

Exercise 4.6. The dye rhodamine 6G in ethylene glycol has a lifetime of 3.5 ns. For an emission wavelength of 570 nm, what is the coefficient of stimulated emission? (Take the refractive index of the solvent to be 1.4.)

Solution: Equation (4.14) gives the coefficient of stimulated emission as

$$B_{21} = \frac{c^3}{8\pi h \nu^3 \tau_0}.$$

The refractive index (n) of the solvent is 1.4. Therefore, the speed of light in this medium is c/n. The lifetime (τ_0) is 3.5×10^{-9} s. The frequency (ν) corresponding to 570 nm is 5×10^{14} Hz. Using the value of $h = 6.6 \times 10^{-34}$ J s, the value of B_{21} obtained is 1.5×10^4 m^3 J^{-1} s^{-2}.

4.4.4.2 The ratio and the magic of stimulated emission

Similarly, equation (4.11) can now be rewritten as follows:

$$\frac{A_{21}}{B_{21}\rho(\nu)} = e^{h\nu/k_B T} - 1. \tag{4.15}$$

The quantity $\frac{A_{21}}{B_{21}\rho(\nu)}$ is purely a number and is known as the ratio (R) of spontaneous to stimulated emission coefficients for a system in thermal equilibrium with a

radiation field. As can be seen from the above equation, its value varies with frequency and the temperature and is extremely important in the development of lasers. Table 4.1 gives typical values of R at various temperatures for a wide range of the EM spectrum.

Exercise 4.7. Evaluate the ratio (R) of the rate of spontaneous radiation to that of stimulated radiation for a tungsten filament for the visible frequency range at 2000 K.

Solution: At $T = 2000$ K, for the visible frequency range (5×10^{14} Hz), the value of this ratio from equation (4.15) is approximately e^{12} (or 1.5×10^5).

This is the reason why the majority of the radiation emitted by tungsten lamps takes the form of spontaneous emission and the probability of stimulated emission is minimal.

Exercise 4.8. Use equation (4.15) and assume a wavelength of 570 nm. If we wish to make the rate of spontaneous emission (A_{21}) equal to the factor $B_{21}\rho(\nu)$, what temperature could be used?

Solution: According to the question, to make the value of ratio R in equation (4.15) equal one, we need

$$e^{h\nu/k_B T} = 2.$$

The frequency (ν) corresponding to 570 nm is 5×10^{14} Hz. Using the values $h = 6.6 \times 10^{-34}$ J s^{-1} and $k_B = 1.38 \times 10^{-23}$ J K^{-1}, the value of

$$\frac{h\nu}{k_B T} = \frac{2.53 \times 10^4}{T}.$$

Therefore, $\frac{2.53 \times 10^4}{T} = \ln 2$,

or the required temperature $T = \frac{2.53 \times 10^4}{\ln 2} = 3.64 \times 10^4$ K

A glance at table 4.1 shows that in the microwave region, the level of stimulated emission dominates that of spontaneous emission, as the value of R is small. This was the obvious reason for the invention of Microwave Amplification by Stimulated Emission of Radiation (MASER) before the invention of LASER. To obtain stimulated emission in the visible/IR region, the denominator of R in equation (4.15) should be increased. This can be achieved by increasing the value of $\rho(\nu)$ between the two energy levels. This is the subject of the next chapter.

♣ The research groups of Townes (1955) and Basov and Prokhorov [4] independently demonstrated amplification in the microwave region in ammonia.

♣ Basov and Prokhorov [4] wrote a paper on their molecular generator for the journal '*Zhurnal Èksperimental'noi i Teoreticheskoi Fiziki*' (later known as '*Soviet Physics—JETP*'), which they submitted in December 1953, but this paper was delayed by a year due to a typographical error in 2π that needed to be corrected!

Table 4.1. The ratio (R) of spontaneous emission to stimulated emission at various temperatures for different frequencies.

Wavelength[a] (nm)	Frequency[a] (Hz)	Value of R at various temperatures				
		1 K	10 K	100 K	1000 K	10000 K
180000000	10^{10}	0.008003	0.000797	0.000266	7.97×10^{-05}	7.97×10^{-06}
18000000	10^{11}	0.082973	0.008003	0.002661	0.000797	7.97×10^{-05}
1800000	10^{12}	1.219099	0.082973	0.026926	0.008003	0.000797
180000	10^{13}	2894.794	1.219099	0.304344	0.082973	0.008003
18000	10^{14}	4.15×10^{34}	2894.794	13.25353	1.219099	0.082973
1800	10^{15}	—	4.15×10^{34}	3.46×10^{11}	2894.794	1.219099
180	10^{16}	—	—	2.5×10^{115}	4.15×10^{34}	2894.794
18	10^{17}	—	—	—	—	4.15×10^{34}

[a] See figure 2.2 for the ranges of wavelengths and frequencies in the UV, visible, and IR regions.

Questions and problems

1. How do you represent the number of radiation modes per unit volume in a frequency range $d\nu$ in free space, in terms of the frequency ν and the velocity of light, c?

2. The temperature of the Sun's surface is about 6000 K. What is the intensity of the radiation from the Sun?

3. What is the mechanism by which an incandescent bulb and a mercury light work?

4. The temperature of the tungsten filament of a light bulb is 3000 K. What is the peak of its light spectrum?

5. According to Planck's law of black-body radiation, what is the energy density of radiation between the frequencies ν and $\nu + d\nu$?

6. The number of atoms of energy E within a specific energy range (dE) can be given by $N(E)dE = \frac{N}{KT}e^{-E/k_BT}dE$. Calculate the temperature at which you could see a considerable number of 'visible' photons.

7. Find the energy of a particle at a room temperature of ~300 K.

8. Calculated the mean number of photons excited in the radiation field mode of a thermal source that has a wavelength 400 nm at a temperature of 300 K.

9. For nondegenerate atomic levels of a system in thermal equilibrium, what is the ratio of Einstein's A coefficient to Einstein's B coefficient in terms of frequency υ, the velocity of light c, and Planck's constant?

10. Write down the units of the rate constants of spontaneous emission (A) and stimulated emission (B). What is the radiative rate for a molecular system with radiative lifetime of 10 ns?

11. At a constant temperature, compare the ratio of the spontaneous and stimulated emission rates typically obtained for the microwave and UV regions of the EM spectrum.

12. An argon-ion laser works on a single line (514.5 nm) with an output power of 78.50 mW. Take the spectral purity to be 0.001 nm. What is the value of A_{21}/B_{21} for the laser?

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