CHAPTER ONE

Spontaneous and Stimulated Transitions

1

Spontaneous and Stimulated Transitions

1.1 Introduction

A laser is an oscillator that operates at very high frequencies. These *optical* frequencies range to values several orders of magnitude higher than can be achieved by the "conventional" approaches of solid-state electronics or electron tube technology. In common with electronic circuit oscillators, a laser is constructed from an amplifier with an appropriate amount of positive feedback. The acronym LASER, which stands for *light amplification by stimulated emission of radiation*, is in reality therefore a slight misnomer†.

In this chapter we shall consider the fundamental processes whereby amplification at optical frequencies can be obtained. These processes involve the fundamental atomic nature of matter. At the atomic level matter is not a continuum, it is composed of discrete particles – atoms, molecules or ions. These particles have energies that can have only certain discrete values. This discreteness or *quantization*, of energy is intimately connected with the duality that exists in nature. Light sometimes behaves as if it were a wave and in other circumstances it behaves as if it were composed of particles. These particles, called *photons*, carry the discrete packets of energy associated with the wave. For light of frequency ν the energy of each photon is $h\nu$, where h is Planck's constant – 6.6×10^{-34} J s. The energy $h\nu$ is the *quantum* of energy associated

† The more truthful acronym LOSER was long ago deemed inappropriate.

Fig. 1.1.

with the frequency ν. At the microscopic level the amplification of light within a laser involves the emission of these quanta. Thus, the term *quantum electronics* is often used to describe the branch of science that has grown from the development of the maser in 1954 and the laser in 1960.

The widespread practical use of lasers and optical devices in applications such as communications, and increasingly in areas such as signal processing and image analysis has lead to the use of the term *photonics*. Whereas, electronics uses electrons in various devices to perform analog and digital functions, photonics aims to replace the electrons with photons. Because photons have zero mass, do not interact with each other to any significant extent, and travel at the speed of light photonic devices promise small size and high speed.

1.2 Why 'Quantum' Electronics?

In "conventional" electronics, where by the word "conventional" for the present purposes we mean frequencies where solid-state devices such as transistors or diodes will operate, say below 10^{11} Hz, an oscillator is conveniently constructed by applying an appropriate amount of positive feedback to an amplifier. Such an arrangement is shown schematically in Fig. (1.1). The input and output voltages of the amplifier are V_i and V_0 respectively. The overall gain of the system is A, where $A = V_0/V_i$. Now,

$$V_0 = A_0(V_i + \beta V_0)$$

Fig. 1.2.

so

$$V_0 = \frac{A_0 V_i}{1 - \beta A_0}$$

and

$$A = \frac{A_0}{1 - \beta A_0}. \tag{1.1}$$

If $\beta A_0 = +1$ then the gain of the circuit would apparently become infinite, and the circuit would generate a finite output without any input. In practice electrical "noise", which is a random oscillatory voltage generated to a greater or lesser extent in all electrical components in any amplifier system, provides a finite input. Because βA_0 is generally a function of frequency the condition $\beta A_0 = +1$ is generally satisfied only at one frequency. The circuit oscillates at this frequency by amplifying the noise at this frequency which appears at its input. However, the output does not grow infinitely large, because as the signal grows, A_0 falls – this process is called saturation. This phenomenon is fundamental to all oscillator systems. A laser (or maser) is an optical (microwave) frequency oscillator constructed from an optical (microwave) frequency amplifier with positive feedback, shown schematically in Fig. (1.2). Light waves which become amplified on traversing the amplifier are returned through the amplifier by the reflectors and grow in intensity, but this intensity growth does not continue indefinitely because the amplifier saturates. The arrangement of mirrors (and sometimes other components) that provides the feedback is generally referred to as the laser cavity or resonator.

We shall deal with the full characteristics of the device consisting of amplifying medium and resonator later, for the moment we must concern ourselves with the problem of how to construct an amplifier at

Fig. 1.3.

optical frequencies. The frequencies involved are very high, for example lasers have been built which operate from very short wavelengths, for example 109.8 nm, using para-hydrogen gas as the amplifying medium, to 2650 μm using methyl bromide as the amplifying medium. This is a frequency range from 2.73×10^{15} Hz down to 1.13×10^{11} Hz. The operating frequencies of masers overlap this frequency range at the low frequency end, the fundamental difference between the two devices is essentially only one of scale. If the length of the resonant cavity which provides feedback is L, then for $L \gg \lambda$, where λ is the wavelength at which oscillation occurs, we have a laser: for $L \sim \lambda$ we have a maser.

1.3 Amplification at Optical Frequencies

How do we build an amplifier at such high frequencies? We use the energy delivered as the particles that consitute the amplifying medium make jumps between their different energy levels. The medium may be gaseous, liquid, a crystalline or glassy solid, an insulating material or a semiconductor. The electrons that are bound within the particles of the amplifying medium, whether these are atoms, molecules or ions, can occupy only certain discrete energy levels. Consider such a system of energy levels, shown schematically in Fig. (1.3). Electrons can make jumps between these levels in three ways.

1.3.1 Spontaneous Emission

An electron spontaneously falls from a higher energy level to a lower one as shown in Fig. (1.4), the emitted photon has frequency

Fig. 1.4.

$$\nu_{ij} = \frac{E_i - E_j}{h}. \tag{1.2}$$

This photon is emitted in a random direction with arbitrary polarization (except in the presence of magnetic fields, but this need not concern us here). The photon carries away momentum $h/\lambda = h\nu/c$ and the emitting particle (atom, molecule or ion) recoils in the opposite direction. The probability of such a spontaneous jump is given quantitatively by the Einstein A coefficient defined as A_{ij} = "probability" per second of a spontaneous jump from level i to level j.

For example, if there are N_i particles per unit volume in level i then $N_i A_{ij}$ per second make jumps to level j. The total rate at which jumps are made between the two levels is

$$\frac{dN_{ij}}{dt} = -N_i A_{ij}. \tag{1.3}$$

There is a negative sign because the population of level i is decreasing.

Generally an electron can make jumps to more than one lower level, unless it is in the first (lowest) excited level. The total probability that the electron will make a spontaneous jump to any lower level is A_i s^{-1} where

$$A_i = \sum_j A_{ij}. \tag{1.4}$$

The summation runs over all levels j lower in energy than level i and the total rate at which the population of level i changes by spontaneous emission is

$$\frac{dN_i}{dt} = -N_i A_i,$$

which has the solution

$$N_i = \text{ constant} \times \ e^{-A_i t}. \tag{1.5}$$

If at time $t = 0, N_i = N_i^0$ then

$$N_i = N_i^0 e^{-A_i t}, \tag{1.6}$$

so the population of level i falls exponentially with time as electrons leave by spontaneous emission. The time in which the population falls to $1/e$ of its initial value is called the natural lifetime of level i, τ_i, where $\tau_i = 1/A_i$. The magnitude of this lifetime is determined by the actual probabilities of jumps from level i by spontaneous emission. Jumps which are likely to occur are called *allowed* transitions, those which are unlikely are said to be *forbidden*. *Allowed* transitions in the visible region typically have A_{ij} coefficients in the range 10^6–10^8 s^{-1}. *Forbidden* transitions in this region have A_{ij} coefficients below 10^4 s^{-1}. These probabilities decrease as the wavelength of the jump increases. Consequently, levels that can decay by allowed transitions in the visible have lifetimes generally shorter than 1 μs, similar forbidden transitions have lifetimes in excess of 10–100 μs. Although no jump turns out to be absolutely forbidden, some jumps are so unlikely that levels whose electrons can only fall to lower levels by such jumps are very long lived. Levels with lifetimes in excess of 1 hour have been observed under laboratory conditions. Levels which can only decay slowly, and usually only by forbidden transitions, are said to be *metastable*.

When a particle changes its energy spontaneously the emitted radiation is not, as might perhaps be expected, all at the same frequency. Real energy levels are not infinitely sharp, they are smeared out or *broadened*. A particle in a given energy level can actually have any energy within a finite range. The frequency spectrum of the spontaneously emitted radiation is described by the *lineshape function*, $g(\nu)$. This function is usually normalized so that

$$\int_{-\infty}^{\infty} g(\nu) d\nu = 1. \tag{1.7}$$

$g(\nu)d\nu$ represents the probability that a photon will be emitted spontaneously in the frequency range $\nu + d\nu$. The lineshape function $g(\nu)$ is a true probability function for the spectrum of emitted radiation and is usually sharply peaked near some frequency ν_0, as shown in Fig. (1.5). For this reason the function is frequently written $g(\nu_0, \nu)$ to highlight this. Since negative frequencies do not exist in reality the question might properly be asked: "Why does the integral have a lower limit of minus infinity?" This is done because $g(\nu)$ can be viewed as the Fourier transform of a real function of time, so negative frequencies have to be permitted

Fig. 1.5.

mathematically. In practice $g(\nu)$ is only of significant value for some generally small range of positive frequencies so

$$\int_0^\infty g(\nu)d\nu \simeq 1. \tag{1.8}$$

The amount of radiation emitted spontaneously by a collection of particles can be described quantitatively by their *radiant intensity* $I_e(\nu)$. The units of radiant intensity are watts per steradian.† The total power (watts) emitted in a given frequency interval $d\nu$ is

$$W(\nu) = \int_S I_e(\nu)d\nu d\Omega, \tag{1.9}$$

where the integral is taken over a closed surface S surrounding the emitting particles.

The total power emitted is

$$W_0 = \int_{-\infty}^\infty W(\nu)d\nu. \tag{1.10}$$

$W(\nu)$ is closely related to the lineshape function

$$W(\nu) = W_0 g(\nu). \tag{1.11}$$

For a collection of N_i identical particles the total spontaneously emitted power per frequency interval is

$$W(\nu) = N_i A_i h\nu g(\nu). \tag{1.12}$$

Clearly this power decreases with time if the number of excited particles decreases.

For a plane electromagnetic wave we can introduce the concept of *in-*

† The steradian is the unit of solid angle, Ω. The surface of a sphere encompasses a solid angle of 4π steradians.

Fig. 1.6.

tensity, which has units of $W\ m^{-2}$. The intensity is the average amount of energy per second transported across unit area in the direction of travel of the wave. The spectral distribution of intensity, $I(\nu)$, is related to the total intensity, I_0, by

$$I(\nu) = I_0 g(\nu). \tag{1.13}$$

It is worth pointing out that in reality perfect plane waves do not exist, such waves would have a unique propagation direction and infinite radiant intensity. However, to a very good degree of approximation we can treat the light from a small source as a plane wave if we are far enough away from the source. The light coming from a star represents a very good example of this.

1.3.2 Stimulated Emission

Besides being able to make transitions from a higher level to a lower one by spontaneous emission, electrons can also be stimulated to make these jumps by the action of an external radiation field, as shown in Fig. (1.6).

Let the energy density of the externally applied radiation field at frequency ν be $\rho(\nu)$ (energy per unit volume per unit frequency interval; i.e., J m^{-3} Hz^{-1}). If ν is the same frequency as a transition between two levels labelled 2 and 1, the rate at which stimulated emissions occur is $N_2 B'_{21}(\nu)$ s^{-1} Hz^{-1} m^{-3} where $B'_{21}(\nu)$ is a function specific to the electron jump between the two levels and N_2 is the number of particles per unit volume in the upper level of the transition. The frequency dependence of $B'_{21}(\nu)$ is the same as the lineshape function

$$B'_{21}(\nu) = B_{21} g(\nu_0, \nu). \tag{1.14}$$

B_{21} is called the Einstein coefficient for stimulated emission. The total

Fig. 1.7.

rate of change of population density by stimulated emission is

$$\begin{aligned}\frac{dN_2}{dt} &= -N_2 \int_{-\infty}^{\infty} B'_{21}(\nu)\rho(\nu)d\nu \\ &= -N_2 B_{21} \int_{-\infty}^{\infty} g(\nu_0, \nu)\rho(\nu)d\nu. \qquad (1.15)\end{aligned}$$

Note, that for the dimensions of both sides of Eq. (1.15) to balance B_{21} must have units $\mathrm{m}^3\ \mathrm{J}^{-1}\ \mathrm{s}^{-2}$. To evaluate the integral in Eq. (1.15) we must consider how energy density is related to intensity and how these quantitites might actually vary with frequency.

1.4 The Relation Between Energy Density and Intensity

The energy density of a radiation field $\rho(\nu)$ (energy per unit volume per unit frequency interval) can be simply related to the intensity of a plane electromagnetic wave. If the intensity of the wave is $I(\nu)$ (for example, watts per unit area per frequency interval). Then

$$\rho(\nu) = \frac{I(\nu)}{c}, \qquad (1.16)$$

where c is the velocity of light in the medium† This is illustrated in Fig. (1.7). All the energy stored in the volume of length c passes across the plane A in one second so

$$\rho(\nu) \times\ A \times\ c = I(\nu) \times\ A. \qquad (1.17)$$

The energy density in a general radiation field $\rho(\nu)$ is a function of

† $c = c_0/n$, where c_0 is the velocity of light in a vacuum and n is the *refractive index.*

Fig. 1.8.

Fig. 1.9.

frequency ν. If $\rho(\nu)$ is independent of frequency the radiation field is said to be *white*, as shown in Fig. (1.8). If the radiation field is *monochromatic* at frequency ν_{21}, its spectrum is as shown in Fig. (1.9). The ideal *monchromatic* radiation field has an infinitely narrow energy density profile at frequency ν_{21}. This type of profile is called a δ-function. The properties of this function are described in more detail in Appendix 1.

For a general radiation field the total energy stored per unit volume between frequencies ν_1 and ν_2 is

$$\int_{\nu_1}^{\nu} \rho(\nu) d\nu.$$

The energy density of a general radiation field is a function of frequency, for example as shown in Fig (1.10). For a monochromatic radiation field at frequency ν_{21}

$$\rho(\nu) = \rho_{21}\delta(\nu - \nu_0). \tag{1.18}$$

The δ-function has the property

$$\delta(\nu - \nu_{21}) = 0 \text{ for } \nu \neq \nu_{21}, \quad (1.19)$$

and

$$\int_{-\infty}^{\infty} \delta(\nu - \nu_{21}) d\nu = 1. \quad (1.20)$$

So for a monochromatic radiation field the total stored energy per unit volume is

$$\int_{-\infty}^{\infty} \rho(\nu) d\nu = \int_{-\infty}^{\infty} \rho_{21} \delta(\nu - \nu_{21}) d\nu = \rho_{21}. \quad (1.21)$$

For such a monochromatic radiation field Eq. (1.15) can be written as

$$\begin{aligned} \frac{dN_2}{dt} &= -N_2 B_{21} \int_{-\infty}^{\infty} g(\nu_0, \nu) \rho_{21} \delta(\nu - \nu_{21}) d\nu \\ &= -N_2 B_{21} g(\nu_0, \nu_{21}) \rho_{21}. \end{aligned} \quad (1.22)$$

It is very important to note that the rate of stimulated emissions produced by this input monochromatic radiation is directly proportional to the value of the lineshape function at the input frequency. The maximum rate of stimulated emission is produced, all else being equal, if the input radiation is at the line center frequency ν_0.

If the stimulating radiation field has a spectrum that is broad, we can assume that the energy density $\rho(\nu)$ is constant over the narrow range of frequencies where $g(\nu_0, \nu)$ is significant. In this case Eq. (1.15) gives

$$\frac{dN_2}{dt} = -N_2 B_{21} \rho(\nu), \quad (1.23)$$

where $\rho(\nu) \simeq \rho(\nu_0)$ is the energy density in the frequency range where transitions take place.

1.4.1 Stimulated Absorption

As well as making stimulated jumps in a downward direction, electrons may make transitions in an upward direction between energy levels of a particle by absorbing energy from an electromagnetic field, as shown in Fig. (1.11). The rate of such absorptions and the rate at which electrons leave the lower level is,

$$N_1 \rho(\nu) B_{12} g(\nu_0, \nu) \text{ s}^{-1} \text{ Hz}^{-1} \text{ m}^{-3},$$

which yields a result similar to Eq. (1.15)

$$\frac{dN_1}{dt} = -N_1 B_{12} \int_{-\infty}^{\infty} g(\nu_0, \nu) \rho(\nu) d\nu. \quad (1.24)$$

Once again B_{12} is a constant specific to the jump and is called the Einstein coefficient for stimulated absorption. Here again $\rho(\nu)$ is the energy

Fig. 1.10.

density of the stimulating field. There is no analog in the absorption process to spontaneous emission. A particle cannot spontaneously *gain* energy without an external energy supply. Thus, it is unnecessary for us to continue to describe the absorption process as stimulated absorption.

It is interesting to view both stimulated emission and absorption as photon–particle collision processes. In *stimulated* emission the incident photon produces an identical photon by "colliding" with the electron in an excited level, as shown in Fig. (1.12a.) After the stimulated emission process, both photons are travelling in the same direction and with the same polarization as the incident photon originally had. When light is described in particle terms, polarization can be viewed as describing the angular motion or spin of individual photons. Left and right hand circularly polarized light corresponds in this particle picture to beams of photons that spin clockwise and counterclockwise, respectively, about their direction of propagation. Linearly polarized light corresponds to a beam of photons that have no net angular momentum about an axis parallel to their direction of propagation. In stimulated emission the stimulated photon has exactly the same frequency as the stimulating photon. In absorption the incident photon disappears, as shown in Fig. (1.12b). In both stimulated emission and absorption the atom recoils to conserve linear momentum.

1.5 Intensity of a Beam of Electromagnetic Radiation in Terms of Photon Flux

If the intensity of a beam of light is $I(\nu)$ (W m^{-2} per frequency interval) then the number of photons in the beam crossing unit area per unit time

Fig. 1.11.

Fig. 1.12.

is

$$N_{photons} = \frac{I(\nu)}{h\nu}(\text{photons S}^{-1}\ \text{m}^{-1}\ \text{per frequency interval}). \quad (1.25)$$

If the beam is monochromatic and has total intensity $I(\nu_{21})$ then

$$N_{photons} = \frac{I(\nu_{21})}{h\nu}\ \text{photons s}^{-1}\ m^{-2}. \quad (1.26)$$

1.6 Black-Body Radiation

A particularly important kind of radiation field is that emitted by a *black body.* Such a body absorbs with 100% efficiency all the radiation falling on it, irrespective of the radiation frequency. Black-body radiation has a spectral distribution of the kind shown in Fig. (1.13). A close approximation to a black body (absorber and emitter) is an enclosed cavity containing a small hole, as shown in Fig. (1.14). Radiation that enters the hole has very little chance of escaping. If the inside of this cavity

Fig. 1.13.

Fig. 1.14.

is in thermal equilibrium it must lose as much energy as it absorbs and the emission from the hole is therefore characteristic of the equilibrium temperature T inside the cavity. Thus this type of radiation is often called "thermal" or "cavity" radiation.

In the early days of the quantum theory, the problem of describing theoretically the spectral profile of the emission from a black body was a crucial one. In the latter part of the nineteenth century experimental measurements of this spectral profile had already been obtained and the data had even been fitted to an empirical formula. Attempts to explain the form of the data were based on treating the electromagnetic radiation as a collection of oscillators, each oscillator with its own characteristic frequency. The problem was to determine how many oscillations at a given frequency could be fitted inside a cavity.

Thermodynamically, the shape of the cavity for which the calculation is performed is arbitrary (provided it is much larger than the wavelength of any of the oscillations) otherwise we could make a heat engine by connecting together cavities of different shapes. If, for example, two cavities of different shapes, but at the same temperature, were connected together with a reflective hollow pipe, we could imagine placing filters having different narrow frequency bandpass characteristics in the pipe. Unless the radiation emitted in each elemental frequency band from both cavities was identical, one cavity could be made to heat up and the other cool down, thereby violating the second law of thermodynamics. For convenience purposes, we choose a cubical cavity with sides of length L. A plane electromagnetic wave will "fit" inside this cavity if it satisfies appropriate *periodic* boundary conditions. If the wave has a spatial variation written in complex notation as $e^{i\mathbf{k}\cdot\mathbf{r}}$ these boundary conditions can be written as

$$e^{ik_x x} = e^{2k_x(x+L)} \tag{1.27}$$

with similar equations for the y and z directed components of the wave. Equations like (1.27) are satisfied if

$$k_x = \frac{2\pi\ell}{L}, k_y = \frac{2\pi m}{L}, k_z = \frac{2\pi n}{L}, \tag{1.28}$$

where k_x, k_y, k_z are the components of the wave vector $\mathbf{k}$ of the oscillation and ℓ, m, n are integers.

$$\mathbf{k} = \frac{\omega}{c}\hat{\mathbf{k}}, \quad |\,\mathbf{k}\,| = 2\pi/\lambda, \tag{1.29}$$

where ω is the angular frequency of the wave, λ its wavelength, c is the velocity of light and $\hat{\mathbf{k}}$ is a unit vector in the direction of the wave vector.

In a three-dimensional space whose axes are k_x, k_y, and k_z (called $\mathbf{k}$-space) the possible k values that are periodic inside the cube form a lattice as shown in Fig. (1.15). The size of a unit cell of this lattice is $(2\pi/L)^3$. Each cell corresponds to one possible *mode*, characterized by its own values of k_x, k_y, and k_z which are periodic inside the cube. Note that the spacing of adjacent modes, say in the k_x direction, is $2\pi/L$. Thus the permitted values of $k_x, 0, 2\pi/L, 4\pi/L$ etc., correspond to oscillation wavelengths $\infty, L, L/2, L/3$ etc. Thus in counting the permitted values of k_x all the intuitive values of λ which "fit" between the walls of the cavity are included. The total number of modes of oscillation with $|\,\mathbf{k}\,| \leq k$ is

$$N_k = \frac{\text{total volume of k-space with } |\,\mathbf{k}\,| \leq k}{\text{volume of unit cell}} \times 2 = 2 \times \frac{4}{3}\pi k^3/(2\pi/L)^3. \tag{1.30}$$

The factor of 2 enters because we must take account of the two distinct

Fig. 1.15.

polarizations of the radiation field. Therefore,

$$N_k = \frac{k^3 L^3}{3\pi^2}. \tag{1.31}$$

Now since $k = 2\pi\nu/c$, the number of modes with frequency $\leq \nu$ is

$$N_\nu = \frac{8\pi\nu^3}{3c^3} L^3. \tag{1.32}$$

Since L^3 is the volume of the enclosure, V,

$$\frac{N_\nu}{V} = \frac{8\pi\nu^3}{3c^3}. \tag{1.33}$$

The mode-density (per unit volume per unit frequency interval) is

$$p(\nu) = \frac{1}{V}\frac{dN_\nu(\nu)}{d\nu} = \frac{8\pi\nu^2}{c^3}. \tag{1.34}$$

Rayleigh and Jeans attempted to use this type of frequency dependence to describe the spectral composition of black-body radiation. They assumed that the law of equipartition of energy held for the distribution of energy among the various modes of the radiation field. Consequently, they assigned an equal energy kT to each mode of oscillation and predicted that the intensity distribution of the black-body radiation would be

$$I(\nu) \propto \frac{8\pi\nu^2}{c^3}.$$

This did not fit experimental observations of black-body radiation except at relatively low frequencies (in the red and infrared regions of the spectrum). The predicted large increase in $I(\nu)$ at high frequencies was in dramatic conflict with observations made of black-body emission intensities in the ultraviolet. This conflict between theory and experiment was called the *ultraviolet catastrophe*, as shown in Fig. (1.16). Planck

Fig. 1.16.

resolved these difficulties with his quantum hypothesis. He proposed that each oscillation mode could only take certain quantized energies

$$E_{n_\nu} = (n + \frac{1}{2})h\nu, \qquad n = 0, 1, 2, 3..., \tag{1.35}$$

where the contribution $\frac{1}{2}h\nu$ is called the zero point energy. The probability of finding energy E_n in a particular mode of oscillation is given by classical Maxwell–Boltzmann statistics, i.e.,

$$\frac{P(n)}{P(0)} = \frac{e^{-E_n/kT}}{e^{-E_0/kT}} = e^{-nh\nu/kT}, \tag{1.36}$$

where h is Planck's constant, k is Boltzmann's constant, T is the absolute temperature, and $P(0)$ is the probability of finding the lowest energy in the mode. Consequently the average energy of a mode is:

$$\overline{E}_\nu = \sum_{n=0}^{\infty} \text{ energy of excitation } \times \text{ probability} = \sum_{n=0}^{\infty} P(n)E_n, \tag{1.37}$$

giving

$$\overline{E}_\nu = \sum_{n=0}^{\infty} P(0)e^{-nh\nu/kT}(n + \tfrac{1}{2})h\nu. \tag{1.38}$$

Now, if a particular oscillation is excited it must be in one of the quantized states, therefore

$$\sum_{n=0}^{\infty} P(n) = 1,$$

so

$$\sum_{n=0}^{\infty} P(0)e^{-nh\nu/kT} = 1. \tag{1.39}$$

Thus

$$P(0) = \frac{1}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}}, \tag{1.40}$$

and

$$E_\nu = \frac{\sum_{n=0}^{\infty}(n+\frac{1}{2})h\nu e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}} \tag{1.41}$$

$$= \frac{1}{2}h\nu + \frac{(h\nu e^{-h\nu/kT} + 2h\nu e^{-2h\nu/kT} + ...nh\nu e^{-nh\nu/kT})}{1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + ...e^{-nh\nu/kT}} \tag{1.42}$$

$$= \frac{1}{2}h\nu - \frac{\frac{d}{d(1/kT)}(e^{-h\nu/kT} + e^{-2h\nu/kT} + ...)}{1/(1-e^{-h\nu/kT})} \tag{1.43}$$

$$= \frac{1}{2}h\nu - \frac{\frac{d}{d(1/kT}, [(1/(1-e^{-h\nu/kT})]}{1/(1-e^{-h\nu/kT})} \tag{1.44}$$

$$= \frac{1}{2}h\nu + \frac{h\nu e^{-h\nu/kT}}{(1-e^{-h\nu/kT})^2}(1-e^{-h\nu/kT}). \tag{1.45}$$

We have used a mathematical "trick" here to sum the series in the numerator by recognizing that it is the derivative of a geometric series that we can sum easily. So

$$\overline{E}_\nu = \frac{1}{2}h\nu + \frac{h\nu}{(e^{h\nu/kT}-1)}. \tag{1.46}$$

This is the average energy per mode. Consequently, the stored energy in the black-body radiation field treated as a collection of quantized oscillators is

$$\rho(\nu) = p(\nu)\overline{E}_\nu = \frac{8\pi h\nu^3}{c^3}\left(\frac{1}{2} + \frac{1}{e^{h\nu/kT}-1}\right). \tag{1.47}$$

The $\frac{1}{2}$ factor comes from zero point energy that cannot be released, so the available stored energy in the field is

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3}\left(\frac{1}{e^{h\nu/kT}-1}\right) \tag{1.48}$$

This formula predicts exactly the observed spectral character of black-body radiation and was the first spectacular success of quantum theory. Note that

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3}\left(\frac{1}{e^{h\nu/kT}-1}\right) = \frac{8\pi\nu^2}{c^2} \times\ h\nu \times\ \left(\frac{1}{e^{h\nu/kT}-1}\right), \tag{1.49}$$

which is (the number of modes per volume per frequency interval) $\times$ photon energy $\times 1/(e^{h\nu/kT}-1)$. The quantity $1/(e^{h\nu/kT}-1)$ represents the average number of photons in each mode, this is called the *occupation number* of the modes of the field.

Fig. 1.17.

1.7 Relation Between the Einstein A and B Coefficients

We can derive a useful relationship between Einstein's A and B coefficients by considering a collection of atoms in thermal equilibrium inside a cavity at temperature T. The energy density of the radiation within the cavity is given by

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3}\left(\frac{1}{e^{h\nu/kT}-1}\right), \tag{1.50}$$

since the radiation in thermal equilibrium in the cavity will be black-body radiation. Although real atoms in such a cavity possess many energy levels, we can restrict ourselves to considering the dynamic equilibrium between any two of them, as shown in Fig. (1.17). The jumps which occur between two such levels as a result of interaction with radiation essentially occur independently of the energy levels of the system which are not themselves involved in the jump.

In thermal equilibrium the populations N_2 and N_1 of these two levels are constant so

$$\frac{dN_2}{dt} = \frac{dN_1}{dt} = 0, \tag{1.51}$$

and the rates of transfer between the levels are equal. Since the energy density of a black-body radiation field varies very little over the range of frequencies where transitions between levels 2 and 1 take place we can use Eqs. (1.3) and (1.23) and write

$$\frac{dN_2}{dt} = -N_2B_{21}\rho(\nu) - A_{21}N_2 + N_1B_{12}\rho(\nu). \tag{1.52}$$

Therefore, substituting from Eq. (1.48)

$$N_2\left[B_{21}\frac{8\pi h\nu^3}{c^3(e^{h\nu/kT}-1)} + A_{21}\right] = N_1\left[B_{12}\frac{8\pi h\nu^3}{c^3(e^{h\nu/kT}-1)}\right]. \tag{1.54}$$

For a collection of particles that obeys Maxwell–Boltzmann statistics, in thermal equilibrium energy levels of high energy are less likely to be occupied then levels of low energy. In exact terms the ratio of the population densities of two levels whose energy difference is $h\nu$ is

$$\frac{N_2}{N_1} = e^{-h\nu/kT}. \tag{1.54}$$

So,

$$\frac{8\pi h\nu^3}{c^3(e^{h\nu/kT}-1)} = \frac{A_{21}}{B_{12}e^{h\nu/kT} - B_{21}}. \tag{1.55}$$

This equality can only be satisfied if

$$B_{12} = B_{21} \tag{1.56}$$

and

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}, \tag{1.57}$$

so a single coefficient A_{21} (say) will describe both stimulated emission and absorption. Eqs. (1.56) and (1.57) are called the *Einstein relations.* The stimulated emission rate is W_{21}, where

$$W_{21} = B_{21}\rho(\nu) = \frac{c^3 A_{21}}{8\pi h\nu^3}\rho(\nu), \tag{1.58}$$

which is proportional to energy density. The spontaneous emission rate is A_{21}, which is independent of external radiation.

If we ignored A_{21} in describing the equilibration of the two energy levels previously considered, then in equilibrium we would have

$$N_2 B_{21} = N_1 B_{12}, \tag{1.59}$$

and if $B_{12} = B_{21}$, this would imply $N_1 = N_2$, which we know cannot be so.

Although spontaneous emission would appear to be a different kind of radiative process from stimulated emission, in fact it is not. The modes of the radiation field contain photons. Even a mode of the radiation field containing no photons has a zero point energy of $\frac{1}{2}h\nu$. This zero point energy cannot be extracted from the mode, that is detected, whereas photons in the mode can be. Spontaneous emission corresponds to stimulated emission resulting from this zero point energy of the radiation field.

1.8 The Effect of Level Degeneracy

In real systems containing atoms, molecules or ions, it frequently happens that different configurations of the system can have exactly the

Fig. 1.18.

same energy. If a given energy level corresponds to a number of different arrangements specified by an integer g, we call g the *degeneracy* of the level. We call the separate states of the system with the same energy *sub-levels*. The levels 2 and 1 that we have been considering may consist of a number of degenerate sub-levels, where each sub-level has the same energy, as shown in Fig. (1.18), with g_2 sub-levels making up level 2 and g_1 sub-levels making up level 1. For each of the sub-levels of levels 1 and 2 with population n_1, n_2 respectively, the ratio of populations is

$$\frac{n_2}{n_1} = e^{-h\nu/kT}, \tag{1.60}$$

and

$$N_1 = g_1 n_1, \quad N_2 = g_2 n_2. \tag{1.61}$$

Therefore

$$\frac{n_2}{n_1} = \frac{g_1 N_2}{g_1 N_2}, \tag{1.62}$$

and

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-h\nu/kt}. \tag{1.63}$$

From Eqs. (1.53) and (1.63) it follows that in this case, where degenerate levels are involved, that the Einstein relations become

$$g_1 B_{12} = g_2 B_{21}, \tag{1.64}$$

and as before

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}. \tag{1.65}$$

Note that

$$A_{21} = B_{21}\frac{8\pi h\nu^3}{c^3} = B_{21}\frac{8\pi\nu^2}{c^3} h\nu, \tag{1.66}$$

which can be described as

$B_{21}\times$ no. of modes per unit volume per frequency interval

$\times$ photon energy.

If there were only one photon in each mode of the radiation field, then the resulting energy density would be

$$\rho(\nu) = p(\nu)\overline{E}_\nu = \frac{8\pi\nu^2}{c^3}h\nu. \tag{1.67}$$

The resulting number of stimulated transitions would be

$$W_{21} = B_{21}\frac{8\pi\nu^2}{c^3}h\nu = A_{21}, \tag{1.68}$$

thus, the number of spontaneous transitions per second is equal to the number of stimulated transitions per second that would take place if there was just one photon excited in each mode.

1.9 Ratio of Spontaneous and Stimulated Transitions

It is instructive to examine the relative rates at which spontaneous and stimulated processes occur in a system in equilibrium at temperature T. This ratio is

$$R = \frac{A_{21}}{B_{21}\rho(\nu)}. \tag{1.69}$$

We choose the $\rho(\nu)$ appropriate to a black-body radiation field, since such radiation is always present to interact with an excited atom that is contained within an enclosure at temperature T.

$$R = \frac{A}{B\rho(\nu)} = (e^{h\nu/kT} - 1). \tag{1.70}$$

If we use $T = 300$ K and examine the *microwave region*, $\nu = 10^{10}$ (say), then

$$\frac{h\nu}{kT} = \frac{6.626\times 10^{-34}\times 10^{10}}{1.38\times 10^{-23}\times 300} = 1.6\times 10^{-3}$$

so

$$R = e^{0.0016} - 1 \approx 0.0016$$

and stimulated emission dominates over spontaneous. Particularly, in any microwave laboratory experiment

$$\rho(\nu)_{laboratory\ created} > \rho(\nu)_{black-body}$$

and spontaneous emission is negligible. However, spontaneous emission is still observable as a source of noise – the randomly varying component of the optical signal.

In the *visible region*

$$\nu \approx 10^{15} \quad \frac{h\nu}{kT} \approx 160 \text{ and } A >> B\rho(\nu),$$

So, in the visible and near-infrared region spontaneous emission generally dominates unless we can arrange for there to be several photons in a mode. The average number of photons in a mode in the case of black-body radiation is

$$\overline{n}(\nu) = \frac{1}{e^{h\nu/kT} - 1}, \tag{1.71}$$

which is very small in the visible and infrared.

1.10 Problems

(1.1) In a *dispersive* medium the refractive index varies with wavelength. We can define *a group* refractive index by the relation

$$n_g = n - \lambda\frac{dn}{d\lambda},$$

(i) Prove that $n_g = n + \nu dn/d\nu$.

(ii) Prove that if a black-body cavity is filled with such a dispersive material then the radiation mode density, p_ν, satisfies

$$p_\nu = \frac{8\pi\nu^2 n^2 n_g}{c_0^3}.$$

(iii) Prove also that in such a situation

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3 n^2 n_g}{c_0^3}.$$

(1.2) Calculate the photon flux (photons m^{-2} s^{-1}) in a plane monochromatic wave of intensity 100 W m^{-2} at a wavelength of (a) 100 nm, and (b) 100 μm.

(1.3) What is the total number of modes per unit volume for visible light?

(1.4) Prove Wien's displacement law for black-body radiation, namely

$$\lambda_m T = 2898\mu\text{m K}$$

λ_m is the wavelength of peak emission of the black-body at absolute temperature T K

(1.5) What fraction of the total emission of a normalized Lorentzian lineshape of FWHM $\Delta\nu$ occurs between $\nu_0 - \Delta\nu$ and $\nu_0 + \Delta\nu$?

(1.6) Estimate the total force produced by the photon pressure of the sun on an aluminum sheet of area 10^6 m^2 situated on the surface of the earth. Use sensible values for the parameters of the problem in order to produce a numerical result.

(1.7) Calculate the total stored energy in a 1 m^3 box that lies between the wavelengths 10.5 μm and 10.7 μm at a temperature of 3000 K.

(1.8) What would the spectral energy density distribution be if "black-body" radiation could only occupy *two-photon* states? Namely, the only allowed energies for the various modes of a cavity would be

$$E_n = (2n + 1)h\nu.$$

Hint: First calculate mode density, and then average energy per mode.

(1.9) At what temperature would the stimulated and spontaneous emission rates be equal for particles in a cavity and a transition at a wavelength of 1 μm.

(1.10) A point source emits a Lorentzian line of FWHM 1 GHz at $\lambda_0 =$ 500 nm and total radiated power of 1 W. A square bandpass optical filter with transmittance 0.8 between $\nu_0 - \Delta\nu$ and ν_0 covers an optical detector of active surface area 10 mm^2 placed 1 m from the source. What light intensity reaches the detector? Hint: $\int 1/(1 + x^2)/dx = \text{ arc } \tan x$