ATOMIC RADIATION

7

7.1 INTRODUCTION AND PRELIMINARY IDEAS

It is the purpose of this chapter to introduce the elementary concepts leading to gain in an atomic system and thus, with proper feedback, a laser. Since a laser is a quantum device, we first review the necessary concepts from this theory to understand the conditions leading to gain.

These concepts are amazingly simple and are quite palatable, even to those who have not had a formal introduction to quantum mechanics.

1. There are discrete energy levels in an atomic (or molecular, or solid, or semiconductor) system. We represent them by an energy-level diagram as shown in Fig. 7-1.

2. The system can make a transition between these two states by the emission of a photon of energy \( E = E_2 - E_1 = \hbar \nu \), thereby changing an atom labeled by (2) into one identified with (1). Or to reverse the process, an atom in state 1 can absorb a photon of this same energy and be labeled as in state 2.

These two ideas are the only ones we need to “accept”; the rest will follow naturally and with little effort on our part.

In addition to the simple ideas expressed above, we need to understand the origin of the correct description of blackbody radiation theory. (At low frequencies, this radiation is referred to as “white” noise, “Johnson’s” noise, or “Nyquist” noise, all being equal to Planck’s blackbody radiation formula at those limits.) Indeed, it was this problem that inspired Planck to make the quantum hypothesis—namely that electromagnetic energy at a frequency \( \nu \) can be present only in discrete multiples of \( \hbar \nu \).

Understanding the origin of Planck’s development of this formula is essential to appreciate the beauty and simplicity of Einstein’s description of the role of the atoms in arriving at this relation. The importance of Einstein’s approach is that it provides the key to the analysis of systems that are not in thermodynamic equilibrium; a laser is a prime example.

Furthermore, Einstein’s approach provides us with a connection between transition rates between quantum states and quantities that can be measured experimentally. Consequently, we can approach such transitions in a phenomenological manner using the published experimental results, thereby bypassing some very complex and complicated quantum calculations.

The foregoing should not be construed to downgrade the importance of a full quantum description of a laser. There are phenomena which are not predicted by the rate-equation approach and which require a detailed analysis by quantum-theoretical methods. But for the initial understanding, Einstein’s rate equations are quite adequate.

We will also have to modify slightly the picture shown in Fig. 7-1 to account for the uncertainty principle and “real-life” broadening processes. An atom is never isolated; a gas atom is in helter-skelter motion, it collides with other atoms (with same kind or with different ones), and it may be subjected to external fields. As a consequence, the energy levels are not perfectly sharp, and thus there is a finite band of frequencies emitted by a collection of atoms and a finite band for amplification.

Once these ideas are in hand, the laser gain equation is a trivial application and oscillation is merely a matter of providing feedback.
7.2 BLACKBODY RADIATION THEORY

The starting point for the quantum era was the derivation, from first principles, of a formula that described the radiation emerging from a small hole in a highly polished "cavity" such as that shown in Fig. 7-2(a). The experimental facts known from the late 1800s were:

1. The hole acted as a nearly perfect blackbody—one whose emission coefficient\(^1\) as a function of frequency was as high as possible, 1.

2. Thus, the intensity emitted by this hole is directly proportional to the energy density of the electromagnetic radiation inside the cavity.

3. This energy density, in a fixed-frequency interval \(dv\) (determined by the measurement technique), had the functional form of (7-1).

\[
\rho(v) = \frac{a v^3}{e^{\frac{h v}{k T}} - 1}
\]

or

\[
\rho(\lambda) d\lambda = \frac{a' \lambda^2}{e^{\frac{h c}{k \lambda T}} - 1}
\]

(7-1)

---

\(\frac{V}{\lambda}

----

\(\lambda_{\text{max}}\) Rayleigh–Jeans

\(\lambda_{\text{max}} \propto \frac{1}{T}

\(\lambda_{\text{max}}\) \(\propto \frac{1}{T}

\(\lambda_{\text{max}}\) \(\propto \frac{1}{T}

---

Figure 7-2. (a) The cavity used to measure the blackbody spectrum; (b) \(I(\lambda) d\lambda\)

from experiment. (Note: \(\lambda_{\text{max}} T = 2.898 \times 10^7 \text{ A}^{-2} \text{ K}^{-1}\))

---

It is important to realize that these facts were known before the advent of quantum mechanics. Even though these facts were known, they were not understood.

---

\(\frac{V}{\lambda}

----

\(\lambda_{\text{max}}\) Rayleigh–Jeans

\(\lambda_{\text{max}} \propto \frac{1}{T}

\(\lambda_{\text{max}}\) \(\propto \frac{1}{T}

---

1 Kirchhoff's radiation law states that the emissivity of a body is equal to its absorptivity. Thus, the cavity would also absorb all electromagnetic energy entering through the hole.

---

One of the triumphs of nineteenth-century physics was the phenomenal success of Maxwell's theory of electromagnetic radiation. Yet here was an electromagnetic problem, coupled with some elementary thermodynamics, which defied explanation. To illustrate some of the difficulties, let us follow some of the reasoning used to arrive at the wrong answer.

Since Maxwell's theory was so successful, and everyone recognized the electromagnetic character of light, it was natural to approach this problem from that standpoint. We assume that the electromagnetic energy is in the form of a standing wave on the interior of the cavity. It is a straightforward process to count the number of resonant frequencies of a cavity in the form of a cube of volume \(a^3\). Those frequencies are given by

\[
\left(\frac{\omega}{c}\right)^2 = \left(\frac{m \pi}{a}\right)^2 + \left(\frac{n \pi}{a}\right)^2 + \left(\frac{q \pi}{a}\right)^2
\]

or

\[
v = \frac{c}{2\pi} \sqrt{(m^2 + n^2 + q^2)^{1/2}}
\]

(7-2)

If we identify the brackets with a spherical coordinate \(r\) with the corresponding Cartesian coordinates \((m, n, q)\), the resonant frequency is the scale factor \(c/2a\) times this radius:

\[
v = \frac{c}{2a} r, \quad r = (m^2 + n^2 + q^2)^{1/2} = \frac{2\pi v}{c}
\]

Thus, the number of resonant frequencies (or modes) between 0 and \(v\) is equal to one-eighth of the volume of this sphere of radius \(r\) (since only positive Cartesian indices \((m, n, q)\) are allowed), and this must be multiplied by a factor of 2 to account for the two independent polarizations of the field, which have the resonance frequencies given by (7-2).

\[
N = \frac{4\pi r^3}{3} \times \frac{1}{8} \times 2 = \frac{8\pi v^4}{3c^3} a^3
\]

(7-3a)

Thus, the mode density (i.e., the number of modes per unit of frequency per unit of volume) equals

\[
n(v) = \frac{1}{V} \frac{dN}{dv} = \frac{8\pi v^4}{3c^3} \left(\frac{\sqrt{v}}{\sqrt[3]{v}}\right)
\]

(7-3b)

Having counted the number of ways that the energy can be distributed, we are now faced with the problem of assigning an average energy to each mode.

Many other physical quantities such as this could be predicted by assigning \(kT/2\) amount of energy to each degree of freedom in the system.
Thus, gas molecules could move in \(x\), \(y\), and \(z\) directions and thus the average energy of translation was \(\frac{1}{2} kT\), in agreement with experiment. In the electromagnetic case we have two types of fields, \(E\) and \(H\), with equal amounts of the two types of energy in a resonant mode; thus, the average energy per mode should be \(kT\).

\[
\text{average energy per mode } = kT \quad (7-4)
\]

Multiplying (7-3) and (7-4), we obtain the average energy per unit of volume in the frequency interval \(\Delta\nu\) centered at \(\nu\).

\[
\rho(\nu) \Delta\nu \left(\frac{\text{joule}}{\text{volume}}\right) = \left(\frac{8\pi\nu^2}{c^3} kT\right) \Delta\nu \quad (Wrong!)
\]

(7-5)

Equation (7-5) is the Rayleigh–Jeans distribution of blackbody radiation, which, as shown in Fig. 7-2(b), did not agree with experiment. Although it does agree with experiment at long wavelengths (microwaves and lower frequencies), it predicts the absurd conclusion that there is infinite energy in the system when all frequencies are concerned (the ultraviolet catastrophe).

It is hard to argue with the line of reasoning leading to (7-5): the number of modes times the average energy per mode. Thus, the error must be in the computation of one of those quantities. Planck accepted and retained the mode calculation and turned his attention to computing the average energy per mode.

Planck made the initial quantum hypothesis that electromagnetic energy at a frequency \(\nu\) could only appear as a multiple of the step size \(h\nu\). Energies between \(h\nu\) and \(2h\nu\) do not occur! This is in stark contrast to classical ideas where all energies are permitted—by allowing the field to have continuously variable amplitudes. Having made this radical departure from accepted concepts, he returned to classical Boltzmann statistics to compute the average energy.

If \(\epsilon_1, \epsilon_2, \epsilon_3, \ldots\) are the allowed energies, we must weigh each energy by the relative probability that it can occur and then divide by the sum of all relative probabilities. According to Boltzmann statistics, the relative probability that an energy \(\epsilon\) can occur is simply \(e^{-\epsilon/kT}\), the Boltzmann factor. Following the recipe above, we obtain

\[
\epsilon = nh\nu \quad \text{(the quantum hypothesis)} \quad (7-6)
\]

\[
\langle\epsilon\rangle = \frac{\nu e^{-h\nu/kT} + 2\nu e^{-2h\nu/kT} + 3\nu e^{-3h\nu/kT} + \cdots}{e^{-h\nu/kT} + e^{-2h\nu/kT} + e^{-3h\nu/kT} + \cdots} \quad (7-7)
\]

\[
\sum \frac{\nu e^{-nh\nu/kT}}{\sum e^{-nh\nu/kT}} \quad (7-8)
\]

One might be tempted to replace the summation by an integral; a procedure that yields an average energy given by (7-4), which is wrong. Fortunately, the series given in (7-8) can be summed exactly to yield

\[
\langle\epsilon\rangle = \frac{h\nu}{e^{h\nu/kT} - 1} \quad (7-9)
\]

Then the energy density of the electromagnetic field inside the cavity at the center frequency of interest is

\[
\rho(\nu) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1} \quad (7-10)
\]

Equation (7-10) is written as a product of two factors to emphasize the origins: the first is a purely classical electromagnetic result, with the second being the quantum value of the average energy of the classical field. Since the package of energy in the field is a multiple of the quantum of energy \(h\nu\), the term \(1/[\exp(h\nu/kT) - 1]\) is the number of quanta in a cavity mode.

Let us evaluate this number for a reasonable set of circumstances. Let \(T = 1200^\circ\text{K}\) (an "orange" color temperature) and \(\lambda = 6000\text{\AA}\) (an orange color); then \(\nu = 5 \times 10^{14}\) and the average number of photons per mode is \(\sim 10^{-9}\).

One must interpret that number correctly. If the energy comes in discrete steps, one cannot have a fraction of a photon in a mode—rather one has a photon in the particular cavity mode for a small—very small—fraction of the time. This particular point is important and distinguishes a laser that has at least one photon in a particular mode all the time.

### 7.3 Einstein's A and B Coefficients

#### 7.3.1 Definition of Radiative Processes

Einstein was able to arrive at the same functional form for the radiation by considering the interaction of the waves with the atoms in the cavity walls. He accepted the quantum hypothesis that the energy comes in discrete packages of \(h\nu\) each, and as a consequence there must be two energy states in the atoms separated by this value,\(^2\) as shown in Fig. 7-3. He identified three processes by which the atoms could interact with the electromagnetic field.

\(^2\)As a matter of practicality, there is a continuum of states, but this does not argue against his reasoning.
Figure 7.3. Radiative processes in a two level system.

(a) **Spontaneous Emission** \((A_{21})\). As the name implies, it appeared as if the atoms in state 2 decayed spontaneously to state 1; in doing so, they added their excess energy to the cavity field in the form of a photon. If the population density in state 2 was \(N_2\), the decay of this state is given by

\[
\frac{dN_2}{dt} _{\text{spontaneous}} = -A_{21}N_2 \tag{7-11}
\]

Notice that this equation says something very simple and transparent: if no other process took place, the atomic population would run “down hill” with a time constant \(\tau = (A_{21})^{-1}\). Obviously, the bottom of the “hill,” \(N_1\), must increase just as fast as the top decreases.

(b) **Absorption** \((B_{12})\). In this process an atom in state 1 absorbs a photon from the field and thus converts the atom into one of those in state 2. The rate at which this process takes place must depend upon the number of absorbing atoms and the field from which they extract the energy. Thus, we have

\[
\frac{dN_2}{dt} _{\text{absorption}} = +B_{12}N_1 \rho(v) = -\frac{dN_1}{dt} _{\text{absorption}} \tag{7-12}
\]

where the string of equalities expresses the obvious idea again that \(N_1\) must decrease if \(N_2\) increases.

(c) **Stimulated Emission** \((B_{21})\). This process is the reverse of absorption; the atom gives up its excess energy, \(hv\), to the field, adding coherently to the intensity. Thus, the added photon is at the same frequency, at the same phase, in same sense of polarization, and propagates in the same direction as the wave that induced the atom to undergo this type of transition. Obviously, the rate is dependent upon the number of atoms to be stimulated and the strength of the stimulating field.

\[
\frac{dN_2}{dt} _{\text{stimulated emission}} = -B_{21}N_2 \rho(v) = -\frac{dN_1}{dt} _{\text{stimulated emission}} \tag{7-13}
\]

These three processes are shown in Fig. 7-4, where some artifacts have been used to emphasize various issues.

Note that “nothing” comes into Fig. 7-4(a), but a photon comes out, most likely in a direction different from the one you predict. That is spontaneous emission; the atom can radiate into any of 4π steradians with any sense of polarization. The absorption should be familiar to most; the wave decreases in amplitude and the atom in state 1 is converted to state 2. Obviously, that part of the wave not absorbed continues along its path. The picture for stimulated emission is just the inverse of absorption. If one accepts this inverse relation, much of the “magic” about stimulated emission disappears. One would not question the fact that the transmitted wave in Fig. 7-4(b) is at the same frequency, in the same direction, and has the same polarization as the incident wave. By identifying Fig. 7-4(c) as the inverse process to Fig. 7-4(b), one attributes those same characteristics to the portion of the wave that adds to the stimulating wave.

### 7.3.2 Relationship Between the Coefficients

By defining these processes, Einstein was able to reproduce the blackbody formula within the framework of thermodynamic equilibrium. The sum of (7-11) through (7-13) yields the total rate of change of the population density in state 2 (or 1) due to the radiative processes.

Figure 7.4. Effect of radiation on an atom.
\[
\frac{dN_2}{dt} = -A_{21}N_2 + B_{12}N_1 \rho(v) - B_{21}N_2 \rho(v) = -\frac{dN_1}{dt}
\] (7-14)

At equilibrium, the time rate of change must be zero.

\[
\frac{N_2}{N_1} = \frac{B_{12}\rho(v)}{A_{21} + B_{21}\rho(v)}
\] (7-15)

Einstein also used Boltzmann statistics for the ratio of populations in the two energy states at thermodynamic equilibrium.

\[
\frac{N_2}{N_1} = \frac{g_2}{g_1} \exp\left(-\frac{\Delta E}{kT}\right) = \frac{g_2}{g_1} \exp\left(-\frac{\hbar v}{kT}\right)
\] (7-16)

where \(g_2/g_1\) is the degeneracy of the states (i.e., the number of independent ways in which the atom can have the same energy). Combining (7-15) and (7-16) yields

\[
\frac{g_2}{g_1} \exp\left(-\frac{\hbar v}{kT}\right) = \frac{B_{12}\rho(v)}{A_{21} + B_{21}\rho(v)}
\] (7-17)

One can always imagine an extreme temperature such that \(kT \gg \hbar v\), and, under such circumstances, the terms with \(\rho(v)\), the electromagnetic energy density, dominates on the right. This yields a very important relationship between the absorption and stimulated emission coefficients:

\[
\frac{B_{12}}{B_{21}} = \frac{g_2}{g_1} \quad \text{or} \quad g_2B_{21} = g_1B_{21}
\] (7-18)

Having made this identification, we return to (7-17) and solve for \(\rho(v)\):

\[
\begin{align*}
A_{21} & \frac{g_2}{g_1} e^{-\hbar v/kT} + B_{21} \frac{g_2}{g_1} e^{-\hbar v/kT} \rho(v) = \frac{B_{12}}{A_{21}} \frac{g_2}{g_1} B_{21} \rho(v) \\
& \text{or} \\
\rho(v) &= \frac{A_{21}}{B_{21} e^{\hbar v/kT} - 1} \frac{1}{c^2} e^{\hbar v/kT} - 1
\end{align*}
\] (7-19)

Comparing (7-19) with the Planck formula, (7-10), yields the relationship between \(A_{21}\) and \(B_{21}\):

\[
A_{21} = \frac{8\pi\hbar^3}{c^2}\]

or

\[
\frac{A_{21}}{B_{21}} = \frac{8\pi\hbar^3}{c^2}
\] (7-20)

Since \(B_{12} = (g_2/g_1)B_{21}\), all three coefficients, \(A_{21}, B_{21},\) and \(B_{12}\), are thus interrelated. If one is known, all are known. Although a particular experiment may emphasize one or another coefficient, the result may be applied to a completely different one. For instance, an absorption experiment yields vital information on the stimulated emission coefficient.

It is most important to realize that these coefficients are characteristic of the atom. The atom, per se, does not know (or care) whether it is in a thermodynamic equilibrium environment of a heated cavity or in the presence of an intense field (a laser) generated by other atoms. It responds according to the rates indicated by (7-11), (7-12), and (7-13) for electromagnetic radiation.

However, radiation is not the only thing that can affect an excited atom. The atoms can undergo a collision with another atom, an electron, or a lattice vibration (a phonon) which can also cause transitions to take place. Einstein's approach places radiation on an equal footing with these other processes and incorporates the interchange between the states in a natural and straightforward manner. The power of this approach is shown in the next section.

### 7.4 Introduction to the Rate Equations—Lifetime Broadening

The example shown in Fig. 7-5 will illustrate the transparent simplicity of Einstein's approach and will also serve to introduce the concept of level broadening, which in turn leads to the idea of a line shape of an atomic transition.

Here we imagine a very dilute gas in which a small number, \(\Delta N\), is excited to state 2 at \(t = 0\). Then all external sources are removed and the system relaxes back toward its equilibrium state, with all atoms in the lowest-energy state. We assume that this number, \(\Delta N\), although small, is far in excess of the thermodynamic population predicted by Boltzmann statistics.

It is not necessary to specify how this excitation is provided, but it helps in visualization. Thus, to be definitive in the example, we assume that the...