V. Absorption and emission of radiation in gases at high temperatures

§1. Introduction. Types of electronic transitions

It was shown in Chapter II that the light* absorption coefficient is the fundamental optical characteristic of a gas which determines the degree of blackness of a heated body, the spectral radiation intensity, and the energy balance in a fluid undergoing radiant heat exchange. When the absorption coefficient is known, Kirchhoff's law, which is an expression of the general principle of detailed balancing, may be used to determine the emission coefficient of the fluid.

In §2 of Chapter II we have presented a short review and classification of the various mechanisms of absorption and emission. In accordance with the general scheme of allowed energy states of atomic systems (the simplest of which consists of one proton and one electron and constitutes the hydrogen atom in the bound state), all allowed electronic transitions accompanying the absorption and emission of light are subdivided into three types. These are:

(1) free-free transitions (bremsstrahlung emission and absorption);
(2) bound-free transitions (photoelectric absorption);
(3) bound-bound (discrete) transitions.

Free-free and bound-free transitions result in continuous absorption and emission spectra. Bound-bound transitions in atoms result in line spectra, while in molecules they result in the formation of band spectra. Band spectra consist of a great number of spectral lines which are closely spaced with respect to frequency. Under certain conditions the individual lines are so close to one another that they even partially overlap and the resulting spectrum is almost continuous (quasi-continuous).

From an energy point of view continuous (quasi-continuous) spectra are of primary interest. Let us imagine, for example, a body heated to a uniform temperature T. If the body is perfectly black, then the radiation flux emitted from its surface will have the Planck spectral distribution. The spectral flux as a function of the frequency v is shown by the dashed curve in Fig. 5.1. The

* We recall that the terms "light", "light quanta", "photons", and "optical" properties refer to radiation at all frequencies and not just to those frequencies which lie in the visible part of the spectrum.
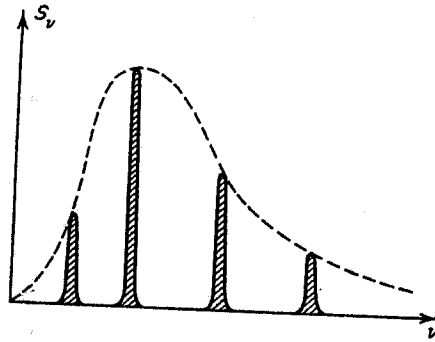
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Fig. 5.1. Emission spectrum of a heated body which is perfectly transparent to the continuous spectrum, but is opaque to a line spectrum. The dashed curve corresponds to the Planck spectrum at the given temperature.

area bounded by this curve gives the integrated radiant energy emitted per unit area of surface per unit time σT^4. Let us now assume that the medium is perfectly transparent to the continuous spectrum and that it absorbs and emits only a line spectrum, where the line radiation for the given frequencies is in thermodynamic equilibrium with the medium. The spectral radiation flux from the body surface is now described by a system of individual narrow lines whose height corresponds to the Planck function, as shown in Fig. 5.1 by the solid curves. The integrated radiant energy emitted per unit area of body surface per unit time is numerically equal to the cross-hatched area of these lines. Since the line widths are very narrow, this energy flux is consider-ably lower than the integrated Planck flux σT^4. The radiant energy losses and also the surface brightness are, in this case, considerably smaller than in the case of a continuous spectrum. Similarly, for radiant energy transfer within the body the line spectra are frequently of little importance in comparison with that of continuous spectra. Therefore, most of our attention in this chapter will be devoted to continuous and quasi-continuous molecular spectra, rather than to line spectra.

At high temperatures, when the molecules are dissociated and the gas consists of atoms or (at even higher temperatures) of ions and electrons, the continuous absorption and emission spectra arise as a result of bound-free and free-free transitions. The calculation of the electronic transition proba-bilities, the results of which could then be used to find the absorption (and emission) coefficient for the case of multi-electron atoms (complex atomic systems), is a quantum-mechanical problem of considerable difficulty. This problem requires a separate analysis for each particular case, for each atom or ion, and also for each quantum state of the system. Such calculations have been carried out only for a few particular cases.

Complete and relatively simple calculations can be carried out only for the simplest hydrogen-like (hydrogenic) systems, that is, for the transitions of a single electron in the Coulomb field of a positive charge Ze. In practice, even when considering the emission and absorption of light in gases composed of complex atoms or ions, it is frequently necessary to use the relations derived for hydrogen-like systems. The atom or ion is in this case represented as an "atomic remainder" with a positive point charge Ze, in the field of which an "optical" electron moves, undergoing transitions from one energy level to another with the absorption or emission of a photon. As will be shown below, this approximation is to some extent justified in many cases of practical importance.

In calculating molecular absorption coefficients, the coefficient is usually determined as a function of frequency and temperature to within a factor termed the oscillator strength for the electronic transition considered; this factor is determined experimentally, as a rule.

In the following sections of this chapter we consider in detail the different mechanisms of light absorption and emission in gases at high temperatures, and the calculations for the corresponding absorption coefficients. We shall be primarily interested in the fundamental physical aspects of the problem and shall not dwell in detail on the various approximate methods for improving the formulas for calculating absorption coefficients.

Very frequently several different mechanisms which are independent of each other participate in the absorption and emission of light in gases under different conditions. The total absorption and emission coefficients in each spectral region are composed of quantities corresponding to these different mechanisms. Therefore, it is quite proper to examine independently the effect of each individual mechanism. At the end of the chapter we shall consider the radiative properties of high-temperature air as the most important practical example illustrating the combined effect of many mechanisms.

1. Continuous spectra

§2. Bremsstrahlung emission from an electron in the Coulomb field of an ion

As is well known from classical electrodynamics, radiation is emitted from a free electron moving in an external electric field, let us say, in the Coulomb field of an ion of positive charge Ze. In the process the electron loses a part of its kinetic energy and slows down. Hence such radiation is called bremsstrahlung.

The radiant energy S emitted by an electron per unit time is determined by its acceleration $\mathbf{w}$

$$S = \frac{2}{3}\frac{e^2}{c^3}\mathbf{w}^2. \tag{5.1}$$

The total radiation emitted during the entire time of travel past an ion is equal to the time integral of this expression

$$\Delta E = \int_{-\infty}^{\infty} S\, dt = \frac{2}{3}\frac{e^2}{c^3}\int_{-\infty}^{\infty}\mathbf{w}^2\, dt. \tag{5.2}$$

The spectral composition of the radiation may be found by expanding the acceleration vector $\mathbf{w}$ in a Fourier integral and substituting the expansion into (5.2). This yields

$$\Delta E = \frac{16\pi^2}{3}\frac{e^2}{c^3}\int_0^{\infty}\mathbf{w}_\nu^2\, d\nu = \int_0^{\infty} S_\nu\, d\nu, \tag{5.3}$$

where

$$\mathbf{w}_\nu = \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathbf{w}(t)\, e^{-i2\pi\nu t}\, dt$$

is the Fourier component of the acceleration vector $\mathbf{w}(t)$. The quantity

$$S_\nu = \frac{16\pi^2}{3}\frac{e^2}{c^3}\mathbf{w}_\nu^2 \tag{5.4}$$

represents the radiant energy per unit frequency interval* emitted with a frequency ν by an electron passing an ion.

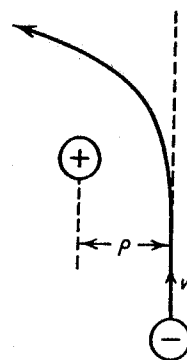According to classical mechanics, when energy losses by radiation are

Fig. 5.2. Trajectory of an electron passing a positive ion.

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* Following astrophysical practice, we shall always use the ordinary frequency ν rather than the angular frequency $\omega = 2\pi\nu$.

absent, a free electron (the sum of whose kinetic and potential energy is positive) passes the ion along a well-defined hyperbolic orbit characterized by the impact parameter ρ, the meaning of which is clear from Fig. 5.2. The total radiant energy and spectral composition of the radiation can be calculated approximately from equations (5.2)–(5.4), by taking for the acceleration $w(t)$ the value corresponding to the motion of the electron in the absence of radiation. This is equivalent to assuming that the radiation is weak.

Let a parallel beam of electrons with initial velocity v at infinity and constant number density N_e (the electron flux is $N_e v$) be incident on the ion from infinity. Through an elementary ring of area $2\pi\rho \, d\rho$ about the ion $N_e v \cdot 2\pi\rho \, d\rho$ electrons pass per unit time. Each electron emits ΔE ergs of energy. The radiant energy emitted by these electrons per unit time is $\Delta E \, N_e v \cdot 2\pi\rho \, d\rho$ erg/sec. The energy emitted per unit time by the electrons passing the ion along all possible orbits can be obtained by integrating this expression with respect to ρ from 0 to ∞. The total emitted energy per ion for a unit electron flux $N_e v = 1 \text{ cm}^{-2} \text{ sec}^{-1}$ is

$$q = \int_0^\infty \Delta E \, 2\pi\rho \, d\rho \; (\text{erg} \cdot \text{cm}^2). \tag{5.5}$$

We can also speak of the energy radiated in the frequency interval v to $v + dv$, the so-called effective radiation dq_v $\left(\int_{v=0}^{v=\infty} dq_v = q\right)$. In accordance with the definition given by (5.3) the effective radiation, the energy emitted in the frequency interval dv per ion and per unit electron flux, is

$$dq_v = dv \int_0^\infty S_v 2\pi\rho \, d\rho \; (\text{erg} \cdot \text{cm}^2). \tag{5.6}$$

The effective radiation determines the spectral emission coefficient of a medium due to bremsstrahlung emission.

If a unit volume contains N_+ ions of a particular species and dN_e electrons with speeds between v and $v + dv$, then the energy in the frequency interval between v and $v + dv$ emitted per unit time by a unit volume as a result of the slowing down of these electrons in the field of the ions is $N_+ v \, dN_e \, dq_v$ (erg/cm$^3 \cdot$ sec).

Let us estimate the effective radiation of electrons in the Coulomb field of an ion. If the electron is at a distance r from the ion (radius vector $\mathbf{r}$), then it is subjected to the force $-Ze^2\mathbf{r}/r^3$. The acceleration due to this force is $\mathbf{w} = -Ze^2\mathbf{r}/r^3 m$, where m is the electron mass. Let the electron have an initial velocity v and impact parameter ρ with respect to the ion. The time during which the force acts t is of the order of ρ/v, and the maximum acceleration interval of the electron during this time w is of the order of $Ze^2/\rho^2 m$. The principal role in the expansion of the acceleration vector in the Fourier integral is

played by frequencies v of the order of $1/2\pi t \sim v/2\pi\rho$ *. We can say that the frequency v is radiated mainly by the electrons passing the ion at the distance $\rho \sim v/2\pi v$, and that frequencies in the interval from v to $v + dv$ are mainly emitted by electrons with impact parameters in the interval $d\rho \sim (v/2\pi v^2)\,dv \sim 2\pi(\rho^2/v)\,dv$. The energy emitted by each of these electrons is given in order of magnitude by

$$\Delta E \sim \frac{2}{3}\frac{e^2}{c^3}\,w^2 t \sim \frac{2}{3}\frac{Z^2 e^6}{m^2 c^3 \rho^3 v}.$$

The effective radiation at the frequency v corresponds to the radiation emitted by electrons with impact parameters from ρ to $\rho + d\rho$ and from the above relation is given by

$$dq_v \sim \Delta E\,2\pi\rho\,d\rho \sim \frac{4\pi}{3}\frac{Z^2 e^6\,d\rho}{m^2 c^3 \rho^2 v} \sim \frac{8\pi^2}{3}\frac{Z^2 e^6}{m^2 c^3 v^2}\,dv. \qquad (5.7)$$

The exact calculation of the effective radiation using (5.6) and (5.4), using the acceleration vector found by solving the mechanical problem of the motion of an electron in a hyperbolic orbit about an ion, is given in the book of Landau and Lifshitz [1]. The result is

$$dq_v = \frac{32\pi^2}{3\sqrt{3}}\frac{Z^2 e^6}{m^2 c^3 v^2}\,dv \qquad \text{for} \quad v \gg \frac{mv^3}{2\pi Z e^2}, \qquad (5.8)$$

$$dq_v = \frac{32\pi}{3}\frac{Z^2 e^6}{m^2 c^3 v^2}\ln\frac{mv^3}{1.78\pi v Z e^2}\,dv \qquad \text{for} \quad v \ll \frac{mv^3}{2\pi Z e^2}. \qquad (5.9)$$

It is evident that the exact result at high frequencies differs from the simple estimate (5.7) only by the numerical factor $4/\sqrt{3} = 2.3$. At low frequencies the exact result differs from the approximate one by a logarithmic factor which is a function of the frequency, as well as by a numerical factor. To explain this we note that the low frequencies radiated come from distant collisions with large impact parameters ρ; as $v \to 0$ and $\rho \to \infty$, the collisions with impact parameters $\rho > v/2\pi v$ give a relatively larger and larger contribution to the radiation at the frequency v in comparison with that from the collisions with impact parameters $\rho \sim v/2\pi v$. The latter collisions are the only ones accounted for in deriving the simple formula (5.7).

The divergence of the effective radiation in the low frequency range is characteristic of a Coulomb field, which decreases slowly with distance; the result is that distant collisions become of considerable importance. This divergence can be eliminated by taking into account the screening effect, which is always present in an actual ionized gas. Actually, the integration

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* For greater accuracy we shall retain the numerical coefficient 2π. (The fundamental role in the expansion is played by the "angular" frequencies such that $\omega t \sim 1$.)

with respect to ρ in (5.6) should be taken not to infinity but, say, to the Debye radius d; the radiation from the low frequency region is then cut off at $v_{min} \sim v/2\pi d$.

It should be noted, however, that the radiation integrated over the spectrum $q = \int dq_v$ converges in the low frequency region, since the divergence in dq_v is only logarithmic and the contribution of the peak value of dq_v in the integral with respect to v is not large as $v \to 0$. Therefore, if we are interested in the integrated radiation only, then the question of cutting off the impact parameters ρ from above and the frequencies from below is not too important.

In the classical theory, the high frequency radiation is independent of frequency and the effective radiation per unit frequency interval dq_v/dv remains finite even as $v \to \infty$ *. Formally, the integrated radiation $q = \int dq_v$ diverges in the high frequency region. This contradiction in the theory is a result of the imperfection of the classical concepts about the motion of an electron and is eliminated in the quantum theory. High frequencies, as we have seen, are radiated when an electron with a small impact parameter passes an ion. But, according to quantum-mechanical concepts, an electron having an initial momentum $p = mv$ cannot be located with greater precision than that allowed by the uncertainty principle $\Delta r \, \Delta p \sim h/2\pi$. Since the uncertainty in the momentum cannot exceed the momentum itself, there is no point in discussing impact parameters smaller than $\rho_{min} \sim h/2\pi mv$. The maximum frequency radiated for such minimum impact parameters is of the order of $v_{max} \sim v/2\pi\rho_{min} \sim mv^2/h$. This upper limit to the emitted frequency has a clear physical meaning. The quantum theory represents the bremsstrahlung as follows. A free electron with an initial energy $E = \frac{1}{2}mv^2$ passing near an ion can emit a photon hv. If the electron remains free after the emission, that is, has a positive energy E' upon moving away from the ion, then, obviously, the electron cannot emit a photon whose energy exceeds the initial energy E. Thus, $v_{max} = E/h = \frac{1}{2}mv^2/h$, which coincides with the frequency limit allowed by the uncertainty principle to within a factor of $\frac{1}{2}$.

In quantum mechanics a free electron is represented by a plane wave and the concept of the impact parameter does not have a precise meaning. We can speak of the probability of emission of a photon of a particular frequency, or, more precisely, about the cross section for the emission of photons with energies between hv and $hv + d(hv)$. The energy emitted in the frequency interval dv per unit flux of electrons interacting with a single ion is equal to the product of the photon energy hv and the emission cross section $d\sigma_v$. This quantity corresponds to the effective radiation of the classical theory

$$dq_v = hv \cdot d\sigma_v \, (\text{erg} \cdot \text{cm}^2). \tag{5.10}$$

* This is true only when the colliding particles are oppositely charged (an electron and a positive ion). For the interaction between similarly charged particles $dq_v/dv \to 0$ as $v \to \infty$.

In the light of the correspondence principle, the effective radiation of frequency v is related to the transition of an electron from one "stationary hyperbolic orbit", corresponding to an electron energy E, to another, corresponding to the energy $E' = E - hv$. The cross section $d\sigma_v$ and, consequently, the effective radiation dq_v, are calculated in quantum mechanics by the usual methods, using the matrix elements of the interaction energy between the electron and the ion.

Before discussing the results of quantum-mechanical calculations of bremsstrahlung emission, let us examine the limits of applicability of the classical relations (5.8) and (5.9) and the conditions under which it is necessary to replace these relations by quantum-mechanical ones. According to the classical derivation, (5.8) is valid for high frequencies where $v \gg mv^3/2\pi Ze^2$. Of course, there is no point in extending the inequality beyond those frequencies given by the upper limit $v_{max} = E/h = \frac{1}{2}mv^2/h$ dictated by quantum-mechanical energy considerations. Let us rewrite the limits imposed upon the frequency in (5.8) in the form

$$1 = \frac{hv_{max}}{E} > \frac{hv}{E} \gg \frac{h}{E} \frac{mv^3}{2\pi Ze^2} = \frac{hv}{\pi Ze^2}. \qquad (5.11)$$

The inequality $hv/\pi Ze^2 \ll 1$, except for a factor of 2, represents nothing else but the condition for quasi-classical motion of an electron in a Coulomb field (see [2], for example)

$$\frac{hv}{2\pi Ze^2} \ll 1. \qquad (5.12)$$

Therefore, the classical formula (5.8) for the effective radiation at a frequency v, limited from above and below by the inequalities (5.11), can be used as an approximation for all electron velocities satisfying the inequality (5.12). If the quasi-classical condition (5.12) is satisfied, then the region of applicability of (5.8) extends down to very low frequencies, those for which $hv/E \sim hv/\pi Ze^2 \ll 1$. Since the energies of the photons which are ordinarily of interest are not too small in comparison with kT, in comparison with the energies of the electrons, and since the contribution of the peak value to the integrated radiation as $v \to 0$ is not too large, (5.8) can be extended to $v = 0$ by replacing it by (5.9). The divergence in dq_v as $v \to 0$ is thus formally eliminated.

Let us transform the quasi-classical condition (5.12), which is also the condition of applicability of (5.8), so as to obtain the condition imposed upon the energy of an electron

$$E = \frac{mv^2}{2} \ll \frac{m}{2}\left(\frac{2\pi Ze^2}{h}\right)^2 = \frac{Z^2e^2}{2a_0} = I_H Z^2 = 13.5 Z^2 \text{ ev}, \qquad (5.13)$$

where $a_0 = h^2/4\pi^2 me^2$ is the Bohr radius, and $I_H = 13.5$ ev is the ionization potential of a hydrogen atom. Thus the quasi-classical condition for the motion of an electron in a Coulomb field is equivalent to the condition of the smallness of the electron energy in comparison with its energy in the first Bohr orbit. In the case of a hydrogen plasma, for example, (5.8) is applicable up to temperatures of the order of 10 ev $\sim$ 100,000°K; in a gas composed of heavier elements it is applicable to even higher temperatures, since the ionic charge Z increases as a result of multiple ionization. Thus, for air at standard density and $T = 10^6$ °K we have $Z \approx 6$, and the average energy of the electrons is still four times less than the " quasi-classical " limit.

At very high temperatures, when conditions opposite to the quasi-classical conditions (5.12) and (5.13) are satisfied, the Born approximation* of quantum mechanics is valid. For nonrelativistic energies ($E \ll mc^2 = 500$ kev) the effective radiation in the Born approximation is given by the expression (see [3])

$$dq_v = h\nu \, d\sigma_v = \frac{32\pi}{3} \frac{Z^2 e^6}{m^2 c^3 v^2} \ln \frac{[E^{1/2} + (E - h\nu)^{1/2}]^2}{h\nu} \, d\nu,$$

where dq_v automatically vanishes for $h\nu = E$ and has a weak logarithmic dependence on the frequency over the entire frequency interval from 0 to v_{max}.

It is remarkable that the quantum-mechanical result yields values of the effective radiation which are quite close to those given by the classical equation (5.8) (with the obvious exception of very low frequencies and frequencies close to the maximum). This is evident from Table 5.1, which gives values of the ratio

$$g_1 = \left(\frac{dq_v}{d\nu}\right)_{quant} \Big/ \left(\frac{dq_v}{d\nu}\right)_{class} = \frac{\sqrt{3}}{\pi} \ln \frac{[E^{1/2} + (E - h\nu)^{1/2}]^2}{h\nu}$$

$$= \frac{\sqrt{3}}{\pi} \ln \frac{[1 + (1 - x)^{1/2}]^2}{x}$$

as a function of the dimensionless quantity $x = h\nu/E = v/v_{max}$. The quantity g_1 which distinguishes the quantum expression for bremsstrahlung from the classical expression is sometimes called the Gaunt factor. The integrated radiation calculated using the quantum-mechanical result is usually written in the form

$$q_{quant} = \int_0^{v_{max}} \left(\frac{dq_v}{d\nu}\right)_{quant} d\nu = \left(\frac{dq_v}{d\nu}\right)_{class} v_{max} \int_0^1 g_1 \, dx = 1.05 \, q_{class}.$$

* The Born approximation requires that both the initial and final electron velocities satisfy the conditions (5.12) and (5.13); otherwise one must use the exact wave functions of an electron in a Coulomb field; this introduces the well-known Coulomb factor into the resulting equations (see [2, 3]).

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g_1	∞

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x	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
g_1	∞	2.01	1.61	1.34	1.13	0.97	0.81	0.68	0.53	0.36	0

Thus, the classical relation (5.8) gives satisfactory approximate results at practically any nonrelativistic temperature.

§2a. Bremsstrahlung emission from an electron scattered by a neutral atom

We now calculate the effective bremsstrahlung emission from an electron in collision with a scattering center, without as yet specifying the interaction law of the electron with the scatterer. The scattering body may be an atom, molecule, or ion. Let us assume that the interaction time τ_0 is small in comparison with the period of electromagnetic oscillations which are radiated, or more precisely that in this case we have $\omega\tau_b \ll 1$, where $\omega = 2\pi\nu$. This assumption may be regarded as valid for visible light frequencies, electron energies of the order of several electron volts, and scattering by a neutral atom*.

If $\omega\tau_b \ll 1$, the scattering takes place "instantaneously", and it is natural to set the acceleration vector $w(t) = \Delta v\,\delta(t)$, where Δv is the change in the electron vector velocity on scattering and δ is the delta function. Then the Fourier component of the acceleration vector is $w_\nu = \Delta v/2\pi$. Substituting this expression into (5.4) we find that the energy radiated in the frequency interval from ν to $\nu + d\nu$ upon scattering is

$$S_\nu\,d\nu = \frac{4}{3}\frac{e^2}{c^3}(\Delta v)^2\,d\nu.$$

This expression should be averaged over the scattering angle ϑ. Assuming approximately that the absolute electron velocity v does not change appreciably on scattering, which corresponds to the emission of photons hv with energies low in comparison with the electron energy $mv^2/2$, we obtain $\overline{(\Delta v)^2} = 2v^2(1 - \overline{\cos\vartheta})$, where $\overline{\cos\vartheta}$ is the average of the cosine of the scattering angle.

In order to find the effective emission we must multiply the quantity $\bar{S}_\nu\,d\nu$, averaged over the scattering angle, by the scattering cross section σ (cf. (5.6)). This yields

$$dq_\nu = \bar{S}_\nu\,d\nu\,\sigma = \frac{8}{3}\frac{e^2v^2\sigma_{tr}}{c^3}\,d\nu, \tag{5.13a}$$

* For example, for red light $\lambda = 7000$ Å, $hv = 1.8$ ev, and $\omega = 2.7\cdot10^{15}$ sec^{-1}. If the radius of the atom is 10^{-8} cm and the electron velocity is 10^8 cm/sec (the energy is 3 ev), then $\tau_b = 10^{-16}$ sec and $\omega\tau_b = 0.27$.