# PHYSICS OF ATOMS AND MOLECULES

B. H. Bransden and C. J. Joachain

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### **Preface**

Modern undergraduate courses in physics invariably include a good deal of material on basic atomic physics, including discussions of atomic structure, the optical and X-ray spectra of atoms, the interaction of atoms with electric and magnetic fields, the theory of simple molecules and some atomic scattering theory. As a rule, part of this material is given in a course on quantum mechanics, and some separately. Correspondingly, most books on quantum mechanics deal with some of these topics, usually in a rather sketchy fashion, while texts on 'Atomic Spectra', 'Collision Theory' and the like, deal with individual topics at considerably greater length than the undergraduate requires.

The aim of this book is to present a unified account of the physics of atoms and molecules, from a modern viewpoint, in adequate detail, but keeping within the undergraduate framework. It is based on courses given by the authors at the Universities of Durham, Glasgow, California (Berkeley), Brussels and Louvainla-Neuve, and is suitable for study at second or third year level of an undergraduate course following some study of elementary quantum theory.

Following a brief historical introduction in Chapter 1, Chapter 2 contains an outline of the ideas and approximation methods of quantum mechanics, which are used later in the book. This is in no sense intended as a substitute for a proper study of quantum mechanics, but serves to establish notation and as a convenient summary of results. In Chapters 3 to 8, the structure of atoms and the interaction of atoms with radiation are discussed, followed in Chapters 9 and 10 by an account of the structure and spectra of molecules. Selected topics dealing with the scattering of electrons by atoms, and of atoms by atoms, are given in Chapters 11 to 13 while in the final chapter, a few of the many important applications of atomic physics are considered. Various special topics and derivations are given in the appendices together with useful tables of units. For a full understanding, the reader should work through the problems given at the end of the chapters. Hints at the solutions of selected problems are given at the end of the book.

We wish to thank our colleagues and students for numerous helpful discussions and suggestions. It is also a pleasure to thank Mme E. Péan and Mrs M. Raine for their patient and careful typing of the manuscript.

B. H. Bransden, Durham C. J. Joachain, Brussels July 1980

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# I Electrons, photons and atoms

The physics of atoms and molecules which constitutes the subject matter of this book rests on a long history of discoveries, both experimental and theoretical. A complete account of the historical development of atomic and molecular physics lies far outside the scope of this volume. Nevertheless, it is important to recognise the key steps which have occurred in this evolution. In the present chapter we shall briefly describe the major experiments and discuss the basic theoretical concepts which are at the root of modern atomic and molecular physics.

### 1.1 THE ATOMIC NATURE OF MATTER

The first recorded speculations as to whether matter is continuous, or is composed of discrete particles, were made by the Greek philosophers. In particular, following ideas of Anaxagoras (500–428 BC) and Empedocles (484–424 BC), Leucippus (circa 450 BC) and his pupil Democritus (460–370 BC) argued that the universe consists of empty space and of indivisible particles, the atoms [1], differing from each other in form, position and arrangement. The atomic hypothesis, however, was rejected by Aristotle (384–322 BC) who strongly supported the concept of the continuity of matter.

In modern times, the question was re-opened following the experimental discovery of the gas laws by R. Boyle in 1662, and the interpretation of these laws in terms of a kinetic model by D. Bernoulli in 1738. The kinetic theory of gases developed throughout the nineteenth century, notably by R. Clausius, J. C. Maxwell and L. Boltzmann, was able to explain the physical properties of gases by assuming that:

- 1. A gas consists of a large number of particles called *molecules* which make elastic collisions with each other and with the walls of the container.
- 2. The molecules of a particular substance are all identical and are small compared with the distances that separate them.

<sup>[1]</sup> The Greek word 'atomos' (atom) means 'indivisible'.

The temperature of a gas is proportional to the average kinetic energy of the molecules.

In parallel with the development of the kinetic theory, the laws of chemical combination were being discovered, which again could be interpreted by making hypotheses about the atomic nature of matter. In 1801, J. L. Proust formulated the law of definite proportions which states that when chemical elements combine to form a given compound, the proportion by weight of each element is always the same. This was followed in 1807 by J. Dalton's law of multiple proportions, according to which when two elements combine in different ways, to form different compounds, then for a fixed weight of one element, the weights of the other element are in the ratio of small integers. These laws were explained by Dalton in 1808, who made the hypothesis that the elements are composed of discrete atoms. For a given element these atoms are all identical and each atom has the same weight. Compounds are formed when atoms of different elements combine in a simple ratio.

Also in 1808, J. L. Gay-Lussac discovered that when two gases combine to form a third, the volumes are in the ratio of simple integers. This result was explained by A. Avogadro in 1811. He was the first to make a clear distinction between atoms, the discrete particles of the elements, and molecules, which are the discrete particles of compounds, composed of two or more atoms bound together. Avogadro was able to show that the Gay-Lussac law is satisfied if equal volumes of different gases, at the same pressure and temperature, contain equal numbers of molecules.

It is interesting that the atomic explanation of chemistry was not fully accepted until late in the nineteenth century [2], largely because chemists tended to ignore the compelling evidence from kinetic theory [3]. In addition to the properties of gases, the kinetic theory was able to explain other phenomena, for example the random motion of small particles suspended in a fluid. This motion, discovered by R. Brown in 1827, is due to the collisions of the molecules of the fluid with the suspended particles.

From the chemical laws the relative weights of atoms can be established. Originally, Dalton proposed a scale in which hydrogen was given, by definition, the atomic weight 1. Later, this was superseded by a scale in which naturally occurring oxygen was assigned the atomic weight 16. On this scale, known as the *chemical scale*, atomic hydrogen has the atomic weight 1.008.

A mole is defined as a quantity of a substance weighing  $\mu$  grams, where  $\mu$  is the atomic (or molecular) weight of that substance. Avogadro's number  $N_A$  is the number of atoms (or molecules) in one mole of any substance. The first estimate of  $N_A$  was made by J. Loschmidt in 1865. In fact,  $N_A$  can be found in several ways, one of the most interesting being from observations of Brownian motion.

<sup>[2]</sup> The nineteenth-century controversies are described in an interesting book by Knight (1967), while a collection of original papers covering the early history of the atomic theory, translated into English, has been given by Borse and Motz (1966).

<sup>[3]</sup> An account of the kinetic theory and its applications can be found in the text by Morse (1966).

1.2 The electron

The number deduced in this way in 1907 by J. Perrin, who performed experiments on the motion of suspended particles, was close to the best modern value of

$$N_{\rm A} = 6.022 \times 10^{23} \, \rm mole^{-1}$$
 [1.1]

### 1.2 THE ELECTRON

The first experimental evidence that electric charge was not infinitely divisible, but existed in discrete units, was obtained by M. Faraday, who discovered the laws of electrolysis in 1833. In his experiments Faraday passed a current through conducting (electrolytic) solutions of chemical compounds. He found that the mass M of a substance (for example, hydrogen, oxygen or metals) liberated at an electrode during a certain time interval was proportional to the quantity of electricity, Q, passed through the solution during that time. He also found that a given quantity of electricity always liberated the same mass of a given substance, and that this mass was proportional to the equivalent weight of the substance, where the equivalent weight is defined as the atomic (or molecular) weight  $\mu$  divided by the valency v. Faraday's laws of electrolysis can be summarised by the formula:

$$M = \frac{Q}{F} \frac{\mu}{v}$$
 [1.2]

where F is a constant called Faraday's constant. Its value in SI units is given by:

$$F = 9.64846 \times 10^4 \text{ coulombs/mole}$$
 [1.3]

Thus, since  $M = \mu$  grams for one mole, we see from [1.2] and [1.3] that it takes 96484.6 C (sometimes called one Faraday) to liberate for example 1.008 g of hydrogen, 107.9 g of silver, 23 g of sodium, 35.5 g of chlorine (which are all monovalent), 8 g of oxygen (having a valency of 2) and so on.

Faraday interpreted his results by assuming that a given amount of electricity is carried by each atom (or group of atoms) during electrolysis. The charged atoms (or groups of atoms) he called *ions*. In electrolysis, the electric current is the result of the motion of the ions through the solution, the positively charged ions (or cations) moving towards the cathode and the negatively charged ions (or anions) moving towards the anode. At the electrodes, the ions are converted to neutral atoms (or radicals) which are liberated or which give rise to secondary reactions.

Faraday's results implied the existence of an elementary unit of electricity, some types of ion carrying one unit, others two units and so on. Indeed, as H. Helmholtz emphasised in 1881 during a speech in honour of Faraday: 'If we assume the existence of atoms of chemical elements, we cannot escape from drawing the further inference that electricity also, positive as well as negative, is divided into definite elementary charges that behave like atoms of electricity'. However, at the time of Faraday's experiments the idea, that electrical charge

existed in discrete units, did not seem to agree with the evidence from other electrical phenomena, such as metallic conduction, and both Faraday and Maxwell were reluctant to accept it. In fact, the hypothesis that there is a 'natural unit of electricity' was only put forward by C. I. Stoney in 1874, who proposed that this unit should be taken to be the quantity of electricity which must pass through an electrolytic solution in order to liberate one atom of a monovalent substance. Since one Faraday (96484.6 C) liberates one mole of a monovalent substance and because one mole contains  $N_A$  atoms, where  $N_A$  is Avagadro's number, the 'natural unit of electricity', e, is given by

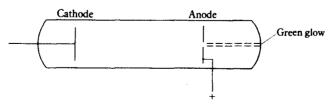
$$e = \frac{F}{N_{\rm A}} \tag{1.4}$$

Stoney suggested the word 'electron' for this unit, and he obtained for e an approximate value of  $10^{-20}$  C, using the rough estimates of  $N_A$  that were available from kinetic theory. In 1880, Helmholtz pointed out that it is apparently impossible to obtain electricity in smaller amounts than e. The first direct measurements of this smallest possible charge were initiated by J. J. Thomson and carried out by his student J. S. Townsend in 1897, and the first accurate value was found in the famous oil-drop experiment of R. M. Millikan in 1909, to which we shall return below.

### Cathode rays and Thomson's measurement of e/m

When electrodes are placed in a gas at normal atmospheric pressure no current presses and the gas acts as an insulator until the electric field is increased to above 3 or 4 MV/m when sparking takes place. In contrast, at low pressures, a steady current can be maintained in a gas. At pressures of about 1 mm of mercury, the discharge is accompanied by the emission of light, but at still lower pressures a dark region forms near the cathode. The dark region, called the Crookes dark space, increases in size as the pressure falls, filling the discharge tube at pressures of  $10^{-3}$  mm and below. If, under these low pressure conditions, a small hole is made in the anode (see Fig. 1.1), a green glow is observed on the glass wall of the discharge tube.

The causative agents of this phenomenon were termed 'cathode rays'. The properties of these rays were studied in the latter part of the nineteenth century



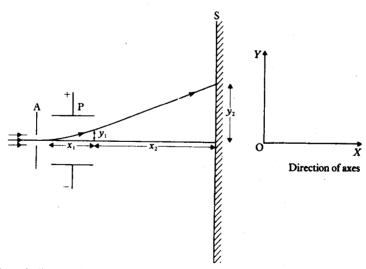
1.1 Low-pressure discharge tube. Cathode rays passing through a hole in the anode cause a green glow on the glass wall of the tube.

4

1.2 The electron

by W. Crookes and P. Lenard, who showed that the rays travelled in straight lines, cast 'shadows' and also carried sufficient momentum to set in motion a light paddle wheel. In 1895, J. Perrin demonstrated that the rays carried negative charge by collecting the charge on an electrometer. At that time very differing views were expressed as to the nature of the cathode rays, but J. J. Thomson set out the hypothesis that the rays consisted of a stream of particles each of mass m and charge -e, originating in the cathode of the discharge tube. Since the earlier investigations showed that the properties of the cathode rays were independent of the material of the cathode and of the gas in the tube, the particles could be assumed to be constituents of all matter.

In Thomson's experiments the deflection of the cathode rays by static electric and magnetic fields was investigated, which allowed the determination of the 'specific charge', the ratio e/m, of the constituent particles. The cathode rays were passed between parallel plates, a distance D apart, to which a potential difference V could be applied, as in Fig. 1.2. The cathode rays emerging from the region of the electric field were detected on a screen S, and the deflection measured as a function of V. Neglecting end effects, the electric field strength  $\mathcal{E}$  between the plates can be taken to be uniform and equal to V/D, and in this field the charged particle experiences a constant acceleration of magnitude  $e\mathcal{E}/m$  in the V direction (see Fig. 1.2). If the initial velocity of a particle is v, the time taken to traverse the region between the plates, of length  $x_1$ , is  $t_1 = x_1/v$ . The subsequent time to reach the screen, placed at distance  $x_2$  from the plates, is  $t_2 = x_2/v$ .



1.2 Schematic diagram of Thomson's apparatus to measure e/m. A stream of cathode rays, passing through a small hole in the anode A of a discharge tube, is deflected by being passed between the plates of a condenser P to which a potential is applied.

During the time  $t_1$ , the deflection in the Y direction is

$$y_1 = \frac{1}{2} \left( \frac{e\mathscr{E}}{m} \right) t_1^2 = \frac{1}{2} \left( \frac{e\mathscr{E}}{m} \right) \left( \frac{x_1}{v} \right)^2$$
 [1.5]

On leaving the region between the plates, the component of the particle velocity in the Y direction is

$$v_{y} = \left(\frac{e\mathscr{E}}{m}\right)t_{1} = \left(\frac{e\mathscr{E}}{m}\right)\left(\frac{x_{1}}{v}\right)$$
 [1.6]

from which the total deflection in reaching the screen is

$$y_2 = v_y t_2 + y_1 = \frac{e}{m} \frac{\mathcal{E} x_1}{v^2} (\frac{1}{2} x_1 + x_2)$$
 [1.7]

Thus, a measurement of the deflection  $y_2$  provides a value of the combination  $(e/mv^2)$ , if  $\mathscr{E}$ ,  $x_1$  and  $x_2$  are known.

To determine e/m, an independent measurement is required from which v can be found. By placing the apparatus within a Helmholtz coil, Thomson could apply a constant magnetic field  $\mathfrak{B}$ , directed in the Z direction, at right angles both to the electric field and to the undeflected path of the cathode rays. The magnetic force on the charged particles is of magnitude  $ev\mathfrak{B}$  and is perpendicular to the particle trajectory, being initially in the Y direction. If both electric and magnetic fields are applied simultaneously, the net force on the particles vanishes provided  $\mathscr E$  and  $\mathscr B$  are adjusted so that

$$ev\mathfrak{B} = e\mathscr{E}$$
 [1.8]

Two experiments can now be performed. In the first, the values of  $\mathfrak{B}$  and  $\mathfrak{E}$  are measured for which the cathode rays are undeflected and this provides the value of v, since from [1.8] we have  $v = \mathfrak{E}/\mathfrak{B}$ . In the second, the magnetic field is switched off and the deflection due to the electric field alone is measured [4]. Knowing v, the specific charge e/m can be calculated from [1.7].

Thomson found a value for the specific charge somewhat smaller than the modern value of  $1.76 \times 10^{11}$  C/kg. The specific charge for the lightest known positive ion (the hydrogen ion) is smaller by a factor of approximately 1840, so either the cathode ray particles are much lighter or they carry a very large charge. Thomson assumed that the charge on a cathode ray particle was equal in magnitude (but opposite in sign) to that on the hydrogen ion, so that each particle was lighter than a hydrogen ion by a factor of about 1840. Particles with this property are now called *electrons*, thus changing the original meaning of the word electron which was applied by Stoney to the magnitude e of the charge carried by a hydrogen ion or a cathode ray particle.

<sup>[4]</sup> If the electric field is switched off the cathode rays move along an arc of a circle of radius R, where  $(mv^2/R) = ev\Re$ . From this the deflection by a magnetic field extending over a region of length x, can be calculated.

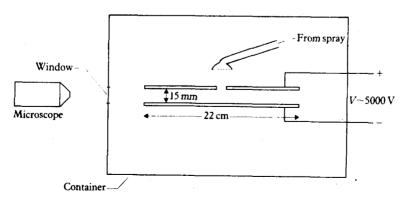
1.2 The electron

### Millikan and the charge of the electron

Following his determination of an accurate value for the charge to mass ratio of the electron, J. J. Thomson, together with his student J. S. Townsend, attempted to measure the electronic charge itself. The method employed was to produce clouds of charged water droplets and to estimate the number of droplets in a cloud from a knowledge of its total mass and the rate at which the cloud settles. The total charge of the cloud could be measured with an electrometer and hence the charge on each drop estimated. In an extension of the method due to H. A. Wilson, the charge on the cloud was measured by applying an electric field in the opposite direction to gravity, and adjusting the strength of the field until the cloud ceased to settle, but remained suspended at rest. Both these methods failed to provide accurate results because of the evaporation of the droplets during the experiment. However, a brilliant modification of Wilson's method, by R. M. Millikan in 1909, gave the first accurate value for the magnitude, e, of the electronic charge.

In Millikan's experiments very small oil droplets a few microns in diameter were formed by spraying mechanically from a nozzle. The droplets became charged by friction as they were formed. They also acquired charges from the surrounding air, which could be ionised by passing X-rays through the apparatus. Some droplets were allowed to fall through a small hole into a region between two parallel plates of a condenser to which an electrostatic potential V could be applied. The motion of the drops was viewed by a microscope with a micrometer eyepiece, and the velocity of fall was measured. The whole apparatus, a schematic diagram of which is shown in Fig. 1.3, was enclosed in a thermostat to avoid convection currents of the air between the condenser plates, which were 22 cm in diameter and separated by about 15 mm.

If the condenser is uncharged (V = 0), a droplet of effective mass M falls under gravity, reaching a terminal velocity  $v_1$  when the gravitational force Mg is balanced by the viscous drag of the air. According to Stokes's law this occurs



1.3 Millikan's experiment for the determination of the charge of the electron.

when

$$Mg = 6\pi \eta r v_1 \tag{1.9}$$

where  $\eta$  is the coefficient of viscosity of air and r the radius of the drop. The mass of the drop is  $4\pi r^3 \rho_{\rm O}/3$  where  $\rho_{\rm O}$  is the density of the oil, and allowing for the buoyancy of the air the effective mass is

$$M = \frac{4}{3} \pi r^3 (\rho_{\rm O} - \rho_{\rm A})$$
 [1.10]

where  $\rho_A$  is the density of the air.

The potential V (of the order of 5 kV) can now be applied. If it is sufficiently large and in the correct direction, the drop will move upwards until a new terminal velocity  $v_2$  is reached. If D is the distance between the plates and q is the charge on the drop

$$q\frac{V}{D} - Mg = 6\pi\eta r v_2 \tag{1.11}$$

Thus, from [1.9] and [1.11], the charge on the drop is

$$q = 6\pi\eta r \left(\frac{D}{V}\right)(v_1 + v_2)$$
 [1.12]

which can be determined by measuring  $v_1$ ,  $v_2$  and (D/V), since the radius of the drop is given by [1.9] and [1.10], provided  $\eta$ ,  $\rho_0$  and  $\rho_A$  are known.

The same drop could be observed for a period of some hours, during which time the charge q varied because positive or negative ions were acquired from the surrounding air. From many thousands of observations, Millikan found that as q altered, it always changed in integral units of a basic charge and in general the magnitude of q was given by

$$|q| = 1.59 \ n \times 10^{-19} \ C$$
 [1.13]

where n was an integer usually between 3 and 30. Thus the basic charge, which he identified with the magnitude of the electronic charge e, was found to have the value  $1.59 \times 10^{-19}$  C. Later measurements in which better values of the viscosity  $\eta$  were used gave an improved value,

$$e = 1.60 \times 10^{-19} \,\mathrm{C}$$
 [1.14]

Combining these results with the modern value of e/m, a value for the mass of the electron is obtained,

$$m = 9.11 \times 10^{-31} \text{ kg}$$
 [1.15]

which is approximately 1840 times lighter than a hydrogen ion, as postulated by Thomson.

### 1.3 BLACK BODY RADIATION

During the later part of the nineteenth century, and in the early years of this century, evidence accumulated that the classical physics, represented by Newton's laws of motion and Maxwell's electromagnetic equations, is inadequate to describe atomic phenomena. The first clues to a new physics, based on the quantisation of energy, came from a study of the properties of radiation from hot bodies. It is a matter of common experience that a hot body radiates electromagnetic energy in the form of heat. In fact, at any temperature, a body emits radiation of all wavelengths, but the distribution in wavelength, the spectral distribution, depends on temperature. At low temperature, most of the energy is in the form of low frequency infra-red radiation, but as the temperature increases more energy is radiated at higher frequencies, until by ~500°C radiation of visible light is observed. At still higher temperatures, such as that of an incandescent lamp filament the spectral distribution has shifted sufficiently to the higher frequencies for the body to be white hot. Not only the spectral distribution changes with temperature, but the total energy radiated also changes, increasing as a body becomes hotter.

In 1874, J. Stefan showed that the power emitted per unit area, R, from a body at the absolute temperature T(K), called the total emittance, could be represented by the empirical law

$$R = e\sigma T^4$$
 [1.16]

where e is called the *emissivity* with  $e \le 1$ . The emissivity varies with the nature of the surface, but the constant  $\sigma$ , known as Stefan's constant, is independent of the nature of the radiating surface and is given by

$$\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$$
 [1.17]

When radiation falls on a body some is reflected and some is absorbed. For example, dark bodies absorb most of the radiation falling on them, while light coloured bodies reflect most of it. The absorptivity, a, of a surface is defined as the fraction of the energy of the radiation falling on unit area which is absorbed, and a black body is defined as a body with a surface having an absorptivity equal to unity, that is a body which absorbs all the radiant energy falling upon it.

If a body is in thermal equilibrium with its surroundings, and therefore is at constant temperature, it must emit and absorb the same amount of radiant energy per unit time, for otherwise its temperature would rise or fall. The radiation emitted or absorbed under these circumstances is called thermal radiation. By considering the thermal equilibrium between objects made of different substances G. R. Kirchoff in 1895 proved, using the laws of thermodynamics, that the absorptivity of a surface is equal to its emissivity, e = a, independently of its temperature, and that this holds for radiation of each particular wavelength. Kirchoff's law thus shows that the emissivity of a black body is unity and that a black body is the most efficient radiator of electromagnetic energy. In 1884, L. Boltzmann derived the relation [1.16] from

thermodynamics for the case of a black body (e = 1). It is now known as the Stefan-Boltzmann law. It follows, from the Stefan-Boltzmann law, that the energy radiated by a black body depends only on the temperature. The spectral distribution of this radiation is of a universal nature and is of particular interest.

A perfect black body is an idealisation, but it can be very closely realised in the following way. Consider a cavity kept at a constant temperature of which the interior walls are blackened. A small hole made in the wall of such a cavity behaves like a black body, because any radiation falling on the hole from outside will pass through it and after multiple reflections will eventually be absorbed by the interior surfaces and the opening has an effective absorptivity of unity. Since the cavity is in thermal equilibrium, the radiation within it and the radiation from the small opening are characteristic of the thermal radiation from a black body. This radiation was studied experimentally as a function of the temperature of the enclosure, and the spectral distribution at each temperature was measured by O. Lummer and E. Pringsheim in 1899.

The power emitted per unit area, from a black body, at wavelengths between  $\lambda$  and  $\lambda + d\lambda$  is denoted by  $R(\lambda) d\lambda$ , so that the total power emitted per unit area is

$$R = \int_0^\infty R(\lambda) \ d\lambda$$
 [1.18]

and by the Stefan-Boltzmann law  $R = \sigma T^4$ . The observed spectral distribution function  $R(\lambda)$  is shown plotted against  $\lambda$ , for a number of different temperatures in Fig. 1.4. We see that, for fixed  $\lambda$ ,  $R(\lambda)$  increases with increasing T. At each temperature, there is a wavelength  $\lambda_{\max}$ , for which  $R(\lambda)$  has its maximum value. Using general thermodynamical arguments it had been predicted in 1893 by W. Wien that  $\lambda_{\max}$  would vary inversely with T and this was confirmed by the later experiments. The relation

$$\lambda_{\max} T = b \tag{1.19}$$

is known as Wien's displacement law, and the constant b has the value  $b = 2.898 \times 10^{-3}$  mK.

The spectral distribution function  $R(\lambda)$ , for the power emitted, is related by a geometrical factor to the spectral distribution function  $\rho(\lambda)$  for the energy density within the cavity. In fact, if  $\rho(\lambda)$  d $\lambda$  is defined as the energy density of the radiation with wavelengths between  $\lambda$  and  $\lambda + d\lambda$ , it can be shown [5] that  $\rho(\lambda) = 4R(\lambda)/c$ , consequently measurements of  $R(\lambda)$  determine the spectral distribution of the energy density within the cavity. It is also interesting to consider the energy density as a function of the frequency  $\nu = c/\lambda$ , in which case a distribution function  $\rho(\nu)$  is defined so that

$$\rho(\nu) = \rho(\lambda) \left| \frac{\mathrm{d}\lambda}{\mathrm{d}\nu} \right| = \lambda^2 \rho(\lambda)/c \qquad [1.20]$$

[5] The details of the calculation are given in the book by Richtmyer, Kennard and Cooper (1969).