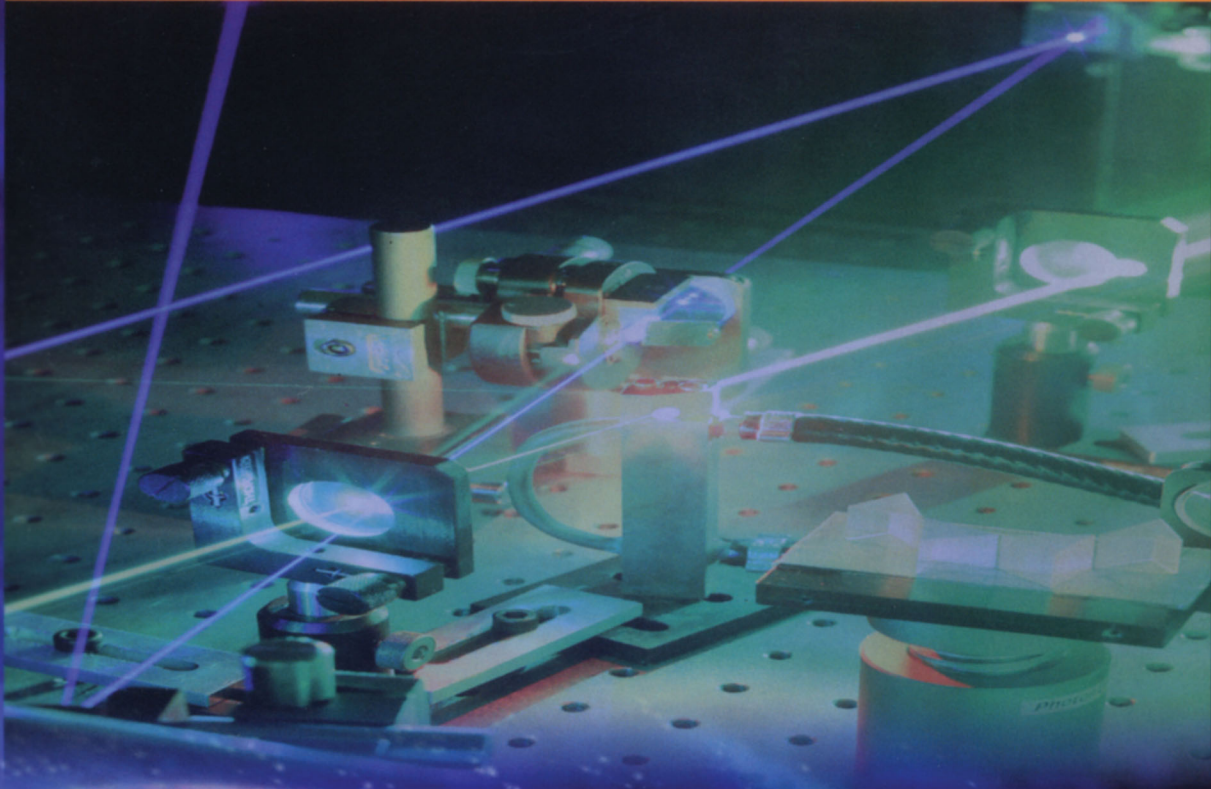# QUANTUM PHYSICS: AN INTRODUCTION

Edited by Joy Manners

The PHYSICAL WORLD

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QUANTUM PHYSICS: AN INTRODUCTION

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Bristol and Philadelphia
in association with

The Open
University

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QUANTUM PHYSICS: AN INTRODUCTION

Introduction

Two of the most remarkable revolutions in the history of science took place in Europe at the beginning of the twentieth century. One began in 1905, when Einstein formulated the special theory of relativity. This is based on two principles, namely, that the same basic physical laws apply in all inertial reference frames and that the velocity of light in a vacuum is constant. Einstein's theory imposed modifications on the Newtonian concepts of space and time, and these modifications led to a radically new and unified interpretation of the *classical* physics of Newton and Maxwell. In this sense, the special theory of relativity can be regarded as the crowning glory of classical physics.

The same is certainly *not* true for the other great revolution, which was brought about by the advent of *quantum physics*. This was entirely new and some of its assumptions conflict with those of classical physics. This does not imply that all the physics you have learnt so far is obsolete and can be discarded. Quantum physics is required only when we try to understand phenomena on the *atomic* scale. This book will first show you how the need for quantum physics arose, and will then outline the new theory of *quantum mechanics*, as developed by Erwin Schrödinger, which aimed to explain the behaviour of particles at the atomic level.

In Chapter 1 we review a set of phenomena for which no explanation could be found within the framework of classical physics. We shall then go on to show how these difficulties were resolved, at least partially, by Planck's quantum hypothesis.

Chapter 2 introduces the revolutionary ideas of quantum mechanics and the basic principles of the theory, while in Chapter 3 these principles are applied to the understanding of atomic structure.

It is important to realize that the postulates and interpretation of quantum theory are completely different from our normal intuitions about natural phenomena. In fact, the debate about the real meaning of quantum-mechanical quantities has been fiercely argued since its inception and continues with unreduced fervour to this day. Chapter 4 is devoted to some of the aspects of the interpretation of quantum theory.

Open University students should view Video 7, *The Search for Reality*, at some stage during their study of this book. This will give you a light-hearted first look at some of these strange philosophical aspects of quantum theory. The video can be viewed at any stage, but might be most effective at the end of Chapter 1.

Chapter 1 The origins of quantum physics

1 The Compton effect — a strange dichotomy in the nature of electromagnetic radiation

In a series of experiments conducted between 1919 and 1923, Arthur Holly Compton (Figure 1.1) investigated the scattering of monochromatic (single-wavelength) X-rays from graphite targets. He found that the radiation scattered at an angle ϕ to the incident beam contained, in addition to radiation of the *same* wavelength as the incident radiation, a second component with a considerably *longer* wavelength. The existence of this second component in the scattered radiation could not be explained by the well-established theory of the scattering of electromagnetic waves by electrons. Compton considered instead the process illustrated in Figure 1.2, in which a *particle* of electromagnetic radiation, collides with a slow moving electron, which then recoils absorbing some of the X-ray particle's energy. Treating the process as a collision between *particles*, and using only the (relativistic) conservation laws of energy and momentum, Compton was able to account for the effect completely. However, at the same time, in the same experiment, Compton was using *interference* effects, depending wholly on the wave model, in order to determine the wavelength of the scattered radiation. So here was an experiment which apparently required the simultaneous use of both the wave and particle models of electromagnetic radiation for the interpretation of the results! The existence of this strange dichotomy in the nature of electromagnetic radiation was just one indication of the need for a radical revision of views regarding the physical world.
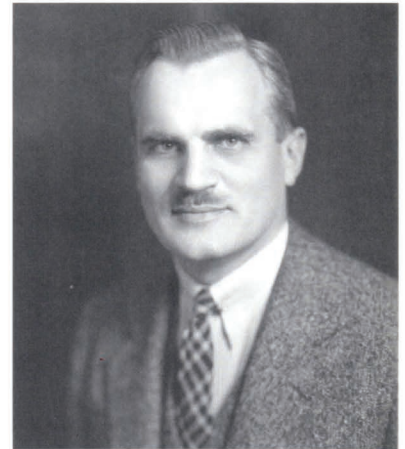
Figure 1.1 Arthur Holly Compton (1892–1962) was a native of Ohio in the United States. After receiving his doctorate at Princeton, he began his career as a research physicist at the Westinghouse Lamp Company before returning to academic circles by moving to Cambridge in 1919. He later held professorships at several American universities. An authority on X-rays, he was awarded the Nobel Prize for physics in 1927 for his discovery and interpretation of the effect that bears his name.
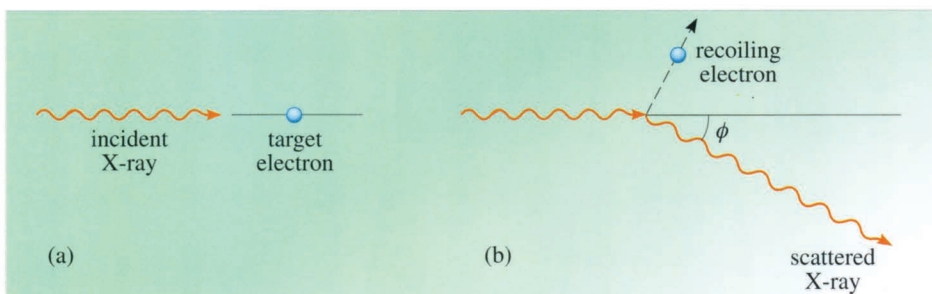
Figure 1.2 (a) The Compton effect. An X-ray or γ-ray 'particle' collides with a slow moving electron in one of the target atoms. (b) The electron recoils, absorbing energy from the X-ray particle which is scattered into a new direction and with increased wavelength.

2 Five problems for classical physics

At the beginning of the twentieth century, physicists were faced with several profound problems that could not be solved by using the classical theories of Newton and Maxwell. In this section we shall describe five of these problems and later in the chapter you will see how all were solved (at least partially) by using the ideas of quantum physics that were formulated between 1900 and 1922.

2.1 Problem 1: Understanding atoms

By the end of the nineteenth century, it was becoming accepted that matter was *not* infinitely divisible (continuous), but that it consisted of discrete parts, which were called *atoms*. Amongst the most persuasive evidence for this was the work of Dalton and Gay-Lussac on the proportions in which chemical elements combine with each other. The fact that these proportions were often in ratios of small integers indicated that the substances that were combining in these reactions were doing so in discrete amounts.

The results of some rather crude experiments had indicated that the atoms that made up the different chemical elements each had a diameter of, very roughly, 10^{-10} m (see Example 1.1). This observation prompted some scientists to ask 'What's so special about 10^{-10} m — why shouldn't atoms have diameters of, say, 10^{-6} m?' This may strike you as rather an odd question — is it reasonable to ask why atoms have a certain size? Shouldn't the typical atomic size be taken as being a fact of nature? Fortunately, the Danish physicist Niels Bohr *did* regard this as a pertinent and extremely important question for physics, and was able to give a clear answer to it.

Another important question concerned the constituents and structure of the atoms themselves. As you will see later in this chapter, important advances in this direction were made by J. J. Thomson and Ernest Rutherford.

Example 1.1

Given that the density of diamond is 3.5×10^3 kg m^{-3} and the relative atomic mass of carbon is 12.0, estimate the radius of a carbon atom.

Solution

From the information provided, we know that one mole of diamond has a mass of 0.012 kg, so that its volume is

$$\frac{\text{mass}}{\text{density}} = \frac{0.012}{3500}\,\text{m}^3 = 3.43 \times 10^{-6}\,\text{m}^3.$$

We know that the number of atoms in a mole is $N_A = 6.02 \times 10^{23}$ (Avogadro's number) and the volume occupied by one atom is therefore

$$\frac{3.43 \times 10^{-6}\,\text{m}^3}{6.02 \times 10^{23}} = 5.70 \times 10^{-30}\,\text{m}^3.$$

If this tiny volume were in the form of a cube, its sides would be of length $(5.70 \times 10^{-30})^{1/3}$ m $= 1.8 \times 10^{-10}$ m. The radius of an atom can be no larger than half of this, that is, about 10^{-10} m.

2.2 Problem 2: Understanding spectroscopy

One branch of science that had developed considerably by the end of the nineteenth century was that of **spectroscopy**, the study of the light emitted by chemical substances when they are heated in a flame.

To find the wavelengths present in, for example, the characteristic yellow light emitted by the element sodium, a beam of the light is shone on a diffraction grating (Figure 1.3a). If the light consisted of *all* wavelengths in the yellow part of the
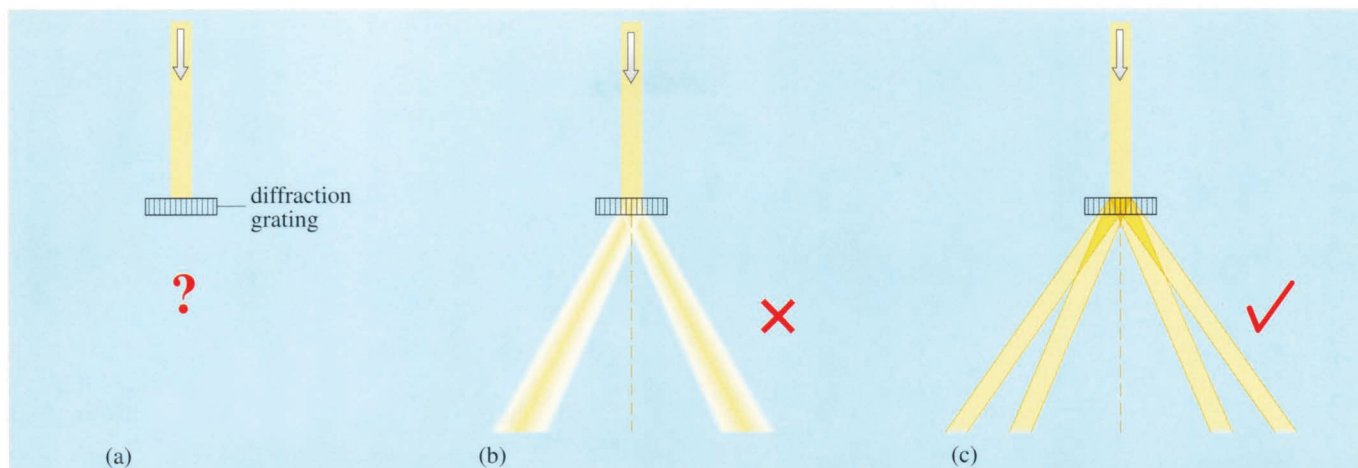
Figure 1.3 (a) What happens when a parallel beam of yellow sodium light is shone onto a diffraction grating? (b) When the light emerges from the grating, it does not fan outwards: this shows that the light does not contain all the frequencies in the range 580–600 nm corresponding to yellow light. (c) Instead, diffraction occurs only at certain definite angles, showing that sodium light consists of discrete frequencies, i.e. spectral lines. (Note that the grating spacing and the angular separation of the spectral lines are grossly exaggerated here. Only the first diffraction order is shown on each side of the straight through direction.)

visible spectrum (580–600 nm), it would simply fan out from the grating to give continuous bands on either side of the straight-through beam (Figure 1.3b). (The abbreviation nm stands for nanometre, 1 nm being equal to 10^{-9} m.) However, *this does not happen*. Instead, the light is diffracted only at certain definite angles (Figure 1.3c). This implies that the yellow sodium light consists of certain, definite wavelengths, which have come to be known as **spectral lines**. The wavelength, λ, of each line in the spectrum can be determined by the angle, θ_n, through which it is diffracted by the grating, provided that the grating spacing, d, is known. As shown in *Dynamic fields and waves*, θ_n is given by the equation $\sin \theta_n = n\lambda/d$, where n is the order of the diffraction. Each element has its own characteristic spectrum, that is, its own individual pattern of spectral lines. You can see examples of different line spectra in Figure 1.4. The fact that the elements have different spectra is the basis of an important experimental technique in chemical analysis. If the spectrum of an

Figure 1.4 The visible atomic spectra of helium, iron and neon.
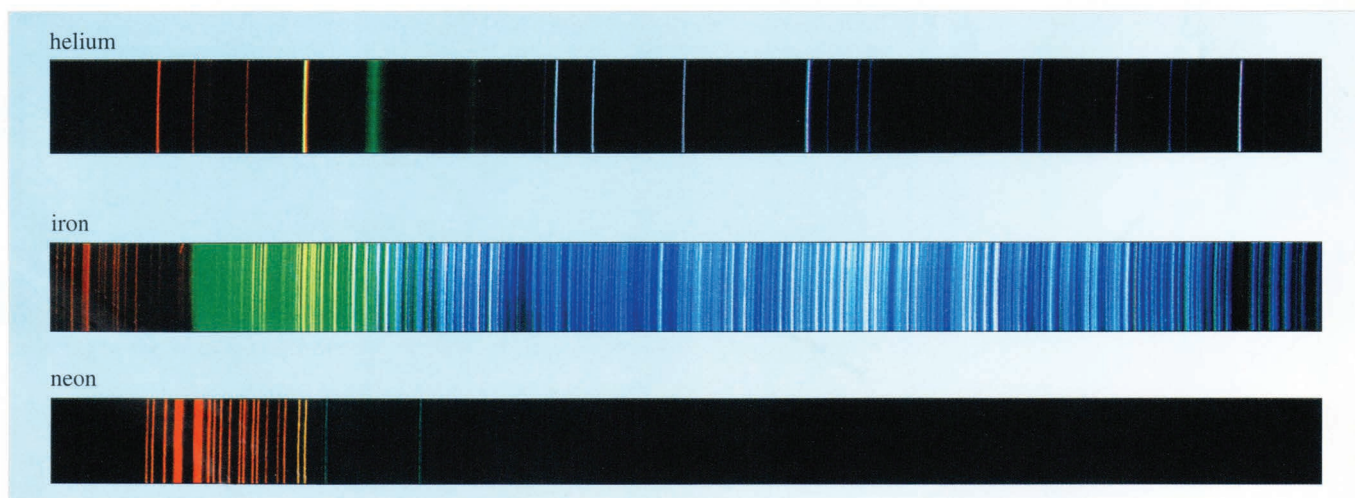
element is identified in the spectrum of a chemical sample, it can be concluded that the sample contains that particular element. This method establishes the existence of particular elements in the outer layers of the Sun and other stars and even provides information about their relative abundance (Figure 1.5).
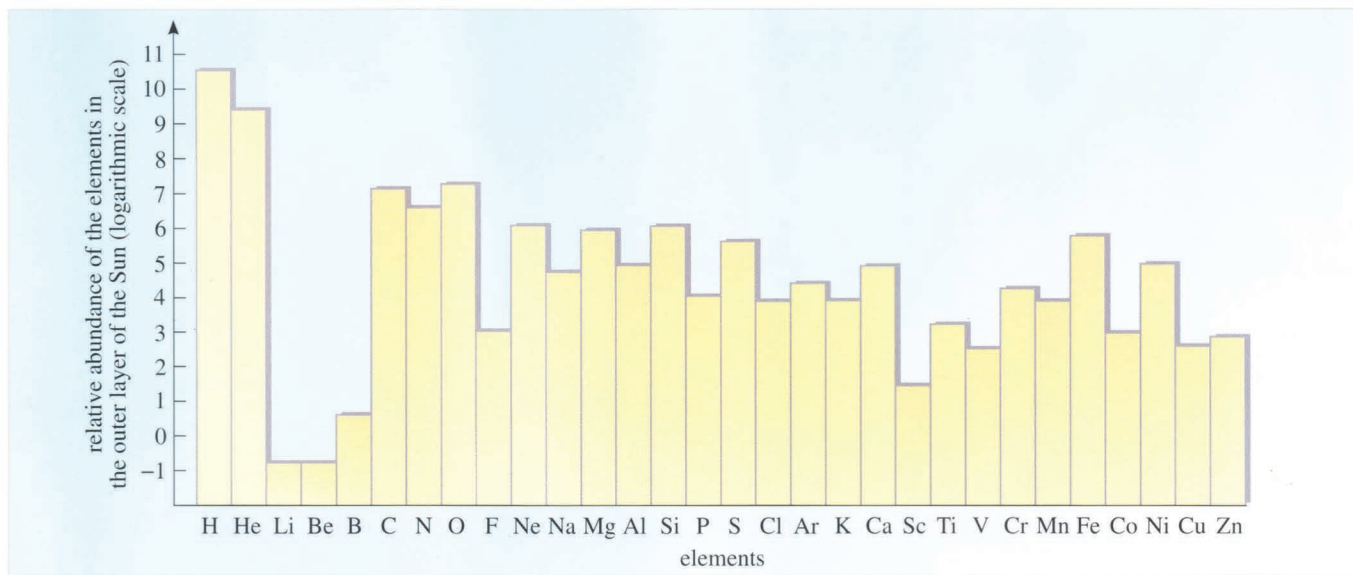
Figure 1.5 Relative abundance of the chemical elements in the solar spectrum. Note the logarithmic scale: an element with a relative abundance of 5 is ten times as abundant as one with a value of 4.

By 1860, spectroscopists had determined the spectra of many elements. That was all very well, but the really difficult problem was to *interpret* these data. What could be concluded from the patterns of spectral lines, and why *do* elements emit light of only certain specific wavelengths? It was evident that these questions were related to still deeper questions about the internal structure of atoms. The way forward was unclear. It seemed no easier for a scientist to learn anything about the structure of atoms from their spectra than for an engineer to deduce the internal construction of a piano from a performance of the 'Moonlight' Sonata.

So far, we have only drawn your attention (in Figure 1.4) to the complicated spectra of elements such as helium, iron and neon. But what about the spectrum of *hydrogen*, the element with the lightest (and simplest?) atoms of all? Perhaps it *would* be feasible to find out something about the least complicated element.

The Swiss mathematician Johann Balmer surmised in 1885 that the best way of tackling the problems of spectroscopy was to concentrate first on trying to understand the visible spectrum of hydrogen, which is shown in Figure 1.6. He made an excellent start on this problem by finding an interesting numerical pattern
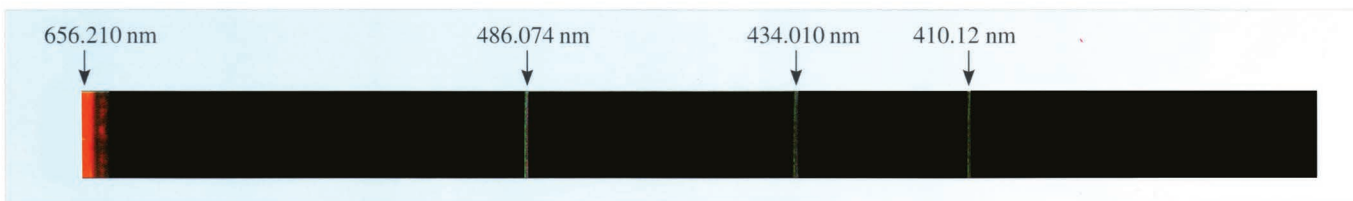
Figure 1.6 The four visible spectral lines of atomic hydrogen.

among the wavelengths of the visible hydrogen lines, which had been determined experimentally as 656.210 nm, 486.074 nm, 434.010 nm and 410.12 nm. Note that these wavelengths had been measured to five or six significant figures, testifying to a very high level of experimental precision. Balmer found that the sequence of the four wavelengths is reproduced to extraordinary accuracy by the expression

$$\lambda = 364.56 \left\{ \frac{n^2}{n^2 - 4} \right\} \text{ nm} \tag{1.1}$$

when the integer n is set equal to 3, 4, 5 and 6. This set of spectral lines came to be known as the **Balmer series** and Equation 1.1 as **Balmer's formula**.

Balmer suggested that n in his formula might take integer (i.e. whole-number) values greater than 6 and that hydrogen might therefore have many other spectral lines which, having wavelengths outside the visible spectrum, had not been observed at that time. This prediction was later borne out by experiments in which several more spectral lines corresponding to $n = 7, 8, 9$, etc. were found in the ultraviolet part of the hydrogen spectrum.

Question 1.1 Substitute the values 3, 4, 5 and 6 for n in Balmer's formula and compare your results with the measured wavelengths of the four visible hydrogen lines. Use the formula to calculate the wavelength of the line corresponding to $n = 7$. ∎

So why should the visible spectral lines of hydrogen be given by this relatively simple formula? Perhaps the most important consequence of Balmer's work on spectroscopy was that it helped to focus attention on the need to account for the spectral lines of *hydrogen* before fruitful attempts could be made to interpret the more complicated spectra of other elements. In 1885, Balmer wrote

> 'It appears to me that hydrogen … more than any other substance is destined to open new paths to the knowledge of the structure of matter and its properties. In this respect, the numerical relations among the wavelengths of the first four hydrogen spectral lines should attract our attention particularly.'

These words were to prove prophetic as you will see later in the chapter.

2.3 Problem 3: Understanding blackbody radiation

It is a familiar fact that a heated body emits electromagnetic radiation and that the intensity of the radiation increases as the temperature rises. When sufficiently hot, the body becomes incandescent and emits visible light, glowing dark red at about 600 °C, orange at about 1000 °C and white at 1400 °C. The spectrum of this *thermal radiation* is continuous (Figure 1.7), i.e. its intensity varies smoothly across all wavelengths, in sharp contrast to the discrete line spectra of gases and vapours. This difference can be understood in the following way. In very low-density material, radiation is emitted or absorbed by individual atoms and these processes are little affected by any interaction *between* atoms. In a solid, such as a lamp filament, the atoms are in very close proximity to each other and they undergo complicated coupled motions as a result of thermal agitation. Radiation generated in these random motions is *thermalized* by repeated absorption and re-emission before escaping from the surface of the solid. Experiments show that the spectra of such 'thermal' sources approximate to a theoretical ideal that depends on the temperature but not on the structure and composition of the source. This ideal thermal spectrum
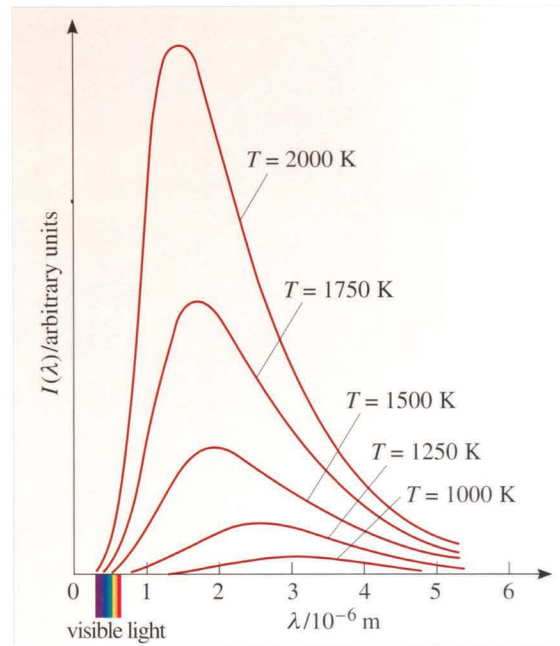
Figure 1.7 The spectrum of blackbody radiation at various temperatures. At any particular temperature, T, the curve shows the variation of intensity I with wavelength λ. (Note that the temperatures are given in kelvin.)

is known as a **blackbody spectrum**. The blackbody spectrum at a number of different temperatures is shown in Figure 1.7. Any radiation that is found to have a blackbody spectrum is said to be **blackbody radiation**.

The reason for the term 'blackbody' is that the *ideal* blackbody spectrum would be that emitted by an object that was a *perfect* emitter and absorber of radiation, and a perfect absorber is referred to as a blackbody. You may have noticed that on a sunny day, a black object in the Sun, warms up more quickly than a white one. This is because it absorbs a greater proportion of the radiation incident on it. However, blackbodies do not necessarily appear black: the Sun and stars provide rough natural approximations to blackbodies at various temperatures, but the best laboratory approximation to a blackbody is a cavity, or box, with all its walls maintained at a fixed temperature T. The cavity is filled with radiation streaming in all directions, which is constantly absorbed and re-emitted by the walls. If there were a small hole in the cavity the radiation emerging from the hole would be blackbody radiation with a spectrum appropriate to the temperature of the cavity walls.

The shape of this blackbody spectrum had already been determined experimentally by the end of the nineteenth century, and a number of attempts had been made to find an equation that would describe the form of the curve at any temperature. Some of these were relatively successful but the equations were empirical and none of them fitted the spectrum everywhere and at all temperatures.

A satisfactory theory of blackbody radiation should provide a precise mathematical expression for the blackbody spectrum. In principle, this should have been straightforward, as it does not depend on knowledge of the internal structure of atoms, but only on the properties of electromagnetic radiation, which were thought to be well understood within the framework of classical physics. However, to the astonishment of physicists at the time, classical physics was quite unable to provide a satisfactory solution.

In simplified terms the problem was this. The walls of the cavity restrict the possible modes of electromagnetic radiation that can exist within it, in much the same way as the allowed modes on a stretched string are restricted to those for which the wavelength

fits with the length of the string (Figure 1.8). Classical physics states that the energy of the blackbody spectrum should be shared out equally among the possible modes of electromagnetic radiation that can fit into the cavity. This is an application of a very important theorem of classical physics: the **equipartition theorem** (see *Classical physics of matter*). This theorem states simply that, if a system in thermal equilibrium at absolute temperature T has n degrees of freedom, each of those degrees of freedom should possess an energy of $\frac{1}{2}kT$ (where k is Boltzmann's constant). Now, each mode of the electromagnetic radiation in the cavity has *two* degrees of freedom, due to the two possible polarizations, and should therefore have an energy of kT. Classical physics predicted the number, Δn, of modes available in any small wavelength range $\Delta\lambda$ between λ and $\lambda + \Delta\lambda$. The blackbody spectrum should then have been obtained by plotting $\Delta n\, kT$ against λ.

So, how many modes are available at different wavelengths? Well, the electromagnetic radiation is simply a set of standing waves fitted inside the cavity. This is a three-dimensional version of fitting standing waves on a one-dimensional string. The modes allowed for a string of length L are given by the formula $n\lambda = 2L$, where n is an integer. The first ten are shown in Figure 1.8. As you can probably see, as the value of n increases, the wavelengths of adjacent modes get closer and closer together: the wavelength of the $n = 9$ mode is very similar to the wavelength of the $n = 10$ mode. This means that the number of modes in a given wavelength range increases as the wavelength decreases. In three dimensions the effect is even more marked, and, in mathematical terms, the number of modes Δn in the range λ to $\lambda + \Delta\lambda$ turns out to be $8\pi V\Delta\lambda/\lambda^4$, where V is the volume of the cavity. The energy density (energy per unit volume) at wavelength λ, in the small range $\Delta\lambda$, in the blackbody spectrum should therefore be given by this expression, multiplied by kT and divided by V, that is $8\pi kT\Delta\lambda/\lambda^4$.

This formula is the classical prediction for the blackbody spectrum. At long wavelengths it fits the experimental spectrum very well (Figure 1.9). However, at short wavelengths the expression simply blows up. Classical physics predicts that all the energy in the blackbody spectrum should be at the short wavelengths. This was clearly a completely unsatisfactory prediction and became known as the '**ultraviolet catastrophe**'. In Section 3 you will see how the application of quantum physics to this problem produced a very satisfactory result.
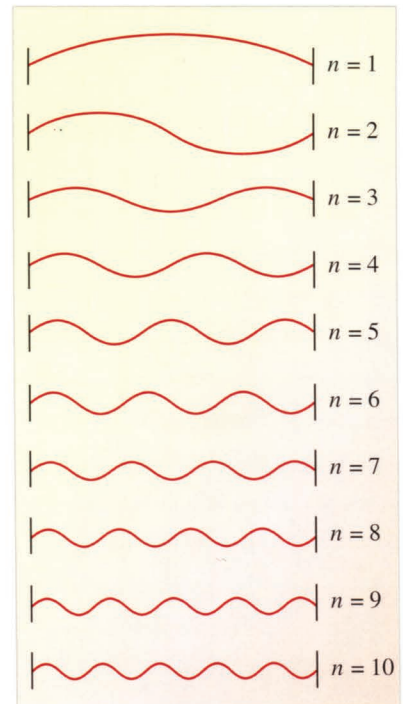
Figure 1.8 The first ten standing wave modes on a string of length L.

Figure 1.9 The ultraviolet catastrophe.

Question 1.2 A blackbody cavity is in the shape of a cube of side 5 cm and is at a temperature of 2000 K. Find the number of modes available in the cavity in the wavelength range 449 nm to 451 nm and hence find the total radiant energy in the cavity in this wavelength range according to the classical theory. ■

2.4 Problem 4: Understanding the photoelectric effect

The ejection of electrons from metals which are illuminated by high frequency electromagnetic radiation was studied in a series of experiments carried out by Philipp Lenard (Figure 1.10) in 1902. This phenomenon is called the **photoelectric effect** (Figure 1.11). Lenard found that the ejected electrons did not all emerge with the same kinetic energy, indicating that some electrons are bound more tightly in the metal than others. Clearly, the *least* strongly bound electrons will emerge with the *greatest* kinetic energy.

That much was fairly easy to understand, problems arose only when it came to accounting for the details of Lenard's observations. In particular, he obtained the two results summarized below. (Recall that the frequency, f, and the wavelength, λ, of electromagnetic radiation are related by $\lambda f = c$, where c is the speed of light.)

Two key results from Lenard's observations

(i) The *maximum* kinetic energy of the ejected electrons is independent of the intensity of the incident electromagnetic radiation: it depends only on the *frequency* of the radiation.

(ii) No electrons are emitted from a metal if the frequency of the incident radiation is lower than a critical threshold frequency f_t that is characteristic of the metal.

Why were these observations so remarkable? Well, think carefully how the photoelectric effect might have been viewed by Maxwell, whose electromagnetic theory had been so successful in accounting for the behaviour of light. He would have pictured the radiation impinging on the metal as *waves*, delivering energy continuously (Figure 1.12). Since the intensity of a wave is defined as the energy it transfers per unit area per unit time, it follows that the energy delivered by these waves is determined only by their intensity and is independent of their frequency.

In this way, it can be argued that a beam of red light should eject electrons with the same maximum kinetic energy as a beam of higher frequency blue light of the same intensity. But Lenard's results showed that this was not the case. For each metal that

Figure 1.10 Philipp Lenard (1862–1947) did his most important and influential work around the beginning of the twentieth of the century, and he was awarded the 1905 Nobel Prize for physics for his experimental investigations into the photoelectric effect. In 1924 he became a Nazi and he expended much effort in attempting to discredit Jewish physicists, in particular, Albert Einstein.

Figure 1.11 When electromagnetic radiation (of sufficiently high frequency) impinges on the surface of a metal, electrons are ejected. This is known as the photoelectric effect.
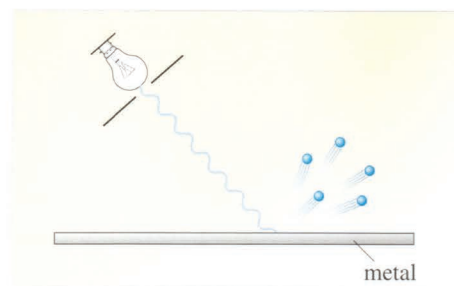
Figure 1.12 According to the classical *wave* theory of radiation, the energy of the beam of radiation is delivered continuously, like the energy of water waves. The energy of the beam should, according to this theory, depend on its intensity, *not* on its frequency. For this reason, it is difficult to understand why the *frequency* of the radiation should determine the maximum kinetic energy of the ejected electrons.

he investigated, the electrons ejected by a beam of light of higher frequency *always* had a greater maximum kinetic energy than that of electrons ejected by a beam of light of a lower frequency. He also found that if the frequency of his beam was below the threshold frequency f_t of the metal, then no electrons were ejected, no matter what the beam's intensity!

Clearly something was wrong somewhere. Maxwell's wave theory seemed to suggest that the energy of radiation should depend crucially on its *intensity*, whereas Lenard's experiments seemed to show that the energy of radiation depended on its *frequency*. This contradiction was perceived very clearly by Albert Einstein, who, in 1905, put forward a new theory. This enabled Lenard's observations to be understood and also explained another observation, namely that there was no measurable time delay between the switching on of the light source and the appearance of ejected electrons, a delay which would be expected using Maxwell's wave theory. Section 3.2 is devoted to Einstein's theory of the photoelectric effect.

2.5 Problem 5: Understanding heat capacities of solids

The molar heat capacity of a substance, denoted by C_m, is the quantity of energy which, when absorbed by a mole of the substance, will raise its temperature by 1 K. For the case of solids, the difference between the molar heat capacity at constant pressure, $C_{P,m}$, and that at constant volume, $C_{V,m}$, is very small, so we will simply refer to C_m.

We assume that the internal (thermal) energy of a solid is contained in its lattice vibrations, i.e. the coordinated vibrations of its constituent atoms. If the solid is in thermal equilibrium at some absolute temperature T, then according to the equipartition theorem, each atomic vibrator has an average energy of $3kT$ since it turns out that there are two degrees of freedom associated with *each* of its three possible directions.

The internal (thermal) energy, $U_m(T)$, of a mole of the solid will therefore be

$$U_m(T) = 3N_m kT = 3RT$$

where N_m is Avogadro's constant and

$$R = N_m k = 8.31\,\mathrm{J\,K^{-1}mol^{-1}}$$

is the molar gas constant. The molar heat capacity at constant volume of the solid is then given by the rate of change of the internal energy with temperature. Thus, using the language of differential calculus:

$$C_m = \frac{dU_m(T)}{dT} = 3R. \quad \text{(CLASSICAL THEORY)} \qquad (1.2)$$

This expression for C_m is clearly independent of the temperature and it has the value $24.93\,\mathrm{J\,K^{-1}mol^{-1}}$. The question we must now ask is 'How does this classical prediction for the molar heat capacity of solids compare with experiment?'

As long ago as 1819 the French researchers Pierre Dulong and Alexis Petit reported experimental values of C_m for a number of elemental solids, including both metals and insulators, at room temperature (Table 1.1). All their samples gave a value close to $25\,\mathrm{J\,K^{-1}mol^{-1}}$. This famous result became known as the **Dulong–Petit law**. To this extent then, classical physics seems to have provided an adequate theory of the heat capacities of solids. There are, however, some serious departures from the law. A notable example is diamond, for which C_m is approximately $6\,\mathrm{J\,K^{-1}mol^{-1}}$ at room

Table 1.1 Dulong and Petit's original data, converted into SI units. These measurements were taken at constant pressure but, for solids, the difference between C_P and C_V is very small (a few per cent).

element	molar heat capacity/ $\mathrm{J\,K^{-1}\,mol^{-1}}$
bismuth	25.77
lead	25.48
gold	24.92
platinum	23.63
tin	25.35
silver	25.38
zinc	25.15
tellurium	24.74
copper	25.19
nickel	25.70
iron	25.06
cobalt	24.80
sulfur	25.50
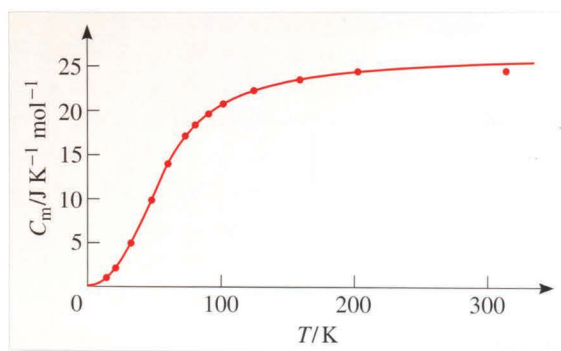
Figure 1.13 Experimentally measured values for the temperature variation of the molar heat capacity of silver.

temperature. Subsequent research has shown that the molar heats of *all* solids decrease at lower temperatures and approach zero as T approaches the absolute zero of temperature. The specific example of silver is shown in Figure 1.13.

In conclusion, the Dulong–Petit law can be regarded as only a partial success for classical physics. Although most solid elements have molar heat capacities that are close to the predicted value, there are several puzzling exceptions and the law breaks down completely at low temperatures. From the viewpoint of classical physics this is very worrying. It is hard to see how the argument that led to Equation 1.2 could ever be modified to get agreement with experiment for all elements at all temperatures. Of course, it turns out that the trouble lies with classical physics itself.

3 Physics saved by the quantum

3.1 The ultraviolet catastrophe tamed

It is appropriate to begin with blackbody radiation because it was the first of the five problems to be solved (in 1900) and because it provided the essential clue to the solution of all of the others.

As you saw in Section 2.3 classical physics predicts that the energy in the blackbody spectrum blows up at short wavelengths — the so-called ultraviolet catastrophe.

The ultraviolet catastrophe would be avoided, however, if, instead of the average energy per mode being kT for *all* modes as required by classical physics, *this average energy actually decreased rapidly with decreasing* λ. This would imply that the equipartition principle is invalid and therefore some aspect of the argument leading to it must be false. Equipartition depends on the assumption that the energy of a standing wave is continuous, in other words, it can vary by infinitesimal amounts. Max Planck (Figure 1.14) wondered what would be the consequences of *assuming* the contrary — that the energy can be changed only by adding or removing a discrete amount or **quantum** of energy? This implies that the energy of a standing wave is contained in a *whole number* of quanta — a fraction of a quantum cannot exist. Planck supposed that the magnitude of the energy quantum must be proportional to the frequency of the wave, which is a reasonable choice qualitatively: as the discrepancies between classical theory and experiment occur at the high-frequency (short-wavelength) end of the spectrum, the quantum of energy should be larger for higher frequencies. In this way Planck was led to his quantum hypothesis, which we will hereafter refer to as **Planck's law** and which may be stated as follows:

The energy E of a standing electromagnetic wave of frequency f (wavelength $\lambda = c/f$) is contained in a whole number of quanta, each of which has the value hf, or equivalently hc/λ, where h is a constant of nature. That is

$$E = hf. \quad \text{(Planck's law)} \qquad (1.3)$$

Max Planck (1858–1947)

Max Planck (Figure 1.14) was born in Kiel in 1858 and studied at Munich. After appointments at Munich and Kiel he was appointed professor of physics at Berlin University in 1892. In 1937, he resigned his position as president of the Kaiser Wilhelm Institute as a protest against the Nazis treatment of Jewish scientists. He lost both his sons, one of whom was executed for plotting against Hitler. After the war Planck was reappointed as president of the Institute, which was renamed the Max Planck Institute, and moved to Göttingen. He died in 1947.

He is famous for his discovery that the key to understanding blackbody radiation is to assume that radiation can be emitted or absorbed only in the form of discrete *quanta*. He was awarded the Nobel Prize for physics in 1918 in recognition of this achievement, which is generally thought to mark the beginning of modern physics.

Figure 1.14 Max Planck.

The constant h is now known as **Planck's constant** and has the value $6.626\,18 \times 10^{-34}\,\text{J s}$. Max Born, writing in 1926, said that Planck's quantum hypothesis 'marked the beginning of an entirely new conception of nature'. Its immediate impact on the problem of blackbody radiation was to provide the following new expression for the average energy of a standing wave

$$\text{average energy per mode} = \frac{hc}{\lambda}(e^{hc/\lambda kT} - 1)^{-1}, \quad \text{(QUANTUM THEORY)} \qquad (1.4)$$

which obviously differs radically from its classical counterpart, namely kT.

In contrast with the constant value kT, Equation 1.4 exhibits just the sort of rapid decrease as the wavelength *shortens* which is required to tame the ultraviolet catastrophe. This result can be understood intuitively as follows. The quantum argument assumes that the energy of a standing wave cannot increase continuously under thermal agitation, but must climb a kind of ladder on which the distance apart of the rungs depends on the wavelength. At long wavelengths, the rungs are close together, many quanta will be excited and as we have seen, the classical case of continuous energy is approached. At the other extreme, when the wavelength is very short, the rungs on the ladder are far apart and the probability of even one quantum being excited is very low. In this situation, the thermodynamic average energy of a standing wave is close to zero.

● What is the significance of the factor $(e^{hc/\lambda kT} - 1)^{-1}$ in Equation 1.4?

○ It is the average number of thermally excited quanta in a standing electromagnetic wave, of wavelength λ, in a cavity at absolute temperature T. (That is, it is the thermodynamic average energy of the wave mode divided by the energy quantum (hc/λ) appropriate to that wavelength.) ■

When the quantum expression (Equation 1.4) is multiplied by the number of modes per unit volume, $\Delta n/V$, in the wavelength range λ to $\lambda + \Delta\lambda$ ($\Delta n/V = 8\pi\Delta\lambda/\lambda^4$ from Section 2.3), the resulting expression for the energy density (energy per unit volume) in blackbody radiation agrees extremely well with experiment (Figure 1.15). This expression is known as **Planck's radiation law**.

Question 1.3   Using Equation 1.4, calculate the total radiant energy in the same wavelength range for the blackbody cavity described in Question 1.2, this time according to Planck's hypothesis. Compare your result with the one you obtained using the classical theory.   ■
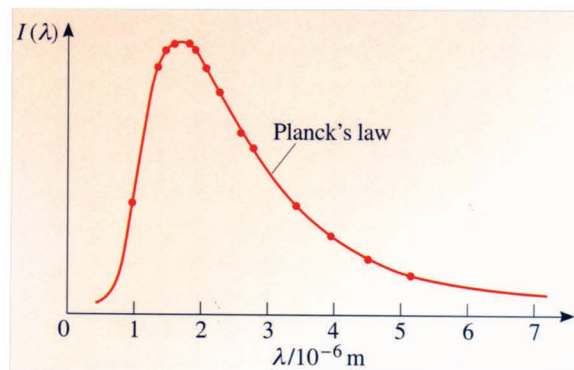

Figure 1.15   The energy density in the blackbody spectrum according to Planck's radiation law (solid line) and experimental measurements (dots). The agreement between the two is very good.

3.2 Einstein's theory of the photoelectric effect

In Section 3.1 we saw how, according to Planck's quantum hypothesis, electromagnetic waves of given frequency, must transfer energy in complete quanta. Albert Einstein (Figure 1.16) sharpened up this idea by arguing that *light quanta* should move through space as localized entities, rather like particles. This would explain how they can be emitted and subsequently absorbed by atoms and suggests a new picture of the radiation in a cavity as comprising a 'gas' of light quanta, which criss-cross the cavity at velocity c and bounce off the walls. The energy E of each light quantum is given by Planck's law, $E = hf$ where h is Planck's constant and f is the frequency of the radiation. Since the magnitude of Planck's constant is so small (6.63×10^{-34} J s), each quantum of light has only a minuscule amount of energy. For example, red light has a frequency of about 4.5×10^{14} Hz so a quantum of red light has an energy of (from Equation 1.3)

$$E = hf = 6.63 \times 10^{-34} \times 4.5 \times 10^{14} \text{ J}$$

$$= 3.0 \times 10^{-19} \text{ J}.$$

Figure 1.16   Albert Einstein (1879–1955). By the age of 27 Albert Einstein had written three of the most famous papers in the canon of physics literature. They concerned the Brownian motion, the special theory of relativity and finally, the quantum theory of radiation, which was cited explicitly when he was awarded the 1921 Nobel Prize for physics.

When a light is switched on, billions upon billions of light quanta are emitted. For example, an ordinary (3% efficient) 100 W light bulb emits roughly 10^{19} quanta of visible light every second! So, in almost all circumstances, the energy in a beam of light appears to be delivered in a constant, uninterrupted stream.

In 1905 Einstein applied the quantum concept to the photoelectric effect by suggesting that electrons in the metal only received energy from the incident radiation in complete quanta of energy $E = hf$ (Figure 1.17). If it is borne in mind that a certain amount of energy must be supplied to an electron just to remove it from the metal, it is straightforward to write down an energy equation for the photoelectric process:

one quantum of incident radiation $-$ energy required to remove the electron from the metal $=$ kinetic energy of the ejected electron.

In Section 2.4 we saw that the electrons emitted from the metal do not all have the same kinetic energy. The least tightly bound ones should emerge as the *most* energetic electrons as they require the *least* energy to remove them from the metal. This *least* energy for removal is usually called the **work function** of the metal, and is conventionally denoted by the Greek letter ϕ (phi).

You should now be able to see that, according to Einstein's theory, when electromagnetic radiation of frequency f impinges on a metal of work function ϕ, the *maximum* kinetic energy of the ejected electrons is given by the difference $hf - \phi$. Then, if m_e is the mass of an electron and v_{max} is the speed with which the most energetic electrons emerge from the metal, it follows that

$$\tfrac{1}{2} m_e v_{max}^2 = hf - \phi. \tag{1.5}$$

This result is known as **Einstein's photoelectric equation**.

Before discussing testable consequences of Equation 1.5 in detail, let us see how Einstein's theory provides an understanding of Lenard's two puzzling results, which were described in Section 2.4.

● Why does the maximum kinetic energy of the ejected electrons depend on the frequency of the incident radiation and not on its intensity?

○ Higher frequency radiation has a higher energy quantum associated with it. Therefore, if each electron is ejected by a single quantum, the energy imparted to the electron will be greater for higher frequency radiation. Raising the intensity of the radiation increases the *number* of quanta, and hence the *number* of ejected electrons, but does not alter the maximum kinetic energy each one may have.

● Why is there a threshold frequency, f_t, below which *no* electrons are ejected from the metal?

○ For electrons to be ejected, the energy quantum ($E = hf$) associated with the incident radiation must be sufficient to remove the least tightly bound electrons (this energy corresponds to the work function ϕ of the metal). Thus, hf must be greater than ϕ. This implies that there is a threshold value f_t for the frequency of the radiation below which electrons will not be ejected. This threshold is given by $f_t = \phi/h$. It is also possible to talk in terms of a threshold wavelength, $\lambda_t = c/f_t$, *above* which no electrons are ejected. ■

An experimental set-up for making photoelectric measurements is shown schematically in Figure 1.18a. Monochromatic light enters the evacuated tube T, and falls on the target or cathode C. The ejected electrons are collected at the anode A, and their flow may be monitored in the external circuit by means of the current meter G. By adjusting the variable resistance R_2, the electrons can be subjected to a retarding potential equal to $R_2 V_0/(R_1 + R_2)$ where R_1 is a fixed resistance and V_0 is the voltage of the power supply. The procedure for checking Einstein's photoelectric equation is to adjust the retarding potential to a value, called the **stopping potential** V_{stop}, which *just* stops the flow of current through G. The maximum initial kinetic energy of the electrons as they are ejected is then eV_{stop}, where e is the charge on an electron and has a value of 1.6×10^{-19} C. A typical plot of the maximum kinetic energy of the ejected electrons (eV_{stop}) against the frequency of the incident radiation is shown in Figure 1.18b. According to Equation 1.5 this should yield a straight-line graph, and this is confirmed by the figure. The gradient or slope of the graph is equal
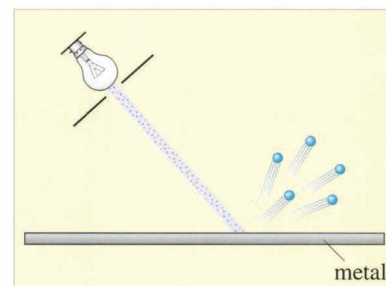
Figure 1.17 According to Einstein's theory, the explanation of the photoelectric effect is that each electron is liberated from the metal by the absorption of a single quantum of energy from the incident radiation.
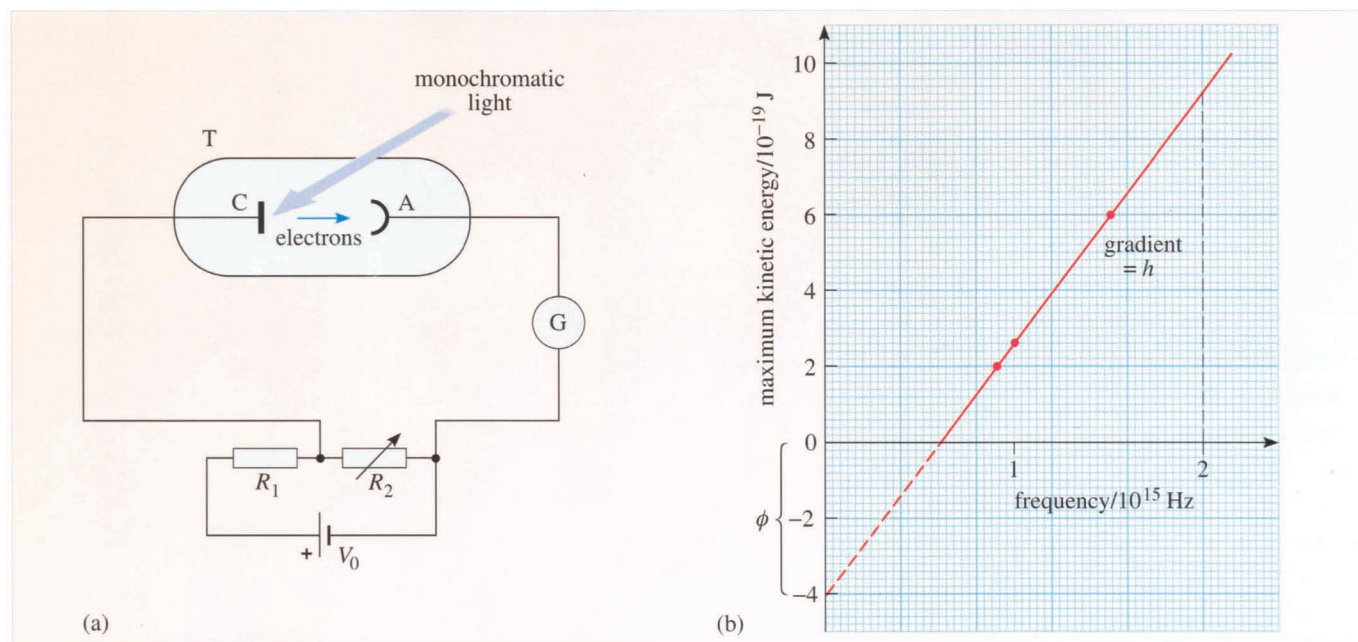
Figure 1.18 (a) An experiment for testing Einstein's theory of the photoelectric effect. For a given frequency of incident radiation, the maximum kinetic energy of the ejected electrons is given by eV_{stop}, where V_{stop} is the stopping potential. (b) The variation of the maximum kinetic energy of the ejected electrons with the frequency, f, of the incident electromagnetic radiation. The straight-line plot confirms the validity of Einstein's photoelectric equation (Equation 1.5).

Figure 1.19 Robert Millikan (1868–1953) was a native of Illinois in the United States. After obtaining his doctorate at Columbia he spent some time at the Universities of Berlin and Göttingen. In 1896 he moved to the University of Chicago where, initially, he was Michelson's assistant. He is famous for his determination of two fundamental constants of nature; e, the charge on an electron and Planck's constant h. He was awarded the Nobel Prize for physics in 1923 for his work on the photoelectric effect.

to Planck's constant h and the threshold frequency f_t is the value of f at which the line crosses the frequency axis. When the line is extrapolated to lower frequencies (dashed portion), its intercept on the maximum kinetic energy axis is $-\phi$, i.e. the negative of the work function of the metal.

● How would you expect the graph in Figure 1.18b to differ for different metals?

○ If different metals are used, the graphs obtained would have the same slope h, but different intercepts, because different metals have different work functions. This reflects the fact that the amount of energy required to remove the least tightly bound electrons will vary from metal to metal. ■

Question 1.4 Use Figure 1.18b to find the value of (a) Planck's constant and (b) the work function of the metal involved. ■

Einstein's photoelectric equation was verified in 1916 in a series of experiments carried out by the American physicist Robert Millikan (Figure 1.19). These experiments led to the award of two separate Nobel prizes: one for Millikan himself and another for Albert Einstein who, according to the citation, was awarded the prize principally for his theory of the photoelectric effect. There was no explicit reference in the citation to his more famous work on the special and general theories of relativity!

Millikan's measurements also provided yet more supporting evidence for the quantum theory of electromagnetic radiation. The time was measured between the moment the radiation impinged on the metals, and the moment that electrons were first ejected from them. It was found that the electrons were emitted immediately, that is, at the instant the metal was illuminated. (The time delay is now known to be

less than 10^{-9} s.) This result is easily understood from Einstein's theory, since it is reasonable to expect that an electron in a metal might be ejected as soon as the first quantum of energy is transferred from the incident radiation. (See also Box 1.1.) Yet the simple wave theory of light predicts that about a *minute* should pass before an amount of energy sufficient to release electrons could be transferred to any individual atom in the metal!

You can verify that this long time delay is predicted by the wave theory by working through Question 1.5.

Question 1.5   A source of light emits, at a rate of 8 W, electromagnetic radiation of frequency sufficient to eject electrons from a piece of potassium that is 1 m away.

(a) Assuming that the radiation is emitted with equal intensity in all directions and that the wave theory of light is correct, show that approximately 5×10^{-21} J of energy will, in each second, be incident on an atom at the surface of the metal.
(Take the radius of a potassium atom to be 0.5×10^{-10} m.)

(b) The work function of potassium is 3.4×10^{-19} J. Assuming that a potassium atom absorbs all of the energy incident on it, estimate the time that would elapse between the instant that the waves of light impinge on the metal and the instant that the first electron is ejected.

(c) Compare your answer to part (b) with the experimentally determined upper limit on the time lag, which is about 10^{-9} s. What do you conclude?

Question 1.6   Light of wavelength 450 nm is incident on a sample of lithium. If the work function of lithium is 2.13 eV, calculate the speed of the fastest electrons ejected.

Question 1.7   The photoelectric threshold wavelength of sodium is 542 nm. Calculate the work function of sodium.   ■

Box 1.1   From light quanta to photons

The idea that radiation was quantized was first introduced by Planck to explain blackbody radiation. The concept was reinforced by Einstein in his explanation of the photoelectric effect. For Einstein, electromagnetic radiation was not only emitted and absorbed in quantized amounts but could also be thought of as retaining this energy quantization as it propagated through space.

These ideas evolved gradually over the next twenty years or so into the idea of electromagnetic radiation as a stream of particles possessing both energy and *momentum*. The term **photon**, for each light particle, was introduced by the American chemist Gilbert Newton Lewis and nowadays, when physicists discuss phenomena which require the particle theory of electromagnetic radiation, they almost invariably refer to the particles as photons.

3.3   Einstein's theory of heat capacities

In Section 2.5 we discussed how classical physics predicts that the molar heat capacity of all solids at all temperatures should be equal to $3R$, where R is the molar gas constant. Although the result is valid in many cases, there are some exceptions and the prediction is completely wrong at low temperatures. In order to progress beyond the simple classical theory given in Section 2.5, it is necessary to make

some assumption about the nature of the atomic vibrations within the solid. Einstein made the simplest assumption possible: that each atom of the solid oscillates at the same characteristic frequency f_v in all three directions. However, as long as the equipartition theorem is thought to be valid, these details can change nothing: the average energy of an atomic vibration will still be kT. Planck had shown that, according to his quantum hypothesis, the energy of *any* oscillator of frequency f_v should be quantized in steps of hf_v and when Einstein added this quantum condition to his model he found, as we might expect, that it changed the outcome completely. By a chain of reasoning virtually identical to that which led, in the case of blackbody radiation, to Equation 1.4, he obtained the average energy of an atomic mode of vibration as

$$\text{average energy per mode} = \frac{hf_v}{e^{hf_v/kT} - 1}. \qquad (1.6)$$

To find the internal energy $U_m(T)$, of a mole of solid, we multiply Equation 1.6 by the number of independent modes of vibration in one mole, $3N_m$. Thus we have

$$U_m(T) = \frac{3N_m hf_v}{e^{hf_v/kT} - 1} \qquad (1.7)$$

for the internal energy of one mole of the solid. The heat capacity is the rate of change of internal energy with respect to temperature and is obtained by differentiating $U_m(T)$ with respect to T. The result may be written, finally, (remembering that $R = N_m k$) as

$$C_m(T) = 3R\left(\frac{\theta_E}{T}\right)^2 \times \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad \text{(EINSTEIN'S THEORY)} \qquad (1.8)$$

Similar reasoning can be applied to diatomic gases, and used to explain why their room temperature heat capacities are lower than predicted by the equipartition of energy theorem (see *Classical physics of matter*, Chapter 2).

where $\theta_E = hf_v/k$. The value θ_E is known as the **Einstein temperature** of the solid and is proportional to the frequency of vibration, f_v, of the atoms of the lattice. Figure 1.20 shows how Einstein's prediction (Equation 1.8) for $C_m(T)$ varies with temperature. This prediction is clearly in much better agreement with the experimentally observed heat capacity (shown for silver in Figure 1.13) than the classical prediction of a constant value of $3R$.
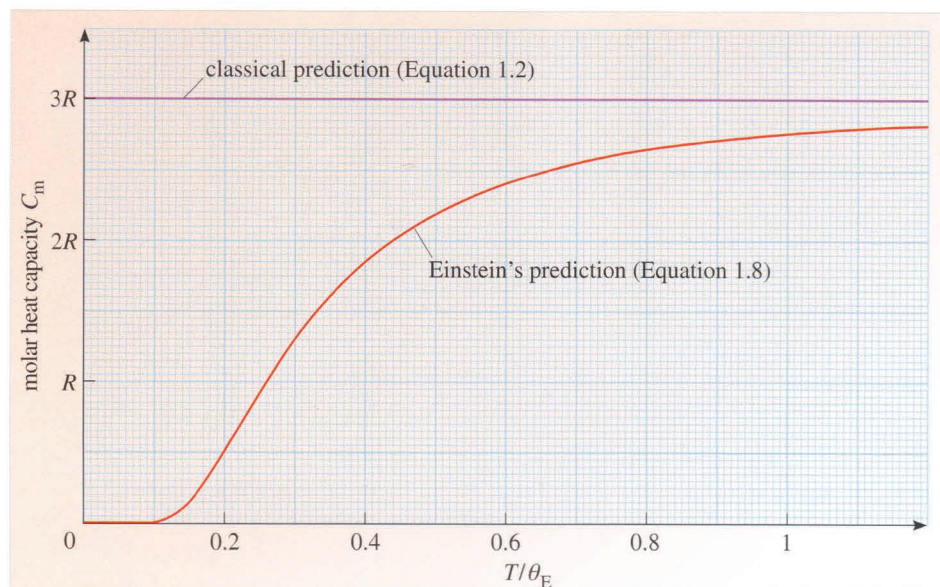

Figure 1.20 Einstein's prediction for the molar heat capacity of a solid as a function of T/θ_E, where T is the actual temperature of the solid and θ_E is its Einstein temperature.