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preface

This book is intended to serve as an introduction to quantum physics. In writing it, I have kept several guidelines in mind.

1. First, it is helpful for the development of intuition in any new field of study to start with a base of detailed knowledge about simple systems. I have therefore worked out a number of problems in great detail, so that the insight thus obtained can be used for more complex systems.

2. Every aspect of quantum mechanics has been helpful in understanding some physical phenomenon. I have therefore laid great stress on applications at every stage of the development of the subject. Although no area of quantum physics is totally developed, my intention is to bridge the gap between a modern physics course and the more formal development of quantum mechanics. Thus, many applications are discussed, and I have stressed order-of-magnitude estimates and the importance of numbers.

3. In keeping with the level of the book, the mathematical structure has been kept as simple as possible. New concepts, such as operators, and new mathematical tools necessarily make their appearance. I have dealt with the former more by analogy than by precise definition, and I have minimized the use of new tools insofar as possible.

In approaching quantum theory, I chose to start with wave mechanics and the Schrödinger equation. Although the state-vector approach gets at the essential structure of quantum mechanics more rapidly, experience has shown that the use of more familiar tools, such as differential equations, makes the theory more accessible and the correspondence with classical physics more transparent.

The book probably contains a little more material than can comfortably be covered in one year. The basic material can be covered in one academic quarter.

It consists of Chapters 1 to 6, 8, and 9, in which the motivation for a quantum theory, the Schrödinger equation, and the general framework of wave mechanics are covered. A number of simple problems are solved in Chapter 5, and their relevance to physical phenomena is discussed. The generalization to many particles and to three dimensions is developed. The second-quarter material deals directly with atomic physics problems and uses somewhat more sophisticated tools. Here we discuss operator methods (Chapter 7), angular momentum (Chapter 11), the hydrogen atom (Chapter 12), operators, matrices, and spin (Chapter 14), the addition of angular momenta (Chapter 15), time-independent perturbation theory (Chapter 16), and the real hydrogen atom (Chapter 17). This material prepares the student to cope with a large variety of problems that are discussed during the third and last quarter. These problems include the interaction of charged particles with a magnetic field (Chapter 13), the helium atom (Chapter 18), problems in the radiation of atoms and related topics (Chapters 22 and 23), collision theory (Chapter 24), and the absorption of radiation in matter (Chapter 25). This material is supplemented by a more qualitative discussion of the structure of atoms and molecules (Chapters 19 to 21). The last chapter on elementary particles and their symmetries serves the dual purpose of describing some of the recent advances on that frontier of physics and of showing how the basic ideas of quantum theory have found applicability in the domain of very short distances.

Several topics arise naturally as digressions in the development of the subject matter. Instead of lengthening some long chapters, I have placed this material in a separate "Special Topics" section. There, relativistic kinematics, the equivalence principle, the WKB approximation, a detailed treatment of lifetimes, line widths and scattering resonances, and the Yukawa theory of nuclear forces are discussed. For the same reason, a brief introduction to the Fourier integral, the Dirac delta function, and some formal material dealing with operators have been placed in mathematical appendices at the end of the book.

I am indebted to my colleagues at the University of Minnesota, especially Benjamin Bayman and Donald Geffen, for many discussions on the subject of quantum mechanics. I am grateful to Eugen Merzbacher, who read the manuscript and made many helpful suggestions for improvements. I also thank my students in the introductory quantum mechanics course that I taught for several years. Their evident interest in the subject led me to the writing of the supplemental notes that later became this book.

Stephen Gasiorowicz

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chapter 1

The Limits of Classical Physics

The end of the nineteenth century and the beginning of the twentieth witnessed a crisis in physics. A series of experimental results required concepts totally incompatible with classical physics. The development of these concepts, in a fascinating interplay of radical conjectures and brilliant experiments, led finally to the *quantum theory*.[1] Our objective in this chapter is to describe the background of this crisis and, armed with hindsight, to expose the new concepts in a manner that, while not historically correct, will make the transition to quantum theory less mysterious for the reader. The new concepts, *the particle properties of radiation*, *the wave properties of matter*, and *the quantization of physical quantities* will emerge in the phenomena discussed below.

A. Black Body Radiation

When a body is heated, it is seen to radiate. In equilibrium the light emitted ranges over the whole spectrum of frequencies ν, with a spectral distribution that depends both on the frequency or, equivalently, on the wavelength of the light λ, and on the temperature. One may define a quantity $E(\lambda, T)$, the emissive power, as the energy emitted at wavelength λ per unit area, per unit time. Theoretical research in the field of thermal radiation began in 1859 with the work of Kirchhoff, who showed that for a given λ, the ratio of the emissive power E to the absorptivity A, defined as the fraction of incident radiation of wavelength λ that is absorbed by the body, is the same for all bodies. Kirchhoff considered two emitting and absorbing parallel plates and showed from the equilibrium condition that the energy emitted was equal to the energy absorbed (for each λ), that the ratios E/A must be the same for the two plates. Soon

[1] An interesting account of the development of quantum theory may be found in M. Jammer, *The Conceptual Development of Quantum Mechanics*, McGraw-Hill, New York, 1966.

thereafter, he observed that for a *black body*, defined as a surface that totally absorbs all radiation that falls on it, so that $A = 1$, the function $E(\lambda, T)$ is a universal function.

In order to study this function it is necessary to obtain the best possible source of black body radiation. A practical solution to this problem is to consider the radiation emerging from a small hole in an enclosure heated to a temperature T. Given the imperfections in the surface of the inside of the cavity, it is clear that any radiation falling on the hole will have no chance of emerging again. Thus the surface presented by the hole is very nearly "totally absorbing," and consequently the radiation coming from it is indeed "black body radiation." Provided the hole is small enough, this radiation will be the same as that which falls on the walls of the cavity. It is therefore necessary to understand the distribution of radiation inside a cavity whose walls are at a temperature T.

Kirchhoff showed that the second law of thermodynamics requires that the radiation in the cavity be isotropic, that is, that the flux be independent of direction; that it be homogeneous, that is, the same at all points; and that it be the same in all cavities at the same temperature—all of this for each wavelength.[2] The emissive power may, by simple geometric arguments, be shown to be connected with the energy density $u(\lambda, T)$ inside the cavity. The relation is

$$u(\lambda, T) = \frac{4E(\lambda, T)}{c} \tag{1-1}$$

The energy density is the quantity of theoretical interest, and further understanding of it came in 1894 from the work of Wien, who, again using very general arguments,[3] showed that the energy density had to be of the form

$$u(\lambda, T) = \lambda^{-5} f(\lambda T) \tag{1-2}$$

with f still an unknown function of a single variable. If, as is convenient, one deals instead with the energy density as a function of frequency, $u(\nu, T)$, then it follows from the fact that

$$\begin{aligned} u(\nu, T) &= u(\lambda, T) \left| \frac{d\lambda}{d\nu} \right| \\ &= \frac{c}{\nu^2} u(\lambda, T) \end{aligned} \tag{1-3}$$

[2] These matters are discussed in many textbooks on modern physics and statistical physics. References can be found at the end of this chapter.

[3] Wien considered a perfectly reflecting spherical cavity contracting adiabatically. The redistribution of the energy as a function of λ has to be caused by the Doppler shift on reflection. See Chapter V in F. K. Richtmyer, E. H. Kennard, and J. N. Cooper *Introduction to Modern Physics*, McGraw-Hill, New York, 1969.

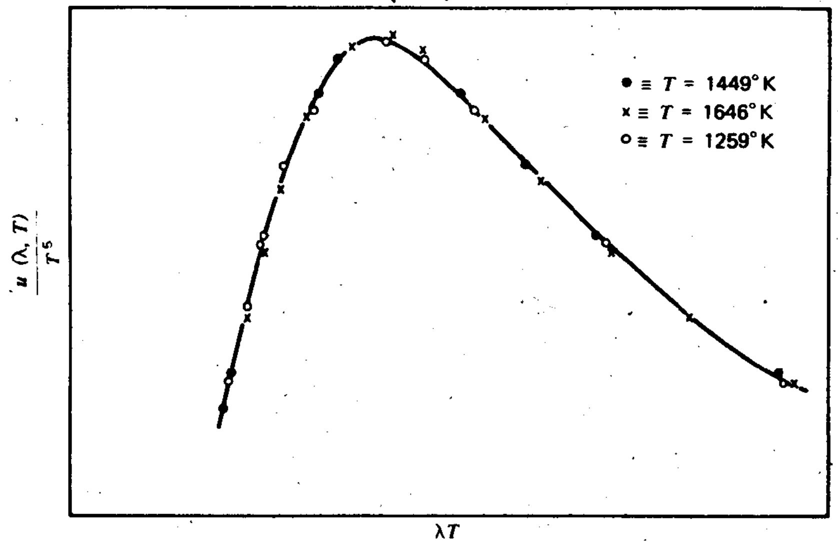

Fig. 1-1. Experimental verification of Eq. 1-2 in the form $u(\lambda,T)/T^5$ = a universal function of λT.

that the Wien law reads

$$u(\nu, T) = \nu^3 g\left(\frac{\nu}{T}\right) \tag{1-4}$$

The implications of this law, which was confirmed experimentally (Fig. 1.1), are twofold:

1. Given the spectral distribution of black body radiation at one temperature, the distribution at any other temperature can be found with the help of the expressions given above.

2. If the function $f(x)$—or, equivalently, the function $g(x)$—has a maximum for some value of $x > 0$, then the wavelength λ_{max} at which the energy density, and hence the emissive power, has its maximum value, has the form

$$\lambda_{max} = \frac{b}{T} \tag{1-5}$$

where b is a universal constant.

Wien used a model (of no interest, except to the historian) to predict a form for $g(\nu/T)$. The form was

$$g(\nu/T) = Ce^{-\beta\nu/T} \tag{1-6}$$

and, remarkably enough, this form, containing two adjustable parameters, fit the high frequency (low wavelength) data very well. The formula is not, how-

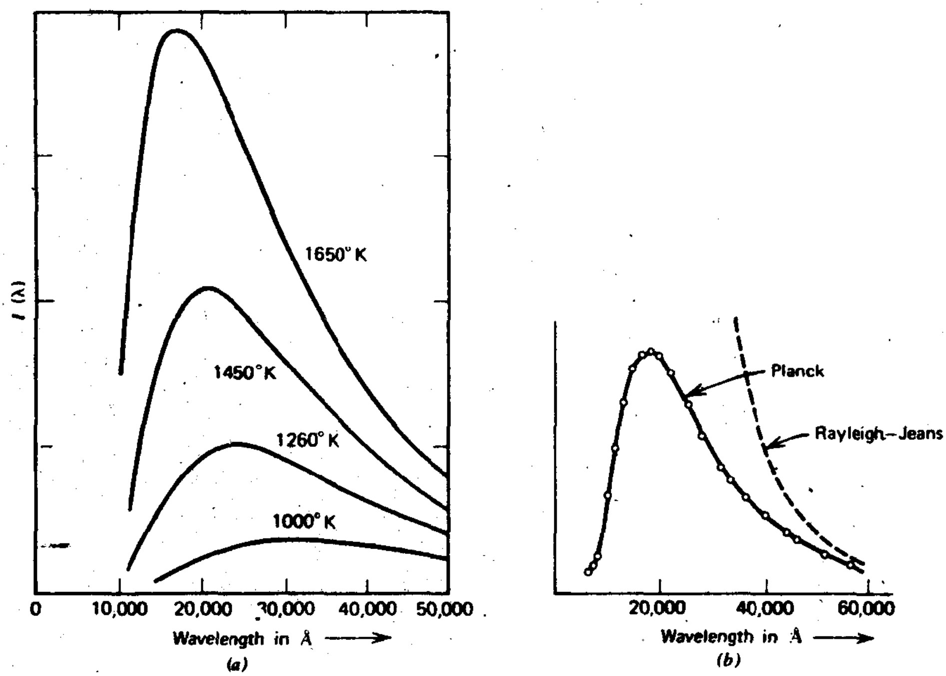

Fig. 1-2. (*a*) Distribution of power radiated by a black body at various temperatures. (*b*) Comparison of data at 1600°K with Planck formula and Rayleigh-Jeans formula.

ever, in accord with some very general notions of classical physics. Rayleigh, in 1900, derived the result

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} kT \tag{1-7}$$

where k is Boltzmann's constant, $k = 1.38 \times 10^{-16}$ erg/deg and c is the velocity of light, $c = 3.00 \times 10^{10}$ cm/sec. The ingredients that went into the derivation were (1) the classical law of equipartition of energy, according to which the average energy per degree of freedom for a dynamical system in equilibrium is, in this context,[4] kT, and (2) the calculation of the number of modes (i.e., degrees of freedom) for electromagnetic radiation with frequency in the interval $(\nu, \nu + d\nu)$, confined in a cavity.[5]

[4] The equipartition law predicts that the energy per degree of freedom is $kT/2$. For an oscillator—and the modes of the electromagnetic field are simple harmonic oscillators—a contribution of $kT/2$ from the kinetic energy is matched by a like contribution from the potential energy, giving kT.

[5] We will need this result again, and derive it in Chapter 23. The number of modes is $4\pi\nu^2/c^3$, further multiplied by a factor of 2 because transverse electromagnetic waves correspond to two-dimensional harmonic oscillators.

The Rayleigh-Jeans law (1-7) (Jeans made a minor contribution to its derivation) does not agree with experiment at high frequencies, where the Wien formula works, though it does fit the experimental curve at low frequencies (Fig. 1.2). The Rayleigh-Jeans law cannot, on general grounds, be correct, since the total energy density (integrated over all frequencies) is predicted to be infinite!

In 1900, Max Planck found a formula by an ingenious interpolation between the high-frequency Wien formula and the low-frequency Rayleigh-Jeans law. The formula is

$$u(\nu, T) = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/kT} - 1} \tag{1-8}$$

where h, *Planck's constant*, is an adjustable parameter whose numerical value was found to be $h = 6.63 \times 10^{-27}$ erg sec. This law approaches the Rayleigh-Jeans form when $\nu \to 0$, and reduces to

$$\begin{aligned} u(\nu, T) &= \frac{8\pi h}{c^3} \nu^3 e^{-h\nu/kT} (1 - e^{-h\nu/kT})^{-1} \\ &\cong \frac{8\pi h}{c^3} \nu^3 e^{-h\nu/kT} \end{aligned} \tag{1-9}$$

when the frequency is large, or, more accurately, when $h\nu \gg kT$. If we rewrite the formula as a product of the number of modes [we obtain this from (1-7) by dividing the energy density by kT] and another factor that can be interpreted as the average energy per degree of freedom

$$\begin{aligned} u(\nu, T) &= \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1} \\ &= \frac{8\pi\nu^2}{c^3} kT \frac{h\nu/kT}{e^{h\nu/kT} - 1} \end{aligned} \tag{1-10}$$

we see that the classical equipartition law is altered whenever the frequencies are not small compared with kT/h. This alteration in the equipartition law shows that the modes have an average energy that depends on their frequency, and that the high frequency modes have a very small average energy. This effective cut-off removes the difficulty of the Rayleigh-Jeans density formula: the total energy in a cavity of unit volume is no longer infinite. We have

$$\begin{aligned} U(T) &= \frac{8\pi h}{c^3} \int_0^\infty d\nu \frac{\nu^3}{e^{h\nu/kT} - 1} \\ &= \frac{8\pi h}{c^3} \left(\frac{kT}{h}\right)^4 \int_0^\infty \frac{(h\nu/kT)^3 \, d(h\nu/kT)}{e^{h\nu/kT} - 1} \\ &= \frac{8\pi k^4}{h^3 c^3} T^4 \int_0^\infty dx \frac{x^3}{e^x - 1} \end{aligned} \tag{1-11}$$

The integral can be evaluated,[6] and the result is the Stefan-Boltzmann expression for the total radiation energy per unit volume

$$U(T) = aT^4 \tag{1-12}$$

with $a = 7.56 \times 10^{-15}$ erg/cm^3 deg^4, derived much earlier, except for the numerical constant in front, on the basis of thermodynamical reasoning. A departure from the pure equipartition law was not entirely unexpected: one consequence of it was the Dulong-Petit law of specific heats, according to which the product of the atomic (or molecular) weight and the specific heat is a constant for all solids; yet departures from the Dulong-Petit predictions were observed as early as 1872.[7] These departures indicated that the specific heat decreased at lower temperatures.[8]

The unqualified success of his formula drove Planck to search for its origin, and within two months he found that he could derive it by assuming that the energy associated with each mode of the electromagnetic field did not vary continuously (with average value kT) but was an integral multiple of some minimum quantum of energy $\mathcal{E}$. Under these circumstances a calculation of the average energy associated with each mode, using the Boltzmann probability distribution in a system of equilibrium at temperature T,

$$P(E) = \frac{e^{-E/kT}}{\sum_E e^{-E/kT}} \tag{1-13}$$

led to

$$\bar{E} = \sum_E EP(E)$$

$$= \frac{\sum_{n=0}^{\infty} n\mathcal{E}\, e^{-n\mathcal{E}/kT}}{\sum_{n=0}^{\infty} e^{-n\mathcal{E}/kT}}$$

$$\int_0^\infty dx\, x^3 (e^x - 1)^{-1} = \int_0^\infty dx\, x^3 e^{-x} \sum_{n=0}^{\infty} e^{-nx}$$
$$= \sum_{n=0}^{\infty} \frac{1}{(n+1)^4} \int_0^\infty dy\, y^3 e^{-y} = 6 \sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{\pi^4}{15}$$

[7] According to the equipartition law an assembly of N oscillators (and a lattice of atoms with elastic forces between them may be so viewed) will have energy $3NkT$, the factor 3 coming from the fact that the oscillators in a solid are three-dimensional, rather than two-dimensional as for the radiation field in an enclosure. The specific heat for a mole is obtained by differentiating with respect to T and setting $N = N_0$, Avogadro's number, so that $C_v = 3N_0k = 3R$ where $R = 8.28 \times 10^7$ erg/deg.

[8] Specific heats will be discussed very briefly in Chapter 20.

$$= \left. \frac{-\mathcal{E} \dfrac{d}{dx} \sum_{n=0}^{\infty} e^{-nx}}{\sum_{n=0}^{\infty} e^{-nx}} \right|_{x=\mathcal{E}/kT}$$

$$= \mathcal{E} \left. \frac{e^{-x}}{1 - e^{-x}} \right|_{x=\mathcal{E}/kT}$$

$$= \frac{\mathcal{E}}{e^{\mathcal{E}/kT} - 1} \tag{1-14}$$

This agrees with (1-10) provided we make the identification

$$\mathcal{E} = h\nu \tag{1-15}$$

and do not change the number of modes.

Planck argued that for some unknown reason the atoms in the walls of the cavity emitted radiation in "quanta" with energy $nh\nu$ ($n = 1,2,3, \ldots$), but consistency demanded, as established by Einstein a few years later, that *electromagnetic radiation behaved as if it consisted of a collection of energy quanta with energy $h\nu$.*[9]

The energy carried per quantum is extremely small. For light in the optical range, with, say, $\lambda = 6000$ Å,

$$h\nu = h\frac{c}{\lambda} = \frac{6.63 \times 10^{-27} \times 3.00 \times 10^{10}}{6 \times 10^{-5}} \simeq 3.3 \times 10^{-12} \text{ erg}$$

so that the number of light quanta of this wavelength, emitted by a 100-watt source, say, is

$$N = \frac{100 \times 10^{7}}{3.3 \times 10^{-12}} \cong 3 \times 10^{20} \text{ quanta/sec}$$

With so many quanta present, it is perhaps not surprising that we do not experience the particle nature of light directly; we shall see that on a macroscopic scale no deviations from classical optics are expected. Nevertheless, Planck's interpretation of his formula radically changes our picture of radiation.

B. The Photoelectric Effect

As successful as the Planck formula was, the conclusion from it of the quantum nature of radiation is hardly compelling. An important contribution to its acceptance came from the work of Albert Einstein, who in 1905 used the

[9] For a given frequency ν there may be any integral number of quanta present, and hence the energy can take on the values $nh\nu$, with $n = 0,1,2,3, \ldots$.