UNIVERSITY PHYSICS

VOLUME III

QUANTUM AND STATISTICAL PHYSICS

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FOREWORD

This book is the third and last volume of a series published under the general title of *Fundamental University Physics*. The purpose of this series is to offer to students of science and engineering a logical and unified presentation of physics at the introductory undergraduate level, with emphasis on the basic ideas which form the core of physics: the conservation laws, the interrelation between particles and fields, and the atomic view of matter. We have tried to present physical concepts in such a way that the student will attain a clear understanding of their theoretical meaning and recognize their experimental foundations, noting the close interrelation between theory and experiment. We also have tried to develop in the student the ability to manipulate the mathematics required for the expression of such concepts. The three volumes cover the equivalent of a two-semester course in general physics plus a one (or two) semester course in modern physics. Volume I treats mechanics and the gravitational interaction. Volume II deals with electromagnetic interactions and waves. Volume III covers quantum and statistical physics (including thermodynamics). Although the three volumes are closely related and follow a logical sequence, each one is self-contained and can be used independently of the others. This is particularly true of Volume III, which covers most of the subject matter usually included in an introductory modern physics course.

The curricula for all sciences are under great pressure to incorporate new subjects that are becoming more relevant. We expect that this series will relieve this pressure by raising the level of the student's understanding of physical concepts and his ability to apply them to concrete situations. This will permit many intermediate courses presently offered in the undergraduate curriculum to be upgraded. The traditional undergraduate courses in mechanics, electromagnetism, and modern physics will benefit most from this upgrading. Thus the student will finish his undergraduate career at a higher level of knowledge than formerly: an important benefit for those who terminate their formal education at this point. Also there will now be room for newer and more exciting courses at the graduate level. This same trend is found in the more recent basic textbooks in other sciences for freshman and sophomore courses.

The first part of this volume is called Quantum Physics. Quantum ideas are the essence of today's physics. Unfortunately, except for a brief introduction to Bohr's ideas and to wave-particle duality in the introductory general physics course, there has often been a delay in exposing students to quantum-mechanical concepts and their applications. Traditionally only the physics and chemistry majors learned quantum mechanics, and then rarely before the senior year. However, physics and chemistry majors should acquire a working knowledge of quantum ideas as early in their curricula as possible so that they may utilize this knowledge in subsequent undergraduate courses. This procedure is strongly endorsed by the Commission on College Physics. Present trends in biology and engineering demand that students in these fields also have a basic understanding of the solid state and of molecular structure. Therefore we have been careful to introduce the student to quantum mechanics in a way which, although elementary, allows him to apply quantum concepts to different situations.

Chapter 1 is an introduction to the foundation of quantum ideas. This is followed in Chapter 2 by the necessary background in quantum mechanics, here we emphasize the way in which physical information about a system is extracted from the shape of the potential-energy function and a knowledge of the general nature of wave functions. In the succeeding chapters, 3 through 9, quantal concepts and techniques are applied to the analysis of atoms, molecules, solids, nuclei, and fundamental particles.

In the second part of the text (designated Statistical Physics), we use statistical methods to consider the properties of matter in bulk. Like quantum mechanics, statistical physics is a well-founded, powerful tool, to which the student should be introduced as early as possible. After discussing classical statistical mechanics in Chapter 10, we present thermodynamics from a statistical point of view in Chapter 11 and apply it to both ideal and real gases in Chapter 12. We are firmly convinced that this is the most appropriate method to follow in introducing the student to the concepts of thermodynamics. The text ends with a brief introduction to quantum statistics in Chapter 13.

Since many students now learn the basic ideas of relativity in their general physics course, the special theory of relativity is discussed in the appendix. (A more complete discussion of relativity appears in Volumes I and II of the series.) Several collateral topics, such as group velocity and the methods of particle detection, are also discussed in the appendix.

We have kept the mathematical requirements within the topics covered by a standard calculus course. We have also often either omitted or relegated to the problem sections those mathematical calculations which are not essential to an understanding of the main trend of physical ideas; one example of such calculations is the sometimes boresome task of finding certain solutions to Schrödinger's equation.

Many applications of the fundamental principles, as well as the discussion of a few more advanced topics, appear in the form of worked examples. The text has been written so that the student may omit all examples at his first reading. During a second reading the student should consider those examples chosen by the instructor. The instructor may discuss these examples at his convenience or propose them on a selective basis. Certain sections of the text may be omitted without loss of continuity. The problems at the end of each chapter follow the sequence of the chapter, with a few more difficult problems at the end. The large number of varied problems means that the instructor can choose problems to match the abilities of his students. Hence by proper selection of the material in this text, the instructor can adapt the text to a one- or two-semester course and at the same time give the student both a challenge and a motivation to meet that challenge.

We want to express our gratitude to all those who, by their assistance and encouragement, have made this work possible. We recognize in particular Professor David Lazarus, whose comments and criticisms helped to improve many aspects of the text. Last—but not least—we thank our wives, who have so patiently stood by us.

Washington, D. C.
January 1968

Marcelo Alonso
Edward J. Finn

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One of the fundamental objectives of physics is to analyze the properties of the basic components of matter and the processes that occur among them as a result of their interactions. These basic components—called fundamental or elementary particles—are electrons, protons, neutrons (and others) which group together to form nuclei, atoms, and molecules. These groups, in turn, combine to form matter in bulk. Although the motion of fundamental particles complies with the principles of conservation of momentum, angular momentum, and energy, the analysis of this motion requires a framework different in several respects from the one developed in classical (or Newtonian) mechanics for the analysis of macroscopic motion. This more refined theory is called *quantum mechanics*. We must understand it well before we embark on a discussion of atoms, molecules, and nuclei. Fortunately, atoms and molecules are essentially the result of *electromagnetic interactions* between the positively charged nuclei and the negatively charged electrons. Thus we can discuss atoms and molecules, without having to appeal to other less-well-understood forces, by combining the laws of electromagnetism with those of quantum mechanics. The same technique may also be used for gases, liquids, and solids. On the other hand, nuclei are basically the result of a new type of force, the so-called *strong* or *nuclear interaction*. Since the strong interaction is not yet well understood, its analysis is much more involved. Consequently, in this text our discussion of nuclei must be of a more descriptive nature.

Perhaps the most dynamic and stimulating field of contemporary physics is the study of the fundamental particles. The interactions observed between these particles require the introduction of another type of force, in addition to the strong interaction. This force is called the *weak interaction*. Another force, the *gravitational interaction*, which is the weakest of all interactions, plays a lesser role insofar as the basic structure of matter is concerned.

The relative value of the four interactions is:

Strong	1
Electromagnetic	10^{-2}
Weak	10^{-13}
Gravitational	10^{-38}

The processes involving fundamental particles have motivated a new formalism, somewhat different from quantum mechanics, called *quantum field theory*. This theory, however, is too complex to be considered in this text.

1 THE FOUNDATIONS OF QUANTUM PHYSICS

1.1 Introduction
1.2 Electromagnetic Radiation
1.3 Blackbody Radiation
1.4 Photoelectric Emission
1.5 Scattering of Radiation by Free Electrons
1.6 Photons
1.7 Stationary States
1.8 Experimental Evidence of Stationary States
1.9 Interaction of Radiation with Matter
1.10 Particles and Fields
1.11 Particles and Wave Packets
1.12 Heisenberg's Uncertainty Principle for Position and Momentum
1.13 The Uncertainty Relation for Time and Energy

1.1 Introduction

By the end of the nineteenth century, and during the first quarter of the twentieth, experimental evidence began to accumulate which indicated that the interaction of electromagnetic radiation with matter was not entirely in accordance with the laws of electromagnetism. These laws were the result of the work of Ampère, Laplace, Faraday, Henry, Maxwell, and many others, and are synthesized in Maxwell's equations for the electromagnetic field. At the same time the theory of the atomic structure of matter was developing, mainly as a result of the discovery of the electron and the confirmation of the nuclear model of the atom. Still another series of experiments forced the physicist to review his concepts of the motion of subatomic particles, since they apparently did not move precisely in accordance with the assumptions of Newtonian mechanics. To explain the new observations, a sequence of new ideas, introduced in a more or less *ad hoc* fashion, were incorporated by several physicists. With the passage of time, and by the efforts of many brilliant men, these ideas evolved until they became what is now known as the *quantum theory*, a theory which is, perhaps, the essence of contemporary physics. In this chapter we shall review the more important experimental bases of quantum physics.

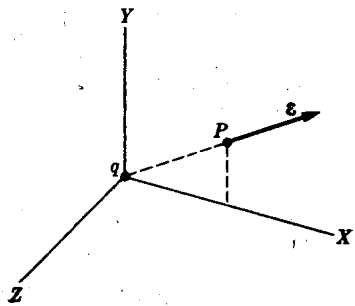

Fig. 1–1. Electric field of a charge at rest.

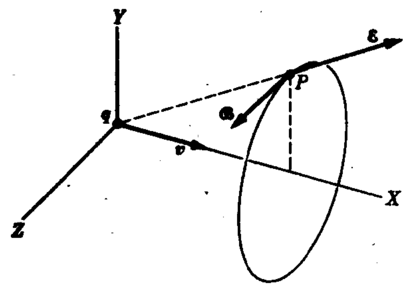

Fig. 1–2. Electric and magnetic fields of a uniformly moving charge.

1.2 Electromagnetic Radiation

The electromagnetic interaction between two charged particles can best be described in terms of the concepts of electric and magnetic fields produced by the charges. When a charged particle is at rest relative to an inertial observer, the observer measures a field which is called the electric field of the charge (Fig. 1–1). However, if the charge is in motion relative to the observer, he observes a different field, called the electromagnetic field of the charge (Fig. 1–2). One component of the field is still called electric, while the remaining component is called the magnetic field. Such fields depend on the velocity and acceleration of the charge relative to the observer. Since the separation of the field produced by a charge into an electric and a magnetic part depends on the relative motion of the charge and the observer, we should speak only of the electromagnetic field of the charged particle. Conversely, when a particle moves through the electromagnetic field produced by other charges, it experiences a force given by

$$\boldsymbol{F} = q(\boldsymbol{\mathcal{E}} + \boldsymbol{v} \times \boldsymbol{\mathcal{B}}),$$

where $\boldsymbol{\mathcal{E}}$ and $\boldsymbol{\mathcal{B}}$ are the electric and magnetic fields, respectively, as measured by an observer who measures the velocity of the particle as $\boldsymbol{v}$. In this way we can describe the electromagnetic interaction of charged particles in terms of fields.

Energy is required to set up an electromagnetic field. The energy per unit volume of an electromagnetic field in vacuum is

$$\mathrm{E} = \tfrac{1}{2}\epsilon_0 \mathcal{E}^2 + \frac{1}{2\mu_0}\mathcal{B}^2, \tag{1.1}$$

where ϵ_0 and μ_0 are the vacuum permittivity and permeability, respectively.

The energy of a *static* electromagnetic field (that is, a field that does not change with time) obviously remains constant. However, when the field is *time dependent*, the electromagnetic energy at each point changes with time. The time variations of an electromagnetic field give rise to an electromagnetic wave which propagates with a velocity

$$c = 1/\sqrt{\epsilon_0 \mu_0} \approx 3 \times 10^8 \text{ m s}^{-1}, \tag{1.2}$$

which is the same as the velocity of light in vacuum. We may say that the wave carries the energy of the electromagnetic field. This energy which is carried by an electromagnetic wave is sometimes called *electromagnetic radiation*.

Since a charge at rest relative to an observer produces a static field, the charge does not radiate electromagnetic energy. Also it can be shown that a charge which is in uniform rectilinear motion does not radiate electromagnetic energy because the total energy of its electromagnetic field remains constant. A very different situation exists for a charge which is in accelerated motion. The total energy of the electromagnetic field of an accelerated charge varies with time. Therefore

an accelerated charge radiates electromagnetic energy.

The rate of energy radiation by a charge q moving with velocity $\boldsymbol{v}$ and acceleration $\boldsymbol{a}$, when the velocity is small relative to the velocity of light, is

$$\frac{dE}{dt} = \frac{q^2 a^2}{6\pi\epsilon_0 c^3}. \tag{1.3}$$

One important conclusion is that, if a charge is to be maintained in accelerated motion, energy must be supplied to compensate for the energy transferred as radiation. This means that when an ion is accelerated, for example in a Van de Graaff accelerator or in a cyclotron, a fraction of the energy supplied to the ion is lost as electromagnetic radiation. This energy loss, however, is negligible except at relativistic energies. Charged particles trapped in the earth's magnetic field, in sun spots, or in distant celestial bodies such as the Crab nebula also emit radiation, called *synchrotron radiation*. This radiation extends from radio frequencies to the extreme ultraviolet.

If the particle is decelerated instead of being accelerated, Eq. (1.3) still holds and the energy radiated is that excess which the electromagnetic field has as a result of the decrease in the velocity of the charge. For example, when a fast charge such as an electron or a proton hits a target and is stopped, a substantial part of its total energy goes off as radiation (Fig. 1-3). This radiation is called deceleration radiation, or more commonly *bremsstrahlung* [from the German words *Bremsung* (deceleration) and *Strahlung* (radiation)]. This is the chief mechanism by which radiation is produced in the x-ray tubes which are used in physical, medical, and industrial applications.

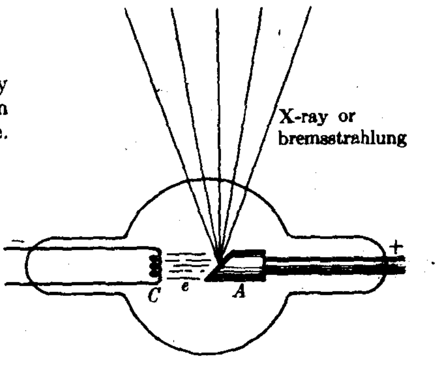

Fig. 1-3. Radiation emitted by a charge which is decelerated when it hits the target in an x-ray tube.

The energy radiated by a charged particle may be absorbed by other charged particles which are subject to the action of the electromagnetic field produced by the first particle. Hence we may describe the interaction of two charged particles as an exchange of energy by means of emission and absorption of radiation. For example, the oscillating electrons in the antenna of a radio broadcasting station radiate energy. Part of this energy is absorbed by the electrons in the antenna of a radio receiver, which results in a signal at the receiving station.

An analysis of the processes of emission and absorption of radiation (that is, the interaction of radiation and matter) is fundamental for understanding the behavior of matter. As we shall see in the following sections, quantum physics evolved as a result of the analysis of such processes.

EXAMPLE 1.1. The rate at which energy is radiated by an oscillating electric dipole.

Solution: Consider a charge q moving along the Z-axis in such a way that at any time its position is given by $z = z_0 \cos \omega t$. This corresponds to an oscillatory motion of amplitude z_0 and angular frequency ω. Thus the charge is equivalent to an oscillating electric dipole. The acceleration of the particle is $a = -\omega^2 z$. Substituting this value of a in Eq. (1.3), we have

$$\frac{dE}{dt} = \frac{q^2 z^2 \omega^4}{6\pi\epsilon_0 c^3}. \tag{1.4}$$

The rate of energy radiation oscillates because of the variation of z with time. To obtain the average rate of energy radiation, we recall that $(z^2)_{ave} = \frac{1}{2}z_0^2$. Thus

$$\left(\frac{dE}{dt}\right)_{ave} = \frac{q^2 z_0^2 \omega^4}{12\pi\epsilon_0 c^3} \tag{1.5}$$

We may say that an oscillating electric dipole radiates energy at an average rate given by Eq. (1.5) and that the radiation corresponds to an electromagnetic field oscillating with the same frequency as the dipole.

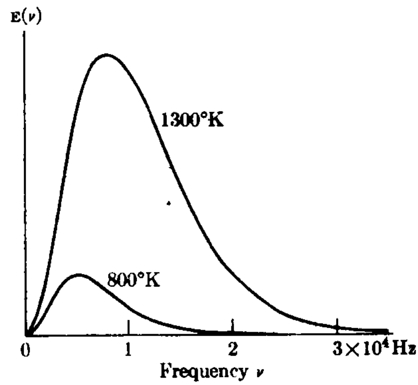

Fig. 1–4. Monochromatic energy density of blackbody radiation at different temperatures as a function of the frequency

1.3 Blackbody Radiation

Consider a cavity whose walls are at a certain temperature. The atoms composing the walls are emitting electromagnetic radiation; at the same time they absorb radiation emitted by other atoms of the walls The electromagnetic radiation field occupies the whole cavity. When the radiation trapped within the cavity reaches equilibrium with the atoms of the walls, the amount of energy emitted by the atoms per unit time is equal to the amount absorbed by them. Hence, when the radiation in the cavity is at equilibrium with the walls, the energy density of the electromagnetic field is constant. Experiment has shown that, at equilibrium, the trapped electromagnetic radiation has a well-defined energy distribution, that is, to each frequency there corresponds an energy density which depends solely on the temperature of the walls and is independent of their material. The energy density corresponding to radiation with frequency between ν and $\nu + d\nu$ is written $E(\nu)\, d\nu$, where $E(\nu)$ is the energy density per unit frequency range, sometimes called *monochromatic energy density* The observed variation of $E(\nu)$ with the frequency ν is illustrated in Fig. 1–4 for two temperatures. Curves like these were first obtained experimentally by Lummer and Pringsheim in 1899. It may be seen from the curves that for each temperature the energy density shows a pronounced maximum at a certain frequency. Note also that the frequency at which the energy density is maximum increases as the temperature increases. This explains the change in color of a radiating body as its temperature varies

If a small hole is opened in one of the walls of the cavity, some of the radiation escapes and may be analyzed The hole appears very bright when the body is at high temperatures and the intensity of the equilibrium radiation within the cavity is high, but it appears completely black at low temperatures, when the intensity of the equilibrium radiation is negligible in the visible region of the spectrum. For that reason the radiation coming out of the cavity was called *blackbody radiation* by those who analyzed it in the nineteenth century.

The problem of finding what mechanism causes radiating atoms to produce the observed energy distribution of blackbody radiation led to the birth of quantum physics. By the end of the last century all attempts to explain this energy distribution using the concepts available at that time had failed completely. The German physicist Max Planck (1858–1947) suggested, about 1900, that if the radiation in the cavity was in equilibrium with the atoms of the walls, there should be a correspondence between the energy distribution in the radiation and the energies of the atoms in the cavity. As a model for the radiating atoms, Planck assumed that atoms behave as harmonic oscillators, and that each one oscillates with a given frequency ν. As a second assumption Planck suggested that

> *each oscillator can absorb or emit radiation energy only in an amount proportional to its frequency* ν.

This latter condition is not required by the classical theory of electromagnetism (as expressed by Maxwell's equations), which permits a continuous emission or absorption of energy. Given that E is the energy absorbed or emitted in a single process of interaction of an oscillator with electromagnetic radiation, Planck's assumption states that

$$E = h\nu, \tag{1.6}$$

where h is a proportionality constant assumed to be the same for all oscillators. Hence, when an oscillator absorbs or emits electromagnetic radiation, its energy increases or decreases by an amount $h\nu$. Equation (1.6) then implies that

> *the energy of atomic oscillators is quantized.*

That is, the energy of an oscillator of frequency ν can attain only certain values, which are (assuming that the minimum energy of the oscillator is zero) 0, $h\nu$, $2h\nu$, $3h\nu$, ... Thus, in general, the possible values of the energy of an oscillator of frequency ν are

$$E_n = nh\nu, \tag{1.7}$$

where n is a positive integer As we know, the energy of an oscillator is proportional to the square of its amplitude and, *a priori*, by properly adjusting the amplitude of the oscillations, we can make an oscillator of a given frequency have any arbitrarily chosen energy. Therefore Planck's idea was an *ad hoc* assumption which could not be explained by means of classical concepts, it was justified only because it "worked," and because physicists at the time lacked a better explanation. We still do not have a better explanation, we must accept the quantization of some physical quantities as a fundamental fact of nature.

By applying some considerations of a statistical nature, together with Eq (1.6), Planck obtained, for the energy density in blackbody radiation, an expression of the form

$$\mathrm{E}(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1}, \tag{1.8}$$

where k is Boltzmann's constant. This expression, which agrees surprisingly well with the experimental values of $\mathrm{E}(\nu)$ at different temperatures, has been accepted as the correct expression for blackbody radiation. It is called *Planck's radiation law.*

An interesting aspect is that Planck's derivation cannot presently be considered as physically sound (which is the reason we have omitted it). In other words, the problem which precipitated the birth of the quantum theory was first solved by means of an unsatisfactory method. The problem had to wait several years until the quantum theory was developed along other lines of thought before an adequate method of calculation was found. This revised derivation will be given in Section 13.6. However, Planck's ideas, especially Eqs (1.6) and (1.7), prompted new thinking by many other physicists who were working on the interpretation of other related phenomena; this led to rapid development of quantum theory.

In Eq. (1.6) we introduced an arbitrary constant h, called *Planck's constant.* Its value, obtained by making Eq. (1.8) fit the experimental results for $\mathrm{E}(\nu)$, is

$$h = 6.6256 \times 10^{-34} \text{ J s}. \tag{1.9}$$

Planck's constant is one of the most important constants in physics.

EXAMPLE 1.2. Express the monochromatic energy density of blackbody radiation in terms of wavelength.

Solution: Sometimes it is preferable to express the monochromatic energy density in terms of wavelength instead of frequency We define $\mathrm{E}(\lambda)$ according to the relation $\mathrm{E}(\lambda)\, d\lambda = -\mathrm{E}(\nu)\, d\nu$ We introduce the minus sign because $d\lambda$ and $d\nu$ have opposite signs, although $\mathrm{E}(\nu)$ and $\mathrm{E}(\lambda)$ are both positive Thus, since $\nu = c/\lambda$, we have

$$d\nu/d\lambda = -c/\lambda^2$$

and

$$\mathrm{E}(\lambda) = -\mathrm{E}(\nu)\, d\nu/d\lambda = \mathrm{E}(\nu)c/\lambda^2.$$

Replacing $\mathrm{E}(\nu)$ by the value given it in Eq (1 8) and setting $\nu = c/\lambda$, we finally obtain

$$\mathrm{E}(\lambda) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}. \tag{1.10}$$

The graph of $\mathrm{E}(\lambda)$ is shown in Fig 1-5 for different temperatures It shows a pronounced peak at a wavelength which depends on the temperature

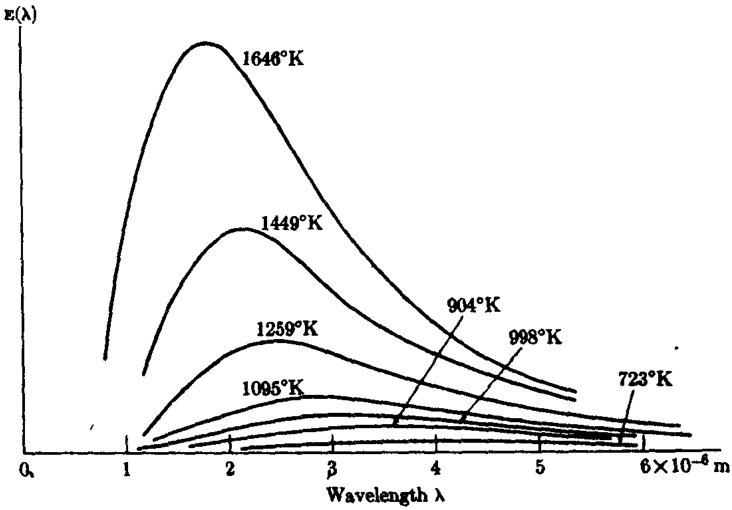

Fig. 1-5. Monochromatic energy density of blackbody radiation at different temperatures as a function of the wavelength.

EXAMPLE 1.3. Find the wavelength at which the monochromatic energy density of blackbody radiation is maximum at a given temperature.

Solution: Let us use Eq. (1.10) and, to simplify our exposition, we shall set $x = hc/\lambda kT$, so that $E(\lambda)$ becomes

$$E(\lambda) = \frac{8\pi k^5 T^5}{c^4 h^4} \frac{x^5}{e^x - 1}.$$

To find the maximum of $E(\lambda)$, we first find dE/dx and equate it to zero. The resulting equation is

$$e^{-x} + \tfrac{1}{5}x - 1 = 0$$

This is a transcendental equation, which we solve by successive approximation to obtain $x = 4.9651$. Thus $\lambda T = b$, where

$$b = hc/4.9651k = 2.8978 \times 10^{-3}\ \text{m°K}$$

is called the *Wien displacement constant*. The expression

$$\lambda T = b \tag{1.11}$$

constitutes *Wien's displacement law*, discovered 1896 by Wilhelm Wien. This law states that the maxima of $E(\lambda)$ at different temperatures $T_1, T_2, T_3, \ldots$ fall at wavelengths $\lambda_1, \lambda_2, \lambda_3, \ldots$ such that

$$\lambda_1 T_1 = \lambda_2 T_2 = \lambda_3 T_3 = \cdots.$$