

Quantum Mechanics Concepts and Applications

Second Edition

Nouredine Zettili

Jacksonville State University, Jacksonville, USA

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Library of Congress Cataloging-in-Publication Data

Zettili, Nouredine.

Quantum Mechanics: concepts and applications / Nouredine Zettili. – 2nd ed.

p. cm.

Includes bibliographical references and index.

ISBN 978-0-470-02678-6 (cloth: alk. paper) – ISBN 978-0-470-02679-3 (pbk.: alk. paper)

1. Quantum theory. I. Title

QC174.12.Z47 2009

530.12 – dc22

2008045022

A catalogue record for this book is available from the British Library

Produced from LaTeX files supplied by the author

Printed and bound in Great Britain by CPI Antony Rowe Ltd, Chippenham, Wiltshire

ISBN: 978-0-470-02678-6 (H/B)

978-0-470-02679-3 (P/B)

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Preface

Preface to the Second Edition

It has been eight years now since the appearance of the first edition of this book in 2001. During this time, many courteous users—professors who have been adopting the book, researchers, and students—have taken the time and care to provide me with valuable feedback about the book. In preparing the second edition, I have taken into consideration the generous feedback I have received from these users. To them, and from the very outset, I want to express my deep sense of gratitude and appreciation.

The underlying focus of the book has remained the same: to provide a well-structured and self-contained, yet concise, text that is backed by a rich collection of fully solved examples and problems illustrating various aspects of nonrelativistic quantum mechanics. The book is intended to achieve a double aim: on the one hand, to provide instructors with a pedagogically suitable teaching tool and, on the other, to help students not only master the underpinnings of the theory but also become effective practitioners of quantum mechanics.

Although the overall structure and contents of the book have remained the same upon the insistence of numerous users, I have carried out a number of streamlining, surgical type changes in the second edition. These changes were aimed at fixing the weaknesses (such as typos) detected in the first edition while reinforcing and improving on its strengths. I have introduced a number of sections, new examples and problems, and new material; these are spread throughout the text. Additionally, I have operated substantive revisions of the exercises at the end of the chapters; I have added a number of new exercises, jettisoned some, and streamlined the rest. I may underscore the fact that the collection of end-of-chapter exercises has been thoroughly classroom tested for a number of years now.

The book has now a collection of almost six hundred examples, problems, and exercises. Every chapter contains: (a) a number of solved examples each of which is designed to illustrate a specific concept pertaining to a particular section within the chapter, (b) plenty of fully solved problems (which come at the end of every chapter) that are generally comprehensive and, hence, cover several concepts at once, and (c) an abundance of unsolved exercises intended for homework assignments. Through this rich collection of examples, problems, and exercises, I want to empower the student to become an independent learner and an adept practitioner of quantum mechanics. Being able to solve problems is an unailing evidence of a real understanding of the subject.

The second edition is backed by useful resources designed for instructors adopting the book (please contact the author or Wiley to receive these free resources).

The material in this book is suitable for three semesters—a two-semester undergraduate course and a one-semester graduate course. A pertinent question arises: How to actually use

the book in an undergraduate or graduate course(s)? There is no simple answer to this question as this depends on the background of the students and on the nature of the course(s) at hand. First, I want to underscore this important observation: As the book offers an abundance of information, every instructor should certainly select the topics that will be most relevant to her/his students; going systematically over all the sections of a particular chapter (notably Chapter 2), one might run the risk of getting bogged down and, hence, ending up spending too much time on technical topics. Instead, one should be highly selective. For instance, for a one-semester course where the students have not taken modern physics before, I would recommend to cover these topics: Sections 1.1–1.6; 2.2.2, 2.2.4, 2.3, 2.4.1–2.4.8, 2.5.1, 2.5.3, 2.6.1–2.6.2, 2.7; 3.2–3.6; 4.3–4.8; 5.2–5.4, 5.6–5.7; and 6.2–6.4. However, if the students have taken modern physics before, I would skip Chapter 1 altogether and would deal with these sections: 2.2.2, 2.2.4, 2.3, 2.4.1–2.4.8, 2.5.1, 2.5.3, 2.6.1–2.6.2, 2.7; 3.2–3.6; 4.3–4.8; 5.2–5.4, 5.6–5.7; 6.2–6.4; 9.2.1–9.2.2, 9.3, and 9.4. For a two-semester course, I think the instructor has plenty of time and flexibility to maneuver and select the topics that would be most suitable for her/his students; in this case, I would certainly include some topics from Chapters 7–11 as well (but not all sections of these chapters as this would be unrealistically time demanding). On the other hand, for a one-semester graduate course, I would cover topics such as Sections 1.7–1.8; 2.4.9, 2.6.3–2.6.5; 3.7–3.8; 4.9; and most topics of Chapters 7–11.

Acknowledgments

I have received very useful feedback from many users of the first edition; I am deeply grateful and thankful to everyone of them. I would like to thank in particular Richard Lebed (Arizona State University) who has worked selflessly and tirelessly to provide me with valuable comments, corrections, and suggestions. I want also to thank Jearl Walker (Cleveland State University)—the author of *The Flying Circus of Physics* and of the Halliday–Resnick–Walker classics, *Fundamentals of Physics*—for having read the manuscript and for his wise suggestions; Milton Cha (University of Hawaii System) for having proofread the entire book; Felix Chen (Powerwave Technologies, Santa Ana) for his reading of the first 6 chapters. My special thanks are also due to the following courteous users/readers who have provided me with lists of typos/errors they have detected in the first edition: Thomas Sayetta (East Carolina University), Moritz Braun (University of South Africa, Pretoria), David Berkowitz (California State University at Northridge), John Douglas Hey (University of KwaZulu-Natal, Durban, South Africa), Richard Arthur Dudley (University of Calgary, Canada), Andrea Durlo (founder of the A.I.F. (Italian Association for Physics Teaching), Ferrara, Italy), and Rick Miranda (Netherlands). My deep sense of gratitude goes to M. Bulut (University of Alabama at Birmingham) and to Heiner Mueller-Krumbhaar (Forschungszentrum Juelich, Germany) and his Ph.D. student C. Gugenberger for having written and tested the C++ code listed in Appendix C, which is designed to solve the Schrödinger equation for a one-dimensional harmonic oscillator and for an infinite square-well potential.

Finally, I want to thank my editors, Dr. Andy Slade, Celia Carden, and Alexandra Carrick, for their consistent hard work and friendly support throughout the course of this project.

N. Zettili
Jacksonville State University, USA
January 2009

Preface to the First Edition

Books on quantum mechanics can be grouped into two main categories: textbooks, where the focus is on the formalism, and purely problem-solving books, where the emphasis is on applications. While many fine textbooks on quantum mechanics exist, problem-solving books are far fewer. It is not my intention to merely add a text to either of these two lists. My intention is to combine the two formats into a single text which includes the ingredients of both a textbook and a problem-solving book. Books in this format are practically nonexistent. I have found this idea particularly useful, for it gives the student easy and quick access not only to the essential elements of the theory but also to its practical aspects in a unified setting.

During many years of teaching quantum mechanics, I have noticed that students generally find it easier to learn its underlying ideas than to handle the practical aspects of the formalism. Not knowing how to calculate and extract numbers out of the formalism, one misses the full power and utility of the theory. Mastering the techniques of problem-solving is an essential part of learning physics. To address this issue, the problems solved in this text are designed to teach the student how to calculate. No real mastery of quantum mechanics can be achieved without learning how to derive and calculate quantities.

In this book I want to achieve a double aim: to give a self-contained, yet concise, presentation of most issues of nonrelativistic quantum mechanics, and to offer a rich collection of fully solved examples and problems. This unified format is not without cost. Size! Judicious care has been exercised to achieve conciseness without compromising coherence and completeness.

This book is an outgrowth of undergraduate and graduate lecture notes I have been supplying to my students for about one decade; the problems included have been culled from a large collection of homework and exam exercises I have been assigning to the students. It is intended for senior undergraduate and first-year graduate students. The material in this book could be covered in three semesters: Chapters 1 to 5 (excluding Section 3.7) in a one-semester undergraduate course; Chapter 6, Section 7.3, Chapter 8, Section 9.2 (excluding fine structure and the anomalous Zeeman effect), and Sections 11.1 to 11.3 in the second semester; and the rest of the book in a one-semester graduate course.

The book begins with the experimental basis of quantum mechanics, where we look at those atomic and subatomic phenomena which confirm the failure of classical physics at the microscopic scale and establish the need for a new approach. Then come the mathematical tools of quantum mechanics such as linear spaces, operator algebra, matrix mechanics, and eigenvalue problems; all these are treated by means of Dirac's bra-ket notation. After that we discuss the formal foundations of quantum mechanics and then deal with the exact solutions of the Schrödinger equation when applied to one-dimensional and three-dimensional problems. We then look at the stationary and the time-dependent approximation methods and, finally, present the theory of scattering.

I would like to thank Professors Ismail Zahed (University of New York at Stony Brook) and Gerry O. Sullivan (University College Dublin, Ireland) for their meticulous reading and comments on an early draft of the manuscript. I am grateful to the four anonymous reviewers who provided insightful comments and suggestions. Special thanks go to my editor, Dr Andy Slade, for his constant support, encouragement, and efficient supervision of this project.

I want to acknowledge the hospitality of the Center for Theoretical Physics of MIT, Cambridge, for the two years I spent there as a visitor. I would like to thank in particular Professors Alan Guth, Robert Jaffe, and John Negele for their support.

Note to the student

We are what we repeatedly do. Excellence, then, is not an act, but a habit.

Aristotle

No one expects to learn swimming without getting wet. Nor does anyone expect to learn it by merely reading books or by watching others swim. Swimming cannot be learned without practice. There is absolutely no substitute for throwing yourself into water and training for weeks, or even months, till the exercise becomes a smooth reflex.

Similarly, physics *cannot be learned passively*. Without tackling various challenging problems, the student has no other way of testing the quality of his or her understanding of the subject. Here is where the student gains the sense of satisfaction and involvement produced by a genuine understanding of the underlying principles. *The ability to solve problems is the best proof of mastering the subject*. As in swimming, the more you solve problems, the more you sharpen and fine-tune your problem-solving skills.

To derive full benefit from the examples and problems solved in the text, avoid consulting the solution too early. If you cannot solve the problem after your first attempt, try again! If you look up the solution only after several attempts, it will remain etched in your mind for a long time. But if you manage to solve the problem on your own, you should still compare your solution with the book's solution. You might find a shorter or more elegant approach.

One important observation: as the book is laden with a rich collection of fully solved examples and problems, one should absolutely avoid the temptation of memorizing the various techniques and solutions; instead, one should focus on understanding the concepts and the underpinnings of the formalism involved. It is not my intention in this book to teach the student a number of tricks or techniques for acquiring good grades in quantum mechanics classes without genuine understanding or mastery of the subject; that is, I didn't mean to teach the student how to pass quantum mechanics exams without a deep and lasting understanding. However, the student who focuses on understanding the underlying foundations of the subject and on reinforcing that by solving numerous problems and thoroughly understanding them will doubtlessly achieve a double aim: reaping good grades as well as obtaining a sound and long-lasting education.

N. Zettili

Chapter 1

Origins of Quantum Physics

In this chapter we are going to review the main physical ideas and experimental facts that defied classical physics and led to the birth of quantum mechanics. The introduction of quantum mechanics was prompted by the failure of classical physics in explaining a number of microphysical phenomena that were observed at the end of the nineteenth and early twentieth centuries.

1.1 Historical Note

At the end of the nineteenth century, physics consisted essentially of classical mechanics, the theory of electromagnetism¹, and thermodynamics. Classical mechanics was used to predict the dynamics of *material bodies*, and Maxwell's electromagnetism provided the proper framework to study *radiation*; *matter* and *radiation* were described in terms of *particles* and *waves*, respectively. As for the interactions between matter and radiation, they were well explained by the Lorentz force or by thermodynamics. The overwhelming success of classical physics—classical mechanics, classical theory of electromagnetism, and thermodynamics—made people believe that the ultimate description of nature had been achieved. It seemed that all known physical phenomena could be explained within the framework of the general theories of matter and radiation.

At the turn of the twentieth century, however, classical physics, which had been quite unsailable, was seriously challenged on two major fronts:

- **Relativistic domain:** Einstein's 1905 theory of relativity showed that the validity of Newtonian mechanics ceases at very high speeds (i.e., at speeds comparable to that of light).
- **Microscopic domain:** As soon as new experimental techniques were developed to the point of probing atomic and subatomic structures, it turned out that classical physics fails miserably in providing the proper explanation for several newly discovered phenomena. It thus became evident that the validity of classical physics ceases at the microscopic level and that *new* concepts had to be invoked to describe, for instance, the structure of atoms and molecules and how light interacts with them.

¹Maxwell's theory of electromagnetism had unified the, then ostensibly different, three branches of physics: electricity, magnetism, and optics.

The failure of classical physics to explain several microscopic phenomena—such as blackbody radiation, the photoelectric effect, atomic stability, and atomic spectroscopy—had cleared the way for seeking new ideas outside its purview.

The first real breakthrough came in 1900 when Max Planck introduced the concept of the *quantum* of energy. In his efforts to explain the phenomenon of blackbody radiation, he succeeded in reproducing the experimental results only after postulating that the energy exchange between *radiation* and its surroundings takes place in *discrete*, or *quantized*, amounts. He argued that the energy exchange between an *electromagnetic wave* of frequency ν and matter occurs *only in integer multiples* of $h\nu$, which he called the energy of a *quantum*, where h is a fundamental constant called *Planck's constant*. The quantization of electromagnetic radiation turned out to be an idea with far-reaching consequences.

Planck's idea, which gave an accurate explanation of blackbody radiation, prompted new thinking and triggered an avalanche of new discoveries that yielded solutions to the most outstanding problems of the time.

In 1905 Einstein provided a powerful consolidation to Planck's quantum concept. In trying to understand the photoelectric effect, Einstein recognized that Planck's idea of the quantization of the *electromagnetic waves* must be valid for *light* as well. So, following Planck's approach, he posited that *light itself is made of discrete bits of energy (or tiny particles)*, called *photons*, each of energy $h\nu$, ν being the frequency of the light. The introduction of the photon concept enabled Einstein to give an elegantly accurate explanation to the photoelectric problem, which had been waiting for a solution ever since its first experimental observation by Hertz in 1887.

Another seminal breakthrough was due to Niels Bohr. Right after Rutherford's experimental discovery of the atomic nucleus in 1911, and combining Rutherford's atomic model, Planck's quantum concept, and Einstein's photons, Bohr introduced in 1913 his model of the hydrogen atom. In this work, he argued that atoms can be found only in *discrete states* of energy and that the interaction of atoms with radiation, i.e., the emission or absorption of radiation by atoms, takes place only in *discrete amounts* of $h\nu$ because it results from transitions of the atom between its various discrete energy states. This work provided a satisfactory explanation to several outstanding problems such as atomic stability and atomic spectroscopy.

Then in 1923 Compton made an important discovery that gave the most conclusive confirmation for the corpuscular aspect of light. By scattering X-rays with electrons, he confirmed that the X-ray photons behave like particles with momenta $h\nu/c$; ν is the frequency of the X-rays.

This series of breakthroughs—due to Planck, Einstein, Bohr, and Compton—gave both the theoretical foundations as well as the conclusive experimental confirmation for the particle aspect of waves; that is, the concept that waves exhibit particle behavior at the microscopic scale. At this scale, classical physics fails not only quantitatively but even qualitatively and conceptually.

As if things were not bad enough for classical physics, de Broglie introduced in 1923 another powerful new concept that classical physics could not reconcile: he postulated that not only does radiation exhibit particle-like behavior but, conversely, *material particles* themselves display *wave-like* behavior. This concept was confirmed experimentally in 1927 by Davisson and Germer; they showed that interference patterns, a property of waves, can be obtained with material particles such as electrons.

Although Bohr's model for the atom produced results that agree well with experimental spectroscopy, it was criticized for lacking the ingredients of a theory. Like the "quantization" scheme introduced by Planck in 1900, the postulates and assumptions adopted by Bohr in 1913

were quite arbitrary and do not follow from the first principles of a theory. It was the dissatisfaction with the arbitrary nature of Planck's idea and Bohr's postulates as well as the need to fit them within the context of a consistent theory that had prompted Heisenberg and Schrödinger to search for the theoretical foundation underlying these new ideas. By 1925 their efforts paid off: they skillfully welded the various experimental findings as well as Bohr's postulates into a refined theory: *quantum mechanics*. In addition to providing an accurate reproduction of the existing experimental data, this theory turned out to possess an astonishingly reliable prediction power which enabled it to explore and unravel many uncharted areas of the microphysical world. This new theory had put an end to twenty five years (1900–1925) of patchwork which was dominated by the ideas of Planck and Bohr and which later became known as the old quantum theory.

Historically, there were two independent formulations of quantum mechanics. The first formulation, called *matrix mechanics*, was developed by Heisenberg (1925) to describe atomic structure starting from the observed spectral lines. Inspired by Planck's quantization of waves and by Bohr's model of the hydrogen atom, Heisenberg founded his theory on the notion that the only allowed values of energy exchange between microphysical systems are those that are discrete: quanta. Expressing dynamical quantities such as energy, position, momentum and angular momentum in terms of matrices, he obtained an eigenvalue problem that describes the dynamics of microscopic systems; the diagonalization of the Hamiltonian matrix yields the energy spectrum and the state vectors of the system. Matrix mechanics was very successful in accounting for the discrete quanta of light emitted and absorbed by atoms.

The second formulation, called *wave mechanics*, was due to Schrödinger (1926); it is a generalization of the de Broglie postulate. This method, more intuitive than matrix mechanics, describes the dynamics of microscopic matter by means of a *wave equation*, called the *Schrödinger equation*; instead of the matrix eigenvalue problem of Heisenberg, Schrödinger obtained a differential equation. The solutions of this equation yield the energy spectrum and the wave function of the system under consideration. In 1927 Max Born proposed his *probabilistic* interpretation of wave mechanics: he took the square moduli of the wave functions that are solutions to the Schrödinger equation and he interpreted them as *probability densities*.

These two ostensibly different formulations—Schrödinger's *wave* formulation and Heisenberg's *matrix* approach—were shown to be equivalent. Dirac then suggested a more general formulation of quantum mechanics which deals with abstract objects such as kets (state vectors), bras, and operators. The representation of Dirac's formalism in a *continuous* basis—the position or momentum representations—gives back Schrödinger's wave mechanics. As for Heisenberg's matrix formulation, it can be obtained by representing Dirac's formalism in a *discrete* basis. In this context, the approaches of Schrödinger and Heisenberg represent, respectively, the *wave* formulation and the *matrix* formulation of the general theory of quantum mechanics.

Combining special relativity with quantum mechanics, Dirac derived in 1928 an equation which describes the motion of electrons. This equation, known as Dirac's equation, predicted the existence of an antiparticle, the positron, which has similar properties, but opposite charge, with the electron; the positron was discovered in 1932, four years after its prediction by quantum mechanics.

In summary, quantum mechanics is the theory that describes the dynamics of matter at the microscopic scale. Fine! But is it that important to learn? This is no less than an otiose question, for quantum mechanics is the *only* valid framework for describing the microphysical world. It is vital for understanding the physics of solids, lasers, semiconductor and superconductor

devices, plasmas, etc. In short, quantum mechanics is the founding basis of all modern physics: solid state, molecular, atomic, nuclear, and particle physics, optics, thermodynamics, statistical mechanics, and so on. Not only that, it is also considered to be the foundation of chemistry and biology.

1.2 Particle Aspect of Radiation

According to classical physics, a particle is characterized by an energy E and a momentum \vec{p} , whereas a wave is characterized by an amplitude and a wave vector \vec{k} ($|\vec{k}| = 2\pi/\lambda$) that specifies the direction of propagation of the wave. Particles and waves exhibit entirely different behaviors; for instance, the “particle” and “wave” properties are mutually exclusive. We should note that waves can exchange *any* (continuous) amount of energy with particles.

In this section we are going to see how these rigid concepts of classical physics led to its failure in explaining a number of microscopic phenomena such as blackbody radiation, the photoelectric effect, and the Compton effect. As it turned out, these phenomena could only be explained by abandoning the rigid concepts of classical physics and introducing a new concept: the *particle* aspect of radiation.

1.2.1 Blackbody Radiation

At issue here is how radiation interacts with matter. When heated, a solid object glows and emits thermal radiation. As the temperature increases, the object becomes red, then yellow, then white. The thermal radiation emitted by glowing solid objects consists of a *continuous* distribution of frequencies ranging from infrared to ultraviolet. The continuous pattern of the distribution spectrum is in sharp contrast to the radiation emitted by heated gases; the radiation emitted by gases has a discrete distribution spectrum: a few sharp (narrow), colored lines with no light (i.e., darkness) in between.

Understanding the continuous character of the radiation emitted by a glowing solid object constituted one of the major unsolved problems during the second half of the nineteenth century. All attempts to explain this phenomenon by means of the available theories of classical physics (statistical thermodynamics and classical electromagnetic theory) ended up in miserable failure. This problem consisted in essence of specifying the proper theory of thermodynamics that describes how energy gets exchanged between radiation and matter.

When radiation falls on an object, some of it might be absorbed and some reflected. An idealized “blackbody” is a material object that absorbs all of the radiation falling on it, and hence appears as black under reflection when illuminated from outside. When an object is heated, it radiates electromagnetic energy as a result of the thermal agitation of the electrons in its surface. The intensity of this radiation depends on its frequency and on the temperature; the light it emits ranges over the entire spectrum. An object in thermal equilibrium with its surroundings radiates as much energy as it absorbs. It thus follows that a blackbody is a perfect absorber as well as a perfect emitter of radiation.

A practical blackbody can be constructed by taking a hollow cavity whose internal walls perfectly reflect electromagnetic radiation (e.g., metallic walls) and which has a very small hole on its surface. Radiation that enters through the hole will be trapped inside the cavity and gets completely absorbed after successive reflections on the inner surfaces of the cavity. The

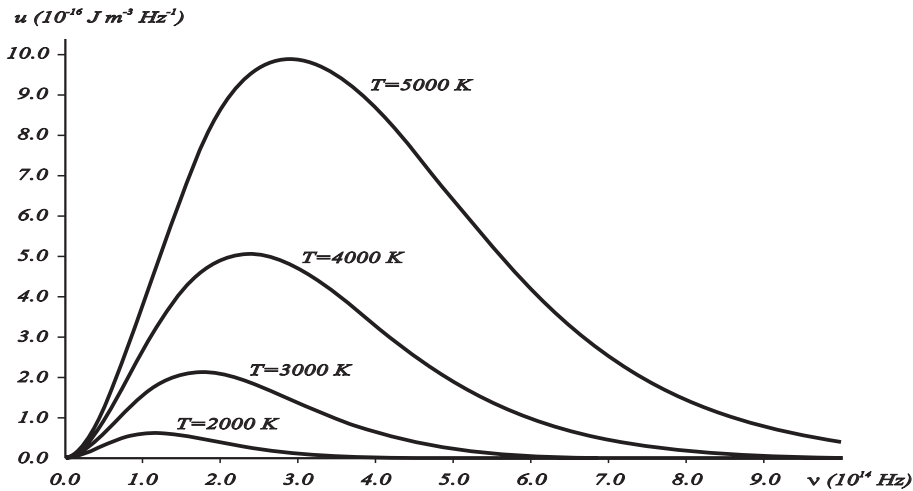


Figure 1.1 Spectral energy density $u(\nu, T)$ of blackbody radiation at different temperatures as a function of the frequency ν .

hole thus absorbs radiation like a black body. On the other hand, when this cavity is heated² to a temperature T , the radiation that leaves the hole is blackbody radiation, for the hole behaves as a perfect emitter; as the temperature increases, the hole will eventually begin to glow. To understand the radiation inside the cavity, one needs simply to analyze the spectral distribution of the radiation coming out of the hole. In what follows, the term *blackbody radiation* will then refer to the radiation leaving the hole of a heated hollow cavity; the radiation emitted by a blackbody when hot is called blackbody radiation.

By the mid-1800s, a wealth of experimental data about blackbody radiation was obtained for various objects. All these results show that, at equilibrium, the radiation emitted has a well-defined, continuous energy distribution: to each frequency there corresponds an energy density which depends neither on the chemical composition of the object nor on its shape, but only on the temperature of the cavity's walls (Figure 1.1). The energy density shows a pronounced maximum at a given frequency, which increases with temperature; that is, *the peak of the radiation spectrum occurs at a frequency that is proportional to the temperature* (1.16). This is the underlying reason behind the change in color of a heated object as its temperature increases, notably from red to yellow to white. It turned out that the explanation of the blackbody spectrum was not so easy.

A number of attempts aimed at explaining the origin of the continuous character of this radiation were carried out. The most serious among such attempts, and which made use of classical physics, were due to Wilhelm Wien in 1889 and Rayleigh in 1900. In 1879 J. Stefan found *experimentally* that the total intensity (or the total power per unit surface area) radiated by a glowing object of temperature T is given by

$$\mathcal{P} = a\sigma T^4, \quad (1.1)$$

which is known as the Stefan–Boltzmann law, where $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ is the

²When the walls are heated uniformly to a temperature T , they emit radiation (due to thermal agitation or vibrations of the electrons in the metallic walls).

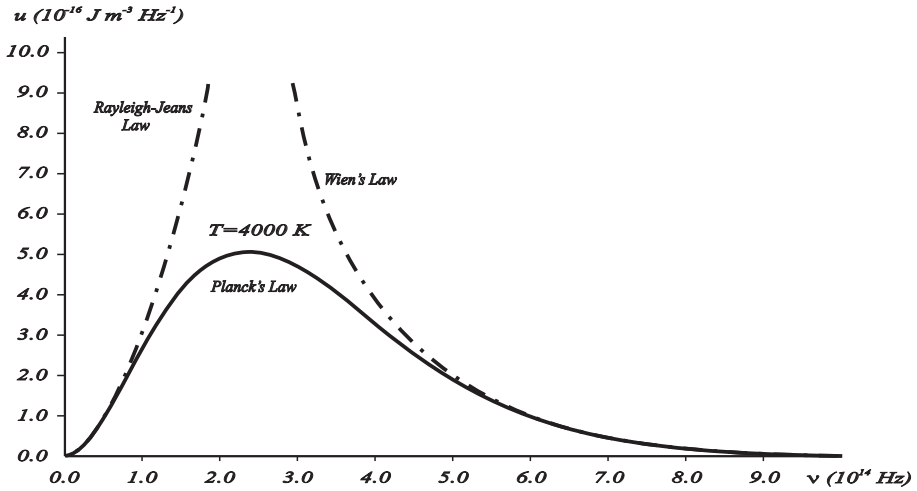


Figure 1.2 Comparison of various spectral densities: while the Planck and experimental distributions match perfectly (solid curve), the Rayleigh–Jeans and the Wien distributions (dotted curves) agree only partially with the experimental distribution.

Stefan–Boltzmann constant, and a is a coefficient which is less than or equal to 1; in the case of a blackbody $a = 1$. Then in 1884 Boltzmann provided a *theoretical* derivation for Stefan’s experimental law by combining thermodynamics and Maxwell’s theory of electromagnetism.

Wien’s energy density distribution

Using thermodynamic arguments, Wien took the Stefan–Boltzmann law (1.1) and in 1894 he extended it to obtain the energy density per unit frequency of the emitted blackbody radiation:

$$u(\nu, T) = A\nu^3 e^{-\beta\nu/T}, \quad (1.2)$$

where A and β are empirically defined parameters (they can be adjusted to fit the experimental data). **Note:** $u(\nu, T)$ has the dimensions of an energy per unit volume per unit frequency; its SI units are $\text{J m}^{-3} \text{Hz}^{-1}$. Although Wien’s formula fits the high-frequency data remarkably well, it fails badly at low frequencies (Figure 1.2).

Rayleigh’s energy density distribution

In his 1900 attempt, Rayleigh focused on understanding the nature of the electromagnetic radiation inside the cavity. He considered the radiation to consist of standing waves having a temperature T with nodes at the metallic surfaces. These standing waves, he argued, are equivalent to harmonic oscillators, for they result from the harmonic oscillations of a large number of electrical charges, electrons, that are present in the walls of the cavity. When the cavity is in thermal equilibrium, the electromagnetic energy density inside the cavity is equal to the energy density of the charged particles in the walls of the cavity; the average total energy of the radiation leaving the cavity can be obtained by multiplying the average energy of the oscillators by the number of modes (standing waves) of the radiation in the frequency interval ν to $\nu + d\nu$:

$$N(\nu) = \frac{8\pi\nu^2}{c^3}, \quad (1.3)$$

where $c = 3 \times 10^8 \text{ m s}^{-1}$ is the speed of light; the quantity $(8\pi\nu^2/c^3)d\nu$ gives the number of modes of oscillation per unit volume in the frequency range ν to $\nu + d\nu$. So the electromagnetic energy density in the frequency range ν to $\nu + d\nu$ is given by

$$u(\nu, T) = N(\nu)\langle E \rangle = \frac{8\pi\nu^2}{c^3}\langle E \rangle, \quad (1.4)$$

where $\langle E \rangle$ is the average energy of the oscillators present on the walls of the cavity (or of the electromagnetic radiation in that frequency interval); the temperature dependence of $u(\nu, T)$ is buried in $\langle E \rangle$.

How does one calculate $\langle E \rangle$? According to the equipartition theorem of classical thermodynamics, all oscillators in the cavity have the same mean energy, irrespective of their frequencies³:

$$\langle E \rangle = \frac{\int_0^\infty E e^{-E/kT} dE}{\int_0^\infty e^{-E/kT} dE} = kT, \quad (1.5)$$

where $k = 1.3807 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant. An insertion of (1.5) into (1.4) leads to the Rayleigh–Jeans formula:

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3}kT. \quad (1.6)$$

Except for low frequencies, this law is in complete disagreement with experimental data: $u(\nu, T)$ as given by (1.6) *diverges* for high values of ν , whereas experimentally it must be finite (Figure 1.2). Moreover, if we integrate (1.6) over all frequencies, the integral *diverges*. This implies that the cavity contains an *infinite* amount of energy. This result is absurd. Historically, this was called the *ultraviolet catastrophe*, for (1.6) *diverges* for *high* frequencies (i.e., in the *ultraviolet* range)—a real catastrophic failure of classical physics indeed! The origin of this failure can be traced to the derivation of the average energy (1.5). It was founded on an erroneous premise: the energy exchange between radiation and matter is *continuous*; any amount of energy can be exchanged.

Planck's energy density distribution

By devising an ingenious scheme—interpolation between Wien's rule and the Rayleigh–Jeans rule—Planck succeeded in 1900 in avoiding the ultraviolet catastrophe and proposed an accurate description of blackbody radiation. In sharp contrast to Rayleigh's assumption that a standing wave can exchange *any* amount (continuum) of energy with matter, Planck considered that the energy exchange between radiation and matter must be *discrete*. He then *postulated* that the energy of the radiation (of frequency ν) emitted by the oscillating charges (from the walls of the cavity) must come *only* in *integer multiples* of $h\nu$:

$$E = nh\nu, \quad n = 0, 1, 2, 3, \dots, \quad (1.7)$$

where h is a universal constant and $h\nu$ is the energy of a “*quantum*” of radiation (ν represents the frequency of the oscillating charge in the cavity's walls as well as the frequency of the radiation emitted from the walls, because the frequency of the radiation emitted by an oscillating charged particle is equal to the frequency of oscillation of the particle itself). That is, the energy of an oscillator of natural frequency ν (which corresponds to the energy of a charge

³Using a variable change $\beta = 1/(kT)$, we have $\langle E \rangle = -\frac{\partial}{\partial\beta} \ln \left(\int_0^\infty e^{-\beta E} dE \right) = -\frac{\partial}{\partial\beta} \ln(1/\beta) = 1/\beta \equiv kT$.

oscillating with a frequency ν) must be an *integral multiple* of $h\nu$; note that $h\nu$ is not the same for all oscillators, because it depends on the frequency of each oscillator. Classical mechanics, however, puts no restrictions whatsoever on the frequency, and hence on the energy, an oscillator can have. The energy of oscillators, such as pendulums, mass–spring systems, and electric oscillators, varies continuously in terms of the frequency. Equation (1.7) is known as *Planck’s quantization rule* for energy or *Planck’s postulate*.

So, assuming that the energy of an oscillator is quantized, Planck showed that the *correct* thermodynamic relation for the average energy can be obtained by merely replacing the integration of (1.5)—that corresponds to an energy continuum—by a *discrete* summation corresponding to the discreteness of the oscillators’ energies⁴:

$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} nh\nu e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}} = \frac{h\nu}{e^{h\nu/kT} - 1}, \quad (1.8)$$

and hence, by inserting (1.8) into (1.4), the energy density per unit frequency of the radiation emitted from the hole of a cavity is given by

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1}. \quad (1.9)$$

This is known as *Planck’s distribution*. It gives an exact fit to the various experimental radiation distributions, as displayed in Figure 1.2. The numerical value of h obtained by fitting (1.9) with the experimental data is $h = 6.626 \times 10^{-34}$ J s. We should note that, as shown in (1.12), we can rewrite Planck’s energy density (1.9) to obtain the energy density per unit wavelength

$$\tilde{u}(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}. \quad (1.10)$$

Let us now look at the behavior of Planck’s distribution (1.9) in the limits of both low and high frequencies, and then try to establish its connection to the relations of Rayleigh–Jeans, Stefan–Boltzmann, and Wien. First, in the case of very low frequencies $h\nu \ll kT$, we can show that (1.9) reduces to the Rayleigh–Jeans law (1.6), since $\exp(h\nu/kT) \simeq 1 + h\nu/kT$. Moreover, if we integrate Planck’s distribution (1.9) over the whole spectrum (where we use a change of variable $x = h\nu/kT$ and make use of a special integral⁵), we obtain the total energy density which is expressed in terms of Stefan–Boltzmann’s total power per unit surface area (1.1) as follows:

$$\int_0^{\infty} u(\nu, T) d\nu = \frac{8\pi h}{c^3} \int_0^{\infty} \frac{\nu^3}{e^{h\nu/kT} - 1} d\nu = \frac{8\pi k^4 T^4}{h^3 c^3} \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{8\pi^5 k^4}{15 h^3 c^3} T^4 = \frac{4}{c} \sigma T^4, \quad (1.11)$$

where $\sigma = 2\pi^5 k^4 / 15 h^3 c^2 = 5.67 \times 10^{-8}$ W m⁻² K⁻⁴ is the Stefan–Boltzmann constant. In this way, Planck’s relation (1.9) leads to a *finite* total energy density of the radiation emitted from a blackbody, and hence avoids the ultraviolet catastrophe. Second, in the limit of *high* frequencies, we can easily ascertain that Planck’s distribution (1.9) yields Wien’s rule (1.2).

In summary, the spectrum of the blackbody radiation reveals the quantization of radiation, notably the particle behavior of electromagnetic waves.

⁴To derive (1.8) one needs: $1/(1-x) = \sum_{n=0}^{\infty} x^n$ and $x/(1-x)^2 = \sum_{n=0}^{\infty} nx^n$ with $x = e^{-h\nu/kT}$.

⁵In integrating (1.11), we need to make use of this integral: $\int_0^{+\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$.

The introduction of the constant h had indeed heralded the end of classical physics and the dawn of a new era: physics of the microphysical world. Stimulated by the success of Planck's quantization of radiation, other physicists, notably Einstein, Compton, de Broglie, and Bohr, skillfully adapted it to explain a host of other outstanding problems that had been unanswered for decades.

Example 1.1 (Wien's displacement law)

(a) Show that the maximum of the Planck energy density (1.9) occurs for a wavelength of the form $\lambda_{max} = b/T$, where T is the temperature and b is a constant that needs to be estimated.

(b) Use the relation derived in (a) to estimate the surface temperature of a star if the radiation it emits has a maximum intensity at a wavelength of 446 nm. What is the intensity radiated by the star?

(c) Estimate the wavelength and the intensity of the radiation emitted by a glowing tungsten filament whose surface temperature is 3300 K.

Solution

(a) Since $\nu = c/\lambda$, we have $d\nu = |d\nu/(d\lambda)| d\lambda = (c/\lambda^2)d\lambda$; we can thus write Planck's energy density (1.9) in terms of the wavelength as follows:

$$\tilde{u}(\lambda, T) = u(\nu, T) \left| \frac{d\nu}{d\lambda} \right| = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}. \quad (1.12)$$

The maximum of $\tilde{u}(\lambda, T)$ corresponds to $\partial\tilde{u}(\lambda, T)/\partial\lambda = 0$, which yields

$$\frac{8\pi hc}{\lambda^6} \left[-5 \left(1 - e^{-hc/\lambda kT} \right) + \frac{hc}{\lambda kT} \right] \frac{e^{hc/\lambda kT}}{(e^{hc/\lambda kT} - 1)^2} = 0, \quad (1.13)$$

and hence

$$\frac{\alpha}{\lambda} = 5 \left(1 - e^{-\alpha/\lambda} \right), \quad (1.14)$$

where $\alpha = hc/(kT)$. We can solve this transcendental equation either graphically or numerically by writing $\alpha/\lambda = 5 - \varepsilon$. Inserting this value into (1.14), we obtain $5 - \varepsilon = 5 - 5e^{-5+\varepsilon}$, which leads to a suggestive approximate solution $\varepsilon \approx 5e^{-5} = 0.0337$ and hence $\alpha/\lambda = 5 - 0.0337 = 4.9663$. Since $\alpha = hc/(kT)$ and using the values $h = 6.626 \times 10^{-34}$ J s and $k = 1.3807 \times 10^{-23}$ J K⁻¹, we can write the wavelength that corresponds to the maximum of the Planck energy density (1.9) as follows:

$$\lambda_{max} = \frac{hc}{4.9663k} \frac{1}{T} = \frac{2898.9 \times 10^{-6} \text{ m K}}{T}. \quad (1.15)$$

This relation, which shows that λ_{max} decreases with increasing temperature of the body, is called *Wien's displacement law*. It can be used to determine the wavelength corresponding to the maximum intensity if the temperature of the body is known or, conversely, to determine the temperature of the radiating body if the wavelength of greatest intensity is known. This law can be used, in particular, to estimate the temperature of stars (or of glowing objects) from their radiation, as shown in part (b). From (1.15) we obtain

$$\nu_{max} = \frac{c}{\lambda_{max}} = \frac{4.9663}{h} kT. \quad (1.16)$$

This relation shows that the peak of the radiation spectrum occurs at a frequency that is proportional to the temperature.

(b) If the radiation emitted by the star has a maximum intensity at a wavelength of $\lambda_{max} = 446 \text{ nm}$, its surface temperature is given by

$$T = \frac{2898.9 \times 10^{-6} \text{ m K}}{446 \times 10^{-9} \text{ m}} \simeq 6500 \text{ K}. \quad (1.17)$$

Using Stefan–Boltzmann’s law (1.1), and assuming the star to radiate like a blackbody, we can estimate the total power per unit surface area emitted at the surface of the star:

$$\mathcal{P} = \sigma T^4 = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \times (6500 \text{ K})^4 \simeq 101.2 \times 10^6 \text{ W m}^{-2}. \quad (1.18)$$

This is an enormous intensity which will decrease as it spreads over space.

(c) The wavelength of greatest intensity of the radiation emitted by a glowing tungsten filament of temperature 3300 K is

$$\lambda_{max} = \frac{2898.9 \times 10^{-6} \text{ m K}}{3300 \text{ K}} \simeq 878.45 \text{ nm}. \quad (1.19)$$

The intensity (or total power per unit surface area) radiated by the filament is given by

$$\mathcal{P} = \sigma T^4 = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \times (3300 \text{ K})^4 \simeq 6.7 \times 10^6 \text{ W m}^{-2}. \quad (1.20)$$

1.2.2 Photoelectric Effect

The photoelectric effect provides a direct confirmation for the energy quantization of light. In 1887 Hertz discovered the photoelectric effect: electrons⁶ were observed to be ejected from metals when irradiated with light (Figure 1.3a). Moreover, the following experimental laws were discovered prior to 1905:

- If the frequency of the incident radiation is smaller than the metal’s threshold frequency—a frequency that depends on the properties of the metal—no electron can be emitted regardless of the radiation’s intensity (Philip Lenard, 1902).
- No matter how low the intensity of the incident radiation, electrons will be ejected *instantly* the moment the frequency of the radiation exceeds the threshold frequency ν_0 .
- At any frequency above ν_0 , the number of electrons ejected increases with the intensity of the light but does not depend on the light’s frequency.
- The kinetic energy of the ejected electrons depends on the frequency but not on the intensity of the beam; the kinetic energy of the ejected electron increases *linearly* with the incident frequency.

⁶In 1899 J. J. Thomson confirmed that the particles giving rise to the photoelectric effect (i.e., the particles ejected from the metals) are electrons.

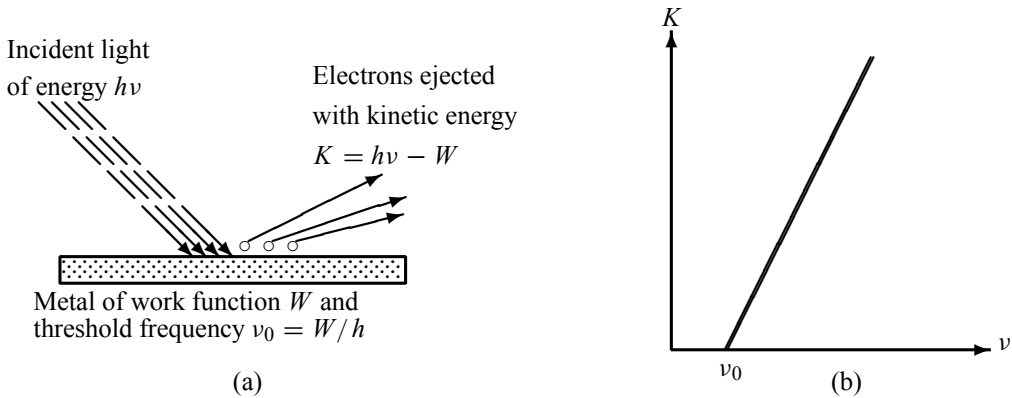


Figure 1.3 (a) Photoelectric effect: when a metal is irradiated with light, electrons may get emitted. (b) Kinetic energy K of the electron leaving the metal when irradiated with a light of frequency ν ; when $\nu < \nu_0$ no electron is ejected from the metal regardless of the intensity of the radiation.

These experimental findings cannot be explained within the context of a purely classical picture of radiation, notably the dependence of the effect on the threshold frequency. According to classical physics, any (continuous) amount of energy can be exchanged with matter. That is, since the intensity of an electromagnetic wave is proportional to the square of its amplitude, *any frequency* with sufficient intensity can supply the necessary energy to free the electron from the metal.

But what would happen when using a *weak* light source? According to classical physics, an electron would keep on absorbing energy—at a *continuous rate*—until it gained a sufficient amount; then it would leave the metal. If this argument is to hold, then when using very weak radiation, the photoelectric effect would not take place for a long time, possibly hours, until an electron gradually accumulated the necessary amount of energy. This conclusion, however, disagrees utterly with experimental observation. Experiments were conducted with a light source that was so weak it would have taken several hours for an electron to accumulate the energy needed for its ejection, and yet some electrons were observed to leave the metal *instantly*. Further experiments showed that an increase in intensity (brightness) alone can in no way dislodge electrons from the metal. But by increasing the frequency of the incident radiation beyond a certain threshold, even at very weak intensity, the emission of electrons starts immediately. These experimental facts indicate that the concept of gradual accumulation, or continuous absorption, of energy by the electron, as predicated by classical physics, is indeed erroneous.

Inspired by Planck's quantization of electromagnetic radiation, Einstein succeeded in 1905 in giving a theoretical explanation for the dependence of photoelectric emission on the frequency of the incident radiation. He assumed that light is made of corpuscles each carrying an energy $h\nu$, called *photons*. When a beam of light of frequency ν is incident on a metal, each photon transmits all its energy $h\nu$ to an electron near the surface; in the process, the photon is entirely absorbed by the electron. The electron will thus absorb energy *only* in quanta of energy $h\nu$, irrespective of the intensity of the incident radiation. If $h\nu$ is larger than the metal's *work function* W —the energy required to dislodge the electron from the metal (every metal has free electrons that move from one atom to another; the minimum energy required to free the electron

from the metal is called the work function of that metal)—the electron will then be knocked out of the metal. Hence no electron can be emitted from the metal's surface unless $h\nu > W$:

$$\boxed{h\nu = W + K}, \quad (1.21)$$

where K represents the kinetic energy of the electron leaving the material.

Equation (1.21), which was derived by Einstein, gives the proper explanation to the experimental observation that the kinetic energy of the ejected electron *increases linearly* with the incident frequency ν , as shown in Figure 1.3b:

$$K = h\nu - W = h(\nu - \nu_0), \quad (1.22)$$

where $\nu_0 = W/h$ is called the threshold or cutoff frequency of the metal. Moreover, this relation shows clearly why no electron can be ejected from the metal unless $\nu > \nu_0$: since the kinetic energy cannot be negative, the photoelectric effect cannot occur when $\nu < \nu_0$ regardless of the intensity of the radiation. The ejected electrons acquire their kinetic energy from the excess energy $h(\nu - \nu_0)$ supplied by the incident radiation.

The kinetic energy of the emitted electrons can be experimentally determined as follows. The setup, which was devised by Lenard, consists of the photoelectric metal (cathode) that is placed next to an anode inside an evacuated glass tube. When light strikes the cathode's surface, the electrons ejected will be attracted to the anode, thereby generating a photoelectric current. It was found that *the magnitude of the photoelectric current thus generated is proportional to the intensity of the incident radiation, yet the speed of the electrons does not depend on the radiation's intensity, but on its frequency*. To measure the kinetic energy of the electrons, we simply need to use a varying voltage source and reverse the terminals. When the potential V across the tube is reversed, the liberated electrons will be prevented from reaching the anode; only those electrons with kinetic energy larger than $e|V|$ will make it to the negative plate and contribute to the current. We vary V until it reaches a value V_s , called the *stopping potential*, at which all of the electrons, even the most energetic ones, will be turned back before reaching the collector; hence the flow of photoelectric current ceases completely. The stopping potential V_s is connected to the electrons' kinetic energy by $e|V_s| = \frac{1}{2}m_e v^2 = K$ (in what follows, V_s will implicitly denote $|V_s|$). Thus, the relation (1.22) becomes $eV_s = h\nu - W$ or

$$\boxed{V_s = \frac{h}{e}\nu - \frac{W}{e} = \frac{hc}{e\lambda} - \frac{W}{e}}. \quad (1.23)$$

The shape of the plot of V_s against frequency is a straight line, much like Figure 1.3b with the slope now given by h/e . This shows that the stopping potential depends linearly on the frequency of the incident radiation.

It was Millikan who, in 1916, gave a systematic experimental confirmation to Einstein's photoelectric theory. He produced an extensive collection of photoelectric data using various metals. He verified that Einstein's relation (1.23) reproduced his data exactly. In addition, Millikan found that his empirical value for h , which he obtained by measuring the slope h/e of (1.23) (Figure 1.3b), is equal to Planck's constant to within a 0.5% experimental error.

In summary, the photoelectric effect does provide compelling evidence for the corpuscular nature of the electromagnetic radiation.
