

PRINCIPLES OF  
*Quantum Mechanics*

Hans C. Ohanian



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## Preface

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**THIS BOOK** is an introduction to the theory of quantum mechanics for advanced undergraduate students. I assume that the student has had some contact with quantum physics and with elementary wave mechanics. Since the first three chapters review the experimental foundations of quantum physics and deal with simple applications of the Schrödinger wave equation, previous contact is not absolutely necessary, but it is certainly helpful.

In their first contact with the quantum-mechanical wavefunction and the Schrödinger wave equation, students often become infected with the misconception that these are the essence of quantum mechanics—if you understand the wavefunction and the Schrödinger wave equation and its solution by separation of variables, you understand everything. To suppress this misconception, I have deliberately placed the wavefunction and the Schrödinger wave equation in a subordinate role, as merely one special representation of the kinematics and the dynamics of a quantum-mechanical system. In this, I adhere to the tradition laid down by Dirac in his great book, *The Principles of Quantum Mechanics*, which is now more than fifty years old, but nevertheless retains its freshness, and still repays close study. Following Dirac, I emphasize the abstract formulation of quantum mechanics in terms of state vectors and operators, and I employ operator techniques for the solution of eigenvalue problems. In most undergraduate textbooks, operator techniques are reserved for the harmonic oscillator and for the treatment of angular momentum, which can be conveniently handled by raising and lowering operators. But, as was shown by Schrödinger in the 1940s, suitable raising and lowering operators can be constructed for all the familiar eigenvalue problems usually solved by separation of variables with the wave equa-

tion. I have adopted Schrödinger's factorization method, expanding his discussions to make them accessible to undergraduates. To some extent, my presentation of the factorization method imitates that by H. S. Green.\*

My book developed out of successive editions of lecture notes I produced for my classes at Rensselaer Polytechnic Institute over several years. I am indebted to the students for their enthusiasm and patience. And I owe a long-standing debt to Professor Frank S. Crawford, whose lectures many years ago, when I was an undergraduate at Berkeley, first gave me an appreciation for the power of operator methods.

H. C. O.

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\*H. S. Green, *Matrix Methods in Quantum Mechanics* (Barnes & Noble, New York, 1965).

# *Contents*

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## **1. *The Origins of Quantum Mechanics* 1**

- 1.1 Early Quantum Theory 2
- 1.2 Wave Mechanics 6
- 1.3 Matrix Mechanics 9
- 1.4 Particle vs. Wave; the Uncertainty Relations 11
- Problems 17

## **2. *The Free Particle in Wave Mechanics* 21**

- 2.1 The Wave Equation 21
- 2.2 Fourier Analysis 26
- 2.3 Solution of the Free-Particle Wave Equation 32
- 2.4 Wave Packets 36
- 2.5 The Gaussian Wave Packet 39
- 2.6 Expectation Values 42
- 2.7 Momentum and Position as Operators 43
- 2.8 Measurement in Quantum Mechanics 50
- Problems 53

## **3. *Particles in Potentials* 58**

- 3.1 The Schrödinger Equation with Potential; Stationary States 58
- 3.2 The Infinite Square Well 63
- 3.3 The Energy Representation 71
- 3.4 The Finite Square Well 78
- 3.5 Barrier Penetration 84
- Problems 91



- 4. Axiomatic Formulation of Quantum Mechanics 97**
  - 4.1 Vector Spaces 97
  - 4.2 The Axioms of Quantum Mechanics 100
  - 4.3 Operators and Eigenvectors 104
  - 4.4 Compatible Observables 116
  - 4.5 The Uncertainty Relations 120
    - Problems 121
  
- 5. The Evolution of States in Time 125**
  - 5.1 The Hamiltonian Operator 126
  - 5.2 Ehrenfest's Equations 132
  - 5.3 The Energy-Time "Uncertainty Relation" 133
  - 5.4 Representations of State Vectors and Their Transformation 139
    - Problems 147
  
- 6. The Factorization Method 150**
  - 6.1 The Harmonic Oscillator 151
  - 6.2 Eigenvectors and Eigenvalues of a General Hamiltonian 162
  - 6.3 Normalization of the Eigenvectors 172
  - 6.4 Power-Series Solution of the Schrödinger Equation 173
    - Problems 177
  
- 7. The Particle in Three Dimensions and Angular Momentum 181**
  - 7.1 The Free Particle 182
  - 7.2 Angular Momentum 184
  - 7.3 Parity 201
  - 7.4 The Kinetic Energy 206
    - Problems 210
  
- 8. Central Potentials 214**
  - 8.1 The Isotropic Harmonic Oscillator 214
  - 8.2 The Hydrogen Atom 220

- 8.3 The Free Particle 234
- Problems 239

## 9. *Spin and the Exclusion Principle* 243

- 9.1 The Spin of the Electron 245
- 9.2 The Magnetic Moment 252
- 9.3 Addition of Angular Momenta 256
- 9.4 Fermions and Bosons; the Exclusion Principle 263
- Problems 268

## 10. *Perturbation Theory* 272

- 10.1 Time-Independent Perturbations 272
- 10.2 Degenerate Perturbations 281
- 10.3 Time-Dependent Perturbations 285
- 10.4 Transitions to the Continuum 290
- 10.5 The Density of States 293
- 10.6 The Photoelectric Effect 294
- Problems 299

## 11. *Scattering and Resonances* 305

- 11.1 Elastic Scattering in One Dimension 305
- 11.2 Scattering by a Square Well 311
- 11.3 Resonances 319
- 11.4 Elastic Scattering in Three Dimensions 328
- 11.5 Partial Waves in a Central Potential; the Optical Theorem 331
- 11.6 The Born Approximation; Rutherford Scattering 335
- Problems 338

## 12. *The Interpretation of Quantum Mechanics* 342

- 12.1 The Copenhagen Interpretation 343
- 12.2 Measurement and the Collapse of the Wavefunction 350
- 12.3 Alternative Interpretations of the Collapse 358
- 12.4 The Einstein-Podolsky-Rosen Paradox 368
- 12.5 Bell's Theorem 373
- Problems 381



***Appendices***

1. Fundamental Constants 385
2. Clebsch–Gordan Coefficients 387
3. Bibliography 389
4. Answers to Odd-Numbered Problems 397

***Index*** 403

# 1

## *The Origins of Quantum Mechanics*

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Quantum mechanics lies at the root of all of the physics of today. It attained this fundamental place early this century, when it supplanted classical mechanics. Quantum mechanics has proved extremely successful in describing the behavior of the world of matter, and it is likely to retain its fundamental place in physics for a long time to come. However, quantum mechanics has some serious deficiencies in that it leads to unacceptable infinite results in some calculations of interactions of particles. Although physicists have devised divers tricks for bypassing or hiding these infinities, it is possible that some radical revision of quantum mechanics will ultimately become inevitable. One speculative suggestion for such a revision is the superstring theory now being investigated by physicists.

In this book we will deal only with nonrelativistic quantum mechanics, and we will concentrate on systems consisting of a single particle interacting with a potential. The relativistic quantum theory of systems of several interacting particles is quite complicated, because the interactions can create and destroy particles. Hence the number of particles in the system is not fixed, and it becomes necessary to consider concurrently a large ensemble of systems with different numbers of particles. The treatment of systems with a variable number of particles requires special mathematical techniques ("second" quantization).

This first chapter is a historical sketch of the origins of quantum mechanics. Full explanations of the concepts and formulas mentioned here are reserved for later chapters.

## 1.1 Early Quantum Theory

Quantum theory began in 1900 with Planck's postulate of the quantization of energy in blackbody radiation, or cavity radiation (the genealogical chart inside the front cover gives a summary of the historical development of quantum physics). Planck's theory of the blackbody spectrum was the culmination of many years of intensive efforts by experimental and theoretical physicists. It had been known for some time that the spectrum of thermal radiation contained in a cavity in thermal equilibrium must be a universal function of the temperature, completely independent of the material of the walls of the cavity. By 1900, detailed measurements by Rubens, Kurlbaum, Lummer, and Pringsheim had determined the shape of the spectrum, and Planck was able to make a clever guess at an empirical formula representing this spectrum. However, he was unable to provide a theoretical derivation of this formula within the context of classical physics. For low frequencies, the spectrum actually did agree with the prediction of classical physics; but for high frequencies, classical physics predicted a monotonic increase of the spectral energy density, whereas the measured energy density decreased toward zero (see Fig. 1.1).

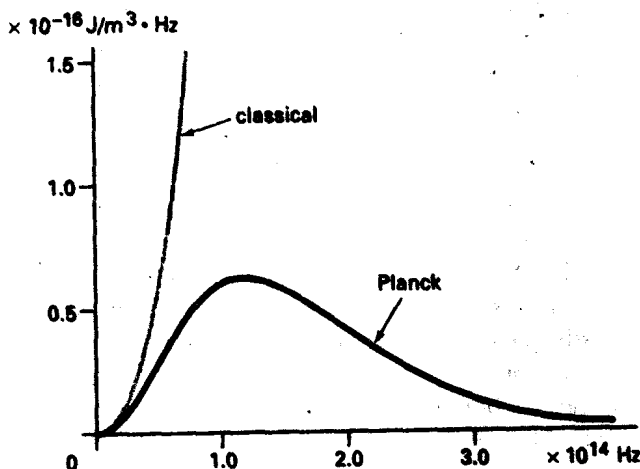


Fig. 1.1 Spectral distribution of the energy density as a function of frequency for the thermal radiation in a cavity at 2000 K. The spectral distribution plotted here is the energy per unit volume and per unit frequency interval. The classical prediction, shown in gray, is based on the equipartition theorem, according to which each mode of electromagnetic oscillation in the cavity should have an average energy  $kT$ .

Planck finally found that he could derive his empirical formula from a postulate of quantization of energy. He adopted a simple model for the walls of the cavity: the walls consist of a large number of electrically charged harmonic oscillators of all possible frequencies (since the final result is independent of the material of the walls, he was free to adopt any convenient model). The oscillators exchange energy with the radiation in the cavity, and hence, at thermal equilibrium, the energy distribution of the radiation matches the energy distribution of the oscillators. Planck postulated that the energy of an oscillator of frequency  $\nu$  could only assume one or another of the values

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

where  $h$  is a universal constant of proportionality, later called Planck's constant. From this quantization condition, Planck derived the thermal energy distribution of the oscillators and of the radiation. Qualitatively, we can understand how the quantization condition leads to a decrease of the spectral energy at high frequencies ( $h\nu \gg kT$ ); the energy quantum  $h\nu$  is then so large that the typical thermal energy  $kT$  is insufficient to provide the minimum energy  $h\nu$  required to excite the oscillator from the ground state  $E = 0$  to the first excited state  $E = h\nu$ ; thus, the oscillator is likely to remain quiescent, and it then does not emit radiation of this frequency into the cavity.

Although Planck quantized the oscillators in the walls of the cavity, he treated the electromagnetic radiation in the cavity as completely smooth and continuous, according to classical electromagnetic theory, that is, according to Maxwell's equations. A few years later, Einstein took quantization a step further by proposing that the electromagnetic radiation exists in the form of packets of energy  $h\nu$ , which came to be called photons. This meant he could view the radiation as a gas of photons. With this picture of the radiation, Einstein could apply statistical mechanics to investigate the behavior of the photon gas at thermal equilibrium, and he was able to supply an alternative derivation of Planck's formula.

Einstein further exploited the concept of photons to explain the puzzling features of the photoelectric effect. Measurements by Hertz, Lenard, and others had shown that when light strikes the surface of a metal, it ejects electrons, or photoelectrons, with an energy that depends on the frequency of the light, but not on its intensity. This contradicts classical electromagnetic theory, according to which the energy available in the light is proportional to

the intensity, and does not depend at all on the frequency. But if light consists of a stream of photons of energy  $h\nu$ , then the maximum energy that an electron in the metal can absorb in a collision with a photon is  $h\nu$ . Of this maximum energy, the electron must give up some fixed amount  $e\phi$  to escape from the metal, where  $\phi$  is a characteristic amount of energy per unit charge, called the work function of the metal. The final maximum kinetic energy of an ejected photoelectron is then

$$K_{\max} = h\nu - e\phi \quad (2)$$

This equation for the energy of the photoelectrons was later verified in detail by Millikan in a series of meticulous experiments.

The photoelectric effect confirmed that the energy in light is packaged in discrete amounts  $h\nu$ . The Compton effect, discovered by Compton in 1922, established that the momentum in light is also packaged in discrete amounts. In an experimental investigation of the scattering of a beam of X rays by a carbon target, Compton noticed that the X rays deflected by large angles always emerged with increased wavelengths. He was able to explain this wavelength shift by assuming that the X-ray photons have not only an energy  $h\nu$ , but also a momentum  $h\nu/c$ . When such a photon collides with an electron, it suffers a loss of energy (and an increase of wavelength) that depends on the angle of deflection.

Einstein also applied quantization to the calculation of the specific heat of solids. Each atom or molecule in a crystalline solid can be regarded as held in its place by springs, and hence each atom or molecule is a three-dimensional harmonic oscillator. According to the equipartition theorem of classical statistical mechanics, at thermal equilibrium each such oscillator should have an average energy of  $3kT$ . But this prediction is contradicted by the measured values of the specific heat, which are found to be much less than  $3kT$  at low temperatures. Einstein explained the dependence of the specific heat on temperature by appealing to the quantization condition (1). Qualitatively, if the temperature is low ( $kT \ll h\nu$ ), the typical thermal disturbances are insufficient to excite oscillations, and the atoms fail to acquire thermal energy.

In 1913, Bohr extended the quantization of energy to the hydrogen atom, with spectacular success. From the experiments on the scattering of alpha particles by atoms, Rutherford had deduced that the atom must consist of a very small, very massive nucleus around which orbit the electrons. But this nuclear model of the atom was in conflict with classical electrodynamics, since an orbit-

ing, accelerated electron should radiate and quickly lose all its orbital energy. Bohr had no explanation for why orbiting electrons do not radiate; but he blithely postulated that they did not. He postulated that the electrons are locked in certain preferred stationary states, with circular orbits, and that they emit radiation only when they make transitions from one stationary state to another. The possible stationary states are characterized by quantized values of the orbital angular momentum:

$$L = \frac{nh}{2\pi} = n\hbar \quad (3)$$

This quantization of angular momentum leads to the quantization of the orbital energy of the hydrogen atom:

$$E_n = -\frac{1}{(4\pi\epsilon_0)^2} \frac{m_e e^4}{2\hbar^2 n^2} \quad (4)$$

In a transition from one stationary state to another, the atom emits a single photon of an energy equal to the difference between the orbital energies. For instance, in the transition from the first excited state (of energy  $E_2$ ) to the ground state (of energy  $E_1$ ), the energy of the emitted photon is  $h\nu = E_2 - E_1$ , and the frequency of the emitted spectral line is

$$\nu = \frac{E_2 - E_1}{h} \quad (5)$$

This result for the frequency is in accord with the combination principle, discovered empirically by Rydberg and Ritz, which states that the frequencies of the spectral lines of the atoms can be expressed as differences between terms, taken two at a time.

An experiment performed by Franck and Hertz provided direct evidence for energy quantization in atoms. In this experiment, the atoms in mercury vapor were subjected to collisions with low-energy electrons. Franck and Hertz found that if the electron energy was below 4.9 eV, all the collisions were elastic; the incident electrons did not have enough energy to excite the atoms from the ground state to the first excited state, and they therefore merely bounced off the atoms without any loss of energy. But if the electron energy was above 4.9 eV, some of the incident electrons would give up 4.9 eV to excite the atoms, and the excited atoms would subsequently reradiate this energy in the form of ultraviolet light.

In his simple theory of the hydrogen atom, Bohr had considered only circular orbits. Sommerfeld and, independently, Wilson generalized Bohr's quantization rule for angular momentum to elliptical orbits and to any kind of periodic motion. The general Sommerfeld–Wilson quantization rule states that

$$\int p \, dq = n\hbar \quad (6)$$

where  $q$  and  $p$  are the canonical coordinate and momentum for the motion, respectively.

## 1.2 Wave Mechanics

The early, or “old,” quantum theory relied heavily on classical mechanics, but sought to supplement Newton's law with extra quantization conditions for the selection of the preferred stationary states. Roughly, we can say that the old quantum theory accepted Newtonian kinematics, but sought to modify Newtonian dynamics with supplementary conditions. In the 1920s, physicists finally recognized that this attempt to graft a quantum structure on the Newtonian roots was unworkable, and they recognized that both Newtonian kinematics and dynamics had to be discarded.

The first step toward the new quantum mechanics was de Broglie's conjecture that electrons and other “particles” have wave properties. De Broglie was led to this conjecture by a formal analogy between geometrical optics and mechanics. He noticed that the equations determining the rays of geometrical optics are analogous to the equations determining the trajectories of particles in classical mechanics. Since geometrical optics is the limiting case of wave optics, he conjectured that classical mechanics is the limiting case of some wave motion. De Broglie postulated that the frequency of the wave associated with a particle is related to the energy of the particle by the same equation as for the light wave associated with a photon:

$$\nu = \frac{E}{h} \quad (7)$$

He then exploited the relativistic connection between energy and momentum and frequency and wavelength to deduce that the wavelength of the wave must be related to the momentum of the particle:

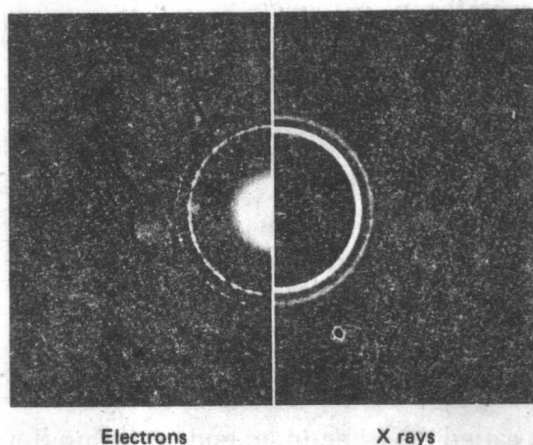
$$\lambda = \frac{h}{p} \quad (8)$$



This is the de Broglie relation. Thus, for the wave associated with a particle moving in the  $x$  direction, de Broglie proposed the harmonic wavefunction<sup>1</sup>

$$\psi = \sin 2\pi \left( \nu t - \frac{x}{\lambda} \right) = \sin \frac{2\pi}{h} (Et - px) \quad (9)$$

He suggested that the wave properties of particles could be confirmed experimentally by the observation of diffraction effects when electrons are incident on crystals. In fact, some data on scattering of electrons by crystals were already available, and Elsasser and Franck recognized diffraction peaks in these data. However, their interpretation was not widely accepted until Davisson and Germer did further detailed experiments with crystals. At about the same time, Thomson succeeded in demonstrating electron diffraction in scattering experiments with thin films of metals. Figure 1.2 shows such a diffraction pattern produced by electrons that have passed through a thin film of aluminum consisting of very many crystallites oriented at random. Additional evidence for the



**Fig. 1.2** This composite photograph strikingly demonstrates the similarity of the diffraction patterns produced by X rays and by electrons upon passage through a thin film of aluminum. The X rays were registered on a photographic plate placed beyond the film of aluminum; the electrons were registered by a fluorescent screen, similar to a television screen. (*Project Physics*, 1975; Holt, Rinehart, Winston, and Education Development Center, Inc., Newton, MA)

<sup>1</sup> The phase velocity of this wave is  $\lambda\nu = E/p$ ; it does not coincide with the velocity of the particle. The group velocity is  $dE/dp$ ; this coincides with the velocity of the particle (phase and group velocities will be discussed in Chapter 2).

wave properties of electrons was provided by the experiments of Rupp, who found that electrons obliquely incident on an optical grating give rise to the familiar multiple-slit interference pattern.

The diffraction and interference patterns observed in these experiments not only established that electrons have wave properties, but also that the waves obey the superposition principle: when waves from two or more sources—such as two or more slits—arrive at some point simultaneously, the net wave amplitude is the sum of the individual wave amplitudes.

Meanwhile, Schrödinger formulated the wave equation obeyed by the de Broglie waves, and he demonstrated that the quantization conditions emerge from the solution of the eigenvalue problem for this wave equation. Schrödinger obtained his wave equation by taking as starting point the standard classical wave equation

$$\frac{\partial^2}{\partial x^2} \psi(x, t) - \frac{1}{u^2} \frac{\partial^2}{\partial t^2} \psi(x, t) = 0 \quad (10)$$

Here,  $u$  is the phase velocity,  $u = \lambda\nu = h\nu/p$ . For a particle of energy  $E$  moving in a potential  $V(x)$ , the momentum is  $p = \sqrt{2m[E - V(x)]}$ , and the phase velocity is  $u = h\nu/\sqrt{2m[E - V(x)]}$ , so

$$\frac{\partial^2}{\partial x^2} \psi(x, t) - \frac{2m[E - V(x)]}{h^2} \frac{1}{\nu^2} \frac{\partial^2}{\partial t^2} \psi(x, t) = 0 \quad (11)$$

Since the frequency of the wave is  $\nu$ , the second time derivative of  $\psi(x, t)$  is  $-(2\pi\nu)^2 \psi(x, t)$ , and Eq. (11) reduces to

$$\frac{\partial^2}{\partial x^2} \psi(x, t) + \frac{2m[E - V(x)]}{h^2} \psi(x, t) = 0 \quad (12)$$

This is called the (time-independent) Schrödinger wave equation.

Note that Eqs. (9) and (10) are actually wrong—we will see in the next chapter that the wavefunction  $\psi$  is a *complex* function, not a real function; and the time-dependent Schrödinger equation involves the *first* derivative with respect to time, not the second derivative. Nevertheless, Schrödinger's approximate argument led him to the correct equation (12). He applied this equation or, rather, its three-dimensional version to the hydrogen atom, and he found that both the quantization of angular momentum and the quantization of energy emerge from the equation. In essence, the Schrödinger equation yields a discrete set of possible energies