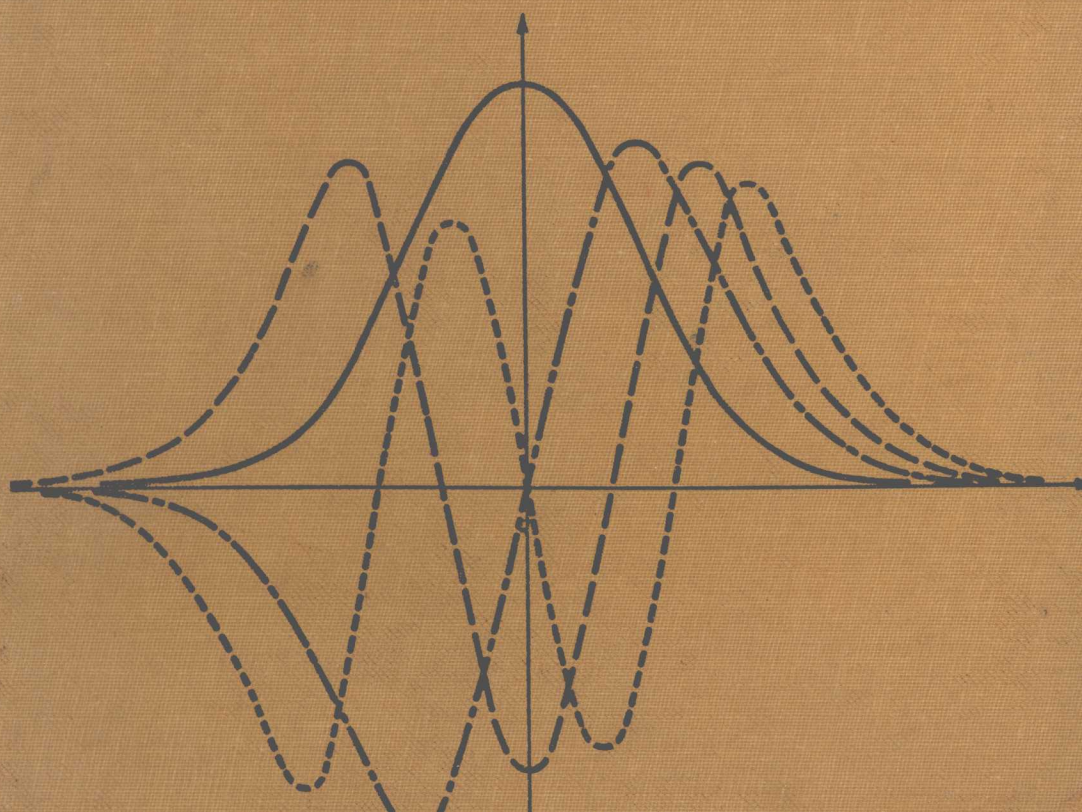


# introduction to wave mechanics



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## preface

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The purpose of this book is to present within the scope of a one-semester course most of the principles of nonrelativistic wave mechanics, together with examples illustrating the applications of these principles. The origin of the book lies in a set of notes issued by the authors over a period of years with the aim of supplementing existing texts and adapting them for students having a background of about two years of college mathematics and physics, including atomic physics.

The change of the role of wave mechanics in science curricula, and its introduction into engineering curricula, has influenced our presentation of the subject. It is no longer realistic to assume that only those students already having a highly specialized preparation in mathematics and physics will study wave mechanics in a quantitative fashion, while all the others can manage with a qualitative model. Rather we wish to acquaint the student as early as possible with the fundamental principles of wave mechanics and to give him practice in applying these principles. By providing incentive for self-study, we hope to make the student sufficiently versatile in coping with future problems in the ever-increasing field of applications of wave mechanics.

The authors have consistently aimed at a logical sequence of topics and a detailed discussion of each. Mathematical topics beyond partial differentiation, integration, and the most elementary differential equations are presented in detail, and with sufficient generality to allow applications outside the immediate scope of this book. Thus a self-contained volume has evolved, in which the important principles are

first illustrated by examples and then again by problems interspersed throughout the text. The emphasis is more on depth in detail than on a broad coverage of topics.

As an introduction to the postulates of wave mechanics such elements of wave theory as expansion in terms of orthogonal functions and the dispersion of wave packets are discussed. The statistical nature of wave mechanics is stressed, and a separate chapter is devoted to the uncertainty principle and operator commutation. The solution of Schroedinger's equation is preceded by various applications of the postulates illustrating how information is extracted from wave functions. Only when the student has had sufficient practice in the use of wave functions is he asked to solve the wave equation. Each analytical solution of Schroedinger's equation is obtained by operator algebra; this method has been found more satisfactory than the polynomial expansion method, because it illustrates quantization more directly, because it gives a more unified approach to the generation of Hermite, Legendre, and Laguerre polynomials, and because it relates the wave mechanical approach to that of matrix mechanics. Moreover, the operator form of these polynomials, as exemplified by Rodrigues's formula for Legendre polynomials, is particularly useful in deriving selection rules. Operator algebra is also used in the discussion of electron spin.

In the chapter on perturbation theory a good deal of the preceding material is applied again. This chapter is based on the foundation laid by the introductory chapter on orthogonal functions, and its application to an anharmonic oscillator further illustrates the usefulness of the operator form of the eigenfunctions of the harmonic oscillator. Finally, this chapter forms the basis for a discussion of direct spin exchange interactions and the helium atom.

The book is concluded by a review of the various interactions that determine the electronic configuration of atoms. An earlier chapter on the resonance of an electron between two identical atoms provides the introductory material for the study of molecular binding.

The authors are aware of many omissions, but in order to restrict the material to a single semester, a choice often had to be made between topics. The decision was always made in favor of wide applicability and of relevance to the remainder of the book. Such topics as the variation method, the continuous spectrum of hydrogen, and the Russell-Saunders and other spin-orbit coupling models regretfully had to be omitted; in each case it was felt that the material in this volume would provide a sufficient basis for continued study. One of the authors has omitted Chaps. 8 and 9 in his class presentation without impairment of the continuity of the material.

It is a pleasure to acknowledge the assistance of our colleagues and students during the development of this text; their names are too numerous to be mentioned separately here. We are particularly grateful to Norman Menyuk, Arthur J. Schneider, and Oscar Grosch for their assistance in the preparation of various drafts of this book. The support of the Westinghouse Educational Foundation and the Westinghouse Research Division is gratefully acknowledged. Special thanks are due Miss Frances M. Doherty and Mrs. Laurence R. Swain, Jr., who typed many drafts of the manuscript.

*Louis Harris*

*Arthur L. Loeb*

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# introduction

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## chapter

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# 1

**1-1 Stationary states.** So much of our knowledge of the structure of atoms and molecules is based on the results of spectroscopy that it is worthwhile to recall the development of ideas that have led to our present concepts.

The correlation between spectroscopic term values and the energy levels of the stationary states of atoms was first postulated by Bohr. He proposed that an atom could exist only in certain stationary states, each of which has a definite energy. The discrete radiation emitted by an atomic system was the result of atoms going from an excited stationary state to a less excited stationary state or to the nonexcited state. This last state is usually designated as the normal or the ground state. The frequency of the radiation emitted, as a result of the transition from one stationary state to another, is found from the relation

$$E_2 - E_1 = h\nu \quad (1-1)$$

where  $E_2$  is the energy of the atom in the more excited state,  $E_1$  is the energy in the less excited state,  $h$  is Planck's radiation constant, and  $\nu$  is the frequency of the radiation.

**1-2 Excitation potentials.** Soon after Bohr's proposal, Franck and Hertz, and others, carried out experiments in which electrons were accelerated through tubes containing elements in their gaseous state. As the accelerating voltage was gradually increased, the electrons

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passed through the gas without change in energy until a critical accelerating voltage was reached, when the electrons were found to have lost most of their energy. The critical accelerating voltages were found to be different for each gaseous element. Franck and Hertz concluded from their measurements that energy was transferred from the electrons to the atoms in the gas by inelastic collisions and that these atoms in turn lost the energy by radiation. When the region in which the inelastic collisions occurred was exposed to the slit of a spectrograph the spectral line observed had a frequency given by the relation

$$(\Delta V)e = h\nu$$

where  $e$  is the charge on the electron and  $(\Delta V)e$  corresponds to the loss in energy of the accelerated electron. The spectral line was the result of transitions from a state with energy  $E_2$  to a state with lower energy,  $E_1$ . The value of the frequency of the spectral line was in agreement with Eq. (1-1).

As the accelerating voltage was increased, additional inelastic collisions corresponding to greater excitation potentials of an atom were observed and simultaneously new spectral lines of the atomic spectrum appeared, corresponding to excitation of atoms to higher levels. As the accelerating voltage was increased still further, the complete atomic spectrum of the element appeared. These experiments provide an excellent experimental confirmation of Bohr's postulate for the mechanism of the emission of spectral lines.

In practice, much greater accuracy for the energy (term value) differences is obtained from spectroscopic than from electron-impact measurements. The latter type of measurements supplemented the former in determining the difference between the energy of the excited states and that of the ground state.

**1-3 Selection rules for transitions.** Early empirical spectroscopic studies showed that the apparent complexity of the spectrum of an element could be resolved as follows. For each element a comparatively small set of numerical terms was found to exist, such that the frequency of each spectral line equals the difference between the numerical value of a pair of terms.

Even before Bohr's postulate it was recognized that every spectral term of an atomic system did not combine with every other term to give a spectral line. Bohr correlated this behavior with certain quantized changes of the angular momentum of the atom in the two energy states involved in a transition. This "selection rule" was partially successful in predicting the presence and absence of certain transitions.

## introduction

The concept of transitions between stationary states to give spectral lines has been found to have general application to nuclear and molecular systems as well as to atomic systems. It is one of the important concepts used in physics today.

*problem 1-1.* As the accelerating voltage of electrons through mercury vapor is gradually increased, one finds excitation potentials at

4.69, 4.91, 5.48, 6.73, 7.75, 7.94 . . . volts

and finally the ionization potential at 10.5 volts. Transitions with radiation emission are observed only from the 4.91, 6.73, and 7.75 excited levels.

(a) Calculate the wavelength (angstroms) of the first spectral line to appear as the accelerating potential is gradually increased (from zero).

(b) Three strong spectral lines in the visible emission spectrum of mercury are at 4040, 4358, and 5460 Å. Demonstrate that these levels have a common upper level, from this information.

*problem 1-2.* When neon gas at a low pressure is exposed to radiation of the following wavelengths:

$\lambda = 745$ Å	the 745-Å resonance line is reemitted
$\lambda = 627$ Å	the 8900-Å, 7180-Å, and 745-Å lines are emitted
$\lambda = 502$ Å	photoelectrons of 3.11-volt energy as well as the complete spectrum are observed

Predict the results of the following separate experiments:

- (a) Irradiation of neon gas with  $\lambda = 7180$  Å
- (b) Passage of 15-volt accelerated electrons through neon gas
- (c) Passage of 19-volt accelerated electrons through neon gas
- (d) Passage of 22-volt accelerated electrons through neon gas

**1-4 Bohr theory of the hydrogen atom.** Bohr also derived an expression for the energies of the different stationary states of the hydrogen atom, from a consideration of the internal motion of the atom, namely, that of the electron with relation to its proton. He



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assumed that the electron moved in a circular orbit around the nucleus and that the electric force of attraction between the proton and electron just balanced the centrifugal force of the rotating electron. If  $Ze$  represents the charge on the nucleus,  $e$  the charge on the electron,  $r$  the distance of the electron from the nucleus,  $m_e$  the mass of the electron, and  $v$  the velocity of the electron

$$\frac{Ze^2}{r^2} = \frac{m_e v^2}{r} \quad (1-2)$$

In the excited states the electron moved around the proton also in distinct circular orbits, but further from the proton. The postulate of discrete energy levels restricted the circles in which the electron might move. Here, Bohr introduced his second postulate which predicted exactly which circles are permitted for the electron motion. The quantization condition is

$$2\pi m_e r v = nh \quad (1-3)$$

where  $n$  is a quantum number, which may take on integral values from 1 to  $\infty$ , and  $h$  is Planck's constant. According to Eq. (1-3), the angular momentum of the system can assume only multiple values of  $h/2\pi$ .

In terms of the quantum number  $n$ , the velocities of the electron and the radii of the orbits for the different stationary states are therefore

$$v = \frac{2\pi Ze^2}{nh} \quad (1-4)$$

$$r = \frac{n^2 h^2}{4\pi^2 Ze^2 m_e} \quad (1-5)$$

The total energy  $E$  is equal to the sum of the kinetic energy and the potential energy

$$E = \frac{1}{2} m_e v^2 - \frac{Ze^2}{r} \quad (1-6)$$

Substitution of Eq. (1-2) into Eq. (1-6) gives

$$E = -\frac{1}{2} \frac{Ze^2}{r} = -\frac{1}{2} m_e v^2 \quad (1-7)$$

Substitution of Eq. (1-4) into Eq. (1-7) gives

$$E = \frac{-2\pi^2 Z^2 e^4 m_e}{n^2 h^2} \quad (1-8)$$