MAX BORN

THE MECHANICS OF THE ATOM

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Translated from the German by
J. W. FISHER, Ph.D.

and revised by
D. R. HARTREE, Ph.D.

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PREFACE TO THE GERMAN EDITION

THE title "Atomic Mechanics," [1] given to these lectures which I delivered in Göttingen during the session 1923–24, was chosen to correspond to the designation "Celestial Mechanics." As the latter term covers that branch of theoretical astronomy which deals with the calculation of the orbits of celestial bodies according to mechanical laws, so the phrase "Atomic Mechanics" is chosen to signify that the facts of atomic physics are to be treated here with special reference to the underlying mechanical principles; an attempt is made, in other words, at a deductive treatment of atomic theory. It may be argued that the theory is not yet sufficiently developed to justify such a procedure; to this I reply that the work is deliberately conceived as an attempt, an experiment, the object of which is to ascertain the limits within which the present principles of atomic and quantum theory are valid and, at the same time, to explore the ways by which we may hope to proceed beyond these boundaries. In order to make this programme clear in the title, I have called the present book "Vol. I"; the second volume is to contain a closer approximation to the "final" mechanics of the atom. I know that the promise of such a second volume is bold, for at present we have only a few hazy indications as to the departures which must be made from the classical mechanics to explain atomic phenomena. Chief among these indications I include Heisenberg's conception of the laws of multiplets and the anomalous Zeeman effect; some features of the new radiation theory of Bohr, Kramers, and Slater, such as the notion of "virtual oscillators"; the subsequent advances of Kramers towards a quantum theory of dispersion phenomena; as well as some general considerations, which I have recently published, relating to the application of the theory of perturbations to the quantum theory. This mass of material, however, in spite of its

[1] The German title "Atommechanik" corresponds to the title "Himmelsmechanik" (celestial mechanics); the title "Mechanics of the Atom" appeared, however, preferable for this book, although, in the text, the clumsier expression atomic mechanics has often been employed.

extensive range, is not nearly enough for the foundation of a deductive theory. The second volume may, in consequence, remain for many years unwritten. In the meantime let its virtual existence serve to make clear the aim and spirit of this work.

This book is not intended for those who are taking up atomic problems for the first time, or who desire merely to obtain a survey of the theoretical problems which it involves. The short introduction, in which the most important physical foundations of the new mechanics are given, will be of little service to those who have not previously studied these questions ; the object of this summary is not an introduction to this field of knowledge, but a statement of the empirical results which are to serve as a logical foundation for our deductive theory. Those who wish to obtain a knowledge of atomic physics, without laborious consultation of original literature, should read Sommerfeld's *Atombau und Spektrallinien*.[1] When they have mastered this work they will meet with no difficulties in the present volume, indeed a great deal of it will be already familiar. The fact that many portions of this book overlap in subject-matter with sections of Sommerfeld's is of course unavoidable, but, even in these portions, a certain difference will be discernible. In our treatment prominence is always given to the mechanical point of view ; details of empirical facts are given only where they are essential for the elucidation, confirmation, or refutation of theoretical deductions. Again, with regard to the foundations of the quantum theory, there is a difference in the relative emphasis laid on certain points ; this, however, I leave for the reader to discover by direct comparison. My views are essentially the same as those of Bohr and his school ; in particular I share the opinion of the Copenhagen investigators, that we are still a long way from a " final " quantum theory.

For the fact that it has been possible to publish these lectures in book form I am indebted in the first place to the co-operation of my assistant, Dr. Friedrich Hund. Considerable portions of the text have been prepared by him and only slightly revised by me. Many points, which I have only briefly touched on in the lectures, have been worked out in detail by him and expounded in the text. In this connection I must mention, in the first place, the principle of the uniqueness of the action variables which, in my opinion, constitutes the basis of the present-day quantum theory ; the proof worked out by Hund plays an important part in the second chapter (§ 15). Further, the account of Bohr's theory of the periodic system, given in the third

[1] English translation of third edition, 1923, by H. L. Brose, Methuen & Co., Ltd., London.

chapter, has, for the most part, been put together by Hund. I also wish to thank other collaborators and helpers. Dr. W. Heisenberg has constantly helped us with his advice and has himself contributed certain sections (as, for example, the last on the helium atom); Dr. L. Nordheim has assisted in the presentation of the theory of perturbations, and Dr. H. Kornfeld has verified numerous calculations.

MAX BORN.

GÖTTINGEN, *November* 1924.

AUTHOR'S PREFACE TO THE ENGLISH EDITION

SINCE the original appearance of this book in German, the mechanics of the atom has developed with a vehemence that could scarcely be foreseen. The new type of theory which I was looking for as the subject-matter of the projected second volume has already appeared in the new quantum mechanics, which has been developed from two quite different points of view. I refer on the one hand to the quantum mechanics which was initiated by Heisenberg, and developed by him in collaboration with Jordan and myself in Germany, and by Dirac in England, and on the other hand to the wave mechanics suggested by de Broglie, and brilliantly worked out by Schrödinger. There are not two different theories, but simply two different modes of exposition. Many of the theoretical difficulties discussed in this book are solved by the new theory. Some may be found to ask if, in these circumstances, the appearance of an English translation is justified. I believe that it is, for it seems to me that the time is not yet arrived when the new mechanics can be built up on its own foundations, without any connection with classical theory. It would be giving a wrong view of the historical development, and doing injustice to the genius of Niels Bohr, to represent matters as if the latest ideas were inherent in the nature of the problem, and to ignore the struggle for clear conceptions which has been going on for twenty-five years. Further, I can state with a certain satisfaction that there is practically nothing in the book which I wish to withdraw. The difficulties are always openly acknowledged, and the applications of the theory to empirical details are so carefully formulated that no objections can be made from the point of view of the newest theory. Lastly, I believe that this book itself has contributed in some small measure to the promotion of the new theories, particularly those parts which have been worked out here in Göttingen. The discussions with my collaborators Heisenberg, Jordan and Hund which attended the writing of this book have prepared the way for the critical step which we owe to Heisenberg.

It is, therefore, with a clear conscience that I authorise the English translation. It does not seem superfluous to remark that this book is not elementary, but supposes the reader to have some knowledge of the experimental facts and their explanation. There exist excellent books from which such knowledge can easily be acquired. In Germany Sommerfeld's *Atombau und Spektrallinien* is much used: an English translation has appeared under the title *Atomic Structure and Spectral Lines*. I should like also to direct attention to Andrade's book, *The Structure of the Atom*, in which not only the theories but also the experimental methods are explained.

I desire to offer my warmest thanks to Professor Andrade for suggesting an English edition of my book. I also owe my thanks to Mr. Fisher, who prepared the translation in the first place; Professor Andrade, Professor Appleton and Dr. Curtis, who read it over; and finally to Dr. Hartree, who revised the translation, read the proof-sheets, and made many helpful suggestions for elucidating certain points. I also offer my sincere thanks to the publishers for the excellent manner in which they have produced the book.

MAX BORN.

GÖTTINGEN, *January* 1927.

NOTE

THE chief departures from the German text which have been made by Professor Born or with his approval are (1) some modifications in §§ 1, 2 concerning the mechanism of radiation, in view of the experiments of Geiger and Bothe, and of Compton and Simon, (2) a modification of the derivation, on the lines suggested by Bohr, of the Rydberg-Ritz series formula in § 26, and (3) various alterations in §§ 24 and 30–32, made in view of the development of ideas and the additional experimental data acquired since the German edition was written.

D. R. H.

CONTENTS

INTRODUCTION

PHYSICAL FOUNDATIONS

FIRST CHAPTER

THE THEORY OF HAMILTON AND JACOBI

SECOND CHAPTER

PERIODIC AND MULTIPLY PERIODIC MOTIONS

THIRD CHAPTER

SYSTEMS WITH ONE RADIATING ELECTRON

FOURTH CHAPTER

THEORY OF PERTURBATION

APPENDIX

THE MECHANICS OF THE ATOM

INTRODUCTION

PHYSICAL FOUNDATIONS

§ 1.—Development of the Quantum Theory of the Oscillator from the Theory of Radiation

BEFORE dealing with the mathematical theory of atomic mechanics we shall give a brief account of its physical foundations. There are two sources to be considered : on the one hand the theory of thermal radiation, which led to the discovery of the quantum laws ; on the other, investigations of the structure of atoms and molecules.

Among all the characteristics of the atom which can be inferred from the physical and chemical properties of bodies, the radiation phenomena are distinguished by the fact that they provide us with the most direct information regarding the laws and structure of the ultimate constituents of matter. The most universal laws of matter are those manifested in such phenomena as are independent of the nature of the particular substance with which we are dealing. This constitutes the importance of Kirchhoff's discovery that the thermal radiation in an enclosure is independent of the nature of the material forming the walls of the enclosure, or contained in its interior. In an enclosure uniformly filled with radiation in equilibrium with the surroundings, the energy density, for a range of frequency $d\nu$, is equal to $\rho_\nu d\nu$, where ρ_ν is a universal function of ν and the temperature T. From the standpoint of the wave theory the macroscopic homogeneous radiation is to be regarded as a mixture of waves of every possible direction, intensity, frequency, and phase, which is in statistical equilibrium with the particles existing in matter which emit or absorb light.

For the theoretical treatment of the mutual interaction between radiation and matter it is permissible, by Kirchhoff's principle, to replace the actual atoms of the substances by simple models, so long as these do not contradict any of the known laws of nature. The harmonic oscillator has been used as the simplest model of an atom emitting or absorbing light; the moving particle is considered to be an electron, which is bound by the action of quasi-elastic forces to a position of equilibrium at which a positive charge of equal magnitude is situated. We thus have a doublet, whose moment (charge × displacement) varies with time. H. Hertz showed, when investigating the propagation of electric waves, how the radiation from such a doublet may be calculated on the basis of Maxwell's equations. It is an even simpler matter to calculate the excitation of such an oscillator by an external electromagnetic wave, a process which is utilised to explain refraction and absorption in the classical theory of dispersion. On the basis of these two results the mutual interaction between such resonators and a field of radiation may be determined. M. Planck has carried out the statistical calculation of this interaction. He found that the mean energy $\overline{W}$ of a system of resonators of frequency ν is proportional to the mean density of radiation ρ_ν, the proportionality factor depending on ν but not on the temperature T :

$$\rho_\nu = \frac{8\pi\nu^2}{c^2}\overline{W}. \tag{1}$$

The complete determination of $\rho_\nu(T)$ is thus reduced to the determination of the mean energy of the resonators, and this can be found from the laws of the ordinary statistical mechanics.

Let q be the displacement of a linear oscillator and χq the restoring force for this displacement; then $p = m\dot{q}$ is the momentum, and the energy is

$$W = \frac{m}{2}\dot{q}^2 + \frac{\chi}{2}q^2 = \frac{1}{2m}p^2 + \frac{\chi}{2}q^2.$$

The force-coefficient χ is connected with the angular frequency ω and the true frequency ν [1] by the relation

$$\frac{\chi}{m} = \omega^2 = (2\pi\nu)^2.$$

According to the rules of statistical mechanics, in order to calculate the mean value of a quantity depending on p and q the quantity must be multiplied by the weighting factor $e^{-\beta W}$, where $\beta = 1/kT$, and then averaged over the whole of the "phase space" (p, q) corresponding to possible motions. Thus the mean energy becomes

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[1] In the following ω will always be used to denote the number of oscillations or rotations of a system in 2π secs. (the angular frequency), ν will be used to denote the number in 1 sec. (the true frequency).

$$\overline{W}=\frac{\iint We^{-\beta W}dp\,dq}{\iint e^{-\beta W}dp\,dq}.$$

This can clearly also be written

$$\overline{W}=-\frac{\partial}{\partial\beta}\log Z,$$

where

$$Z=\iint e^{-\beta W}dp\,dq$$

is the so-called partition function (Zustandsintegral). The evaluation of Z gives

$$Z=\int_{\infty}^{\infty}e^{-\frac{\beta}{2m}p^2}dp\int_{-\infty}^{\infty}e^{-\frac{\beta\chi}{2}q^2}dq\,;$$

and since

$$\int_{-\infty}^{\infty}e^{-x^2}dx=\sqrt{\pi}$$

we get

$$Z=2\pi\sqrt{\frac{m}{\chi}}\frac{1}{\beta}=\frac{1}{\nu\beta}.$$

Hence

$$\overline{W}=\frac{1}{\beta}=kT. \tag{2}$$

This leads to the following formula for the density of radiation :

$$\rho_\nu=\frac{8\pi\nu^2}{c^3}kT, \tag{3}$$

the so-called Rayleigh-Jeans formula. It is at variance not only with the simple empirical fact that the intensity does not increase continually with the frequency, but also leads to the impossible consequence that the total density of radiation

$$\int_0^\infty \rho_\nu d\nu$$

is infinite.

The formula (3) is valid only in the limiting case of small ν (long waves). W. Wien put forward a formula which represents correctly the observed decrease in intensity for high frequencies. A formula which includes both of these others as limiting cases was found by Planck, first by an ingenious interpolation, and shortly afterwards derived theoretically. It is

$$\rho_\nu=\frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{\frac{h\nu}{kT}}-1}, \tag{4}$$

where h is a new constant, the so-called Planck's Constant. Since it is the fundamental constant of the whole quantum theory, its numerical value will be given without delay, viz.:

$$h = 6{\cdot}54 \,.\, 10^{-27} \text{ erg sec.}$$

Comparison of (4) with (1) shows that this radiation formula corresponds to the following expression for the energy of the resonators:

$$\overline{W} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}. \tag{5}$$

To derive this formula theoretically, a complete departure from the principles of classical mechanics is necessary. Planck discovered that the following assumption led to the required result: *the energy of an oscillator can take not all values, but only those which are multiples of a unit of energy* W_0.

According to this hypothesis of Planck, the integral formula for Z is to be replaced by the sum

$$Z = \sum_{n=0}^{\infty} e^{-\frac{nW_0}{kT}}. \tag{6}$$

The summation of this geometric series gives

$$Z = \frac{1}{1 - e^{-\frac{W_0}{kT}}}.$$

From this it follows that

$$\overline{W} = \frac{\partial}{\partial\beta} \log(1 - e^{-\beta W_0}) = \frac{W_0 e^{-\beta W_0}}{1 - e^{-\beta W_0}},$$

thus

$$\overline{W} = \frac{W_0}{e^{\frac{W_0}{kT}} - 1}. \tag{7}$$

This agrees with Planck's formula (5) if we put $W_0 = h\nu$. This last relation can be established with the help of Wien's displacement law, which can be deduced from thermo-dynamical considerations combined with the Doppler principle. Wien's law states that the density of radiation must depend on the temperature and frequency in the following way:

$$\rho_\nu = \nu^3 f\left(\frac{\nu}{T}\right),$$

the energy of the resonator has therefore the form

$$\overline{W} = \nu F\left(\frac{\nu}{T}\right).$$

Comparison with (7) shows that W_0 must be proportional to ν.

Einstein showed that the behaviour of the specific heat of solid bodies furnished valuable support for Planck's bold hypothesis of energy quanta. The crudest model of a solid consisting of N atoms is a system of 3N linear oscillators, each of which more or less represents the vibration of an atom in one of the three directions of space. If the energy content of such a system be calculated on the assumption of a continuous energy distribution, we get from (2)

$$E=3NkT.$$

If we consider one gram molecule, then $Nk=R$, the absolute gas constant, and we have the law of Dulong and Petit in the form

$$c_v=\frac{dE}{dT}=3R=5{\cdot}9 \text{ calories per degree C.}$$

Experiment shows, however, that this is the case at high temperatures only, while, for low temperatures, c_v tends to zero. Einstein took Planck's value (5) for the mean energy instead of the classical one and obtained for one gram molecule:

$$E=3RT\frac{\frac{h\nu}{kT}}{e^{\frac{h\nu}{kT}}-1}.$$

This represents, with fair accuracy, the decrease in c_v at low temperatures for monatomic substances (*e.g.* diamond). The further development of the theory, taking into account the coupling of the atoms with one another, has confirmed Einstein's fundamental hypothesis.

Whereas Planck's assumption of energy quanta for resonators is well substantiated by this result, a serious objection may be brought against his deduction of his radiation formula, namely, that the relation (1) between the density of radiation ρ_ν and the mean energy $\overline{W}$ of the resonators is derived from classical mechanics and electrodynamics, whereas the statistical calculation of $\overline{W}$ is based on the quantum principle, which cannot be reconciled with classical considerations. Planck has endeavoured to remove this contradiction by the introduction of modified quantum restrictions; but further developments have shown that the classical theory is inadequate to explain numerous phenomena, and plays rather the rôle of a limiting case (see below), whereas the real laws of the atomic world are pure quantum laws.

Let us recapitulate clearly the points in which the quantum principles are absolutely irreconcilable with the classical theory.

According to the classical theory, when a resonator oscillates, it emits an electromagnetic wave, which carries away energy; in consequence the energy of the oscillation steadily decreases. But according to the quantum theory, the energy of the resonator remains constant during the oscillation and equal to $n.h\nu$; a change in the energy of the resonator can occur only as the result of a process in which n changes by a whole number, a " quantum jump."

A radically new connection between radiation and the oscillation of the resonator must therefore be devised. This may be accomplished in two ways. We may either assume that the resonator does not radiate at all during the oscillation, and that it gives out radiation of frequency ν only when a quantum jump takes place, there being some yet unexplained process by which energy lost or gained by the resonator is given to or taken away from the ether. The energy principle is then satisfied in each elementary process. Or we may assume that the resonator radiates during the oscillation, but retains its energy in spite of this. The energy principle is then no longer obeyed by the individual processes; it can only be maintained on an average provided that a suitable relation exists between the radiation and the probabilities of transitions between the states of constant energy.

The first conception was long the prevailing one; the second hypothesis was put forward by Bohr, Kramers, and Slater,[1] but new experiments by Bothe and Geiger,[2] and by Compton and Simon,[3] have provided strong evidence against it. The investigations of this book will, in general, be independent of a decision in favour of either of these two assumptions. The existence of states of motion with constant energy (Bohr's "stationary states") is the root of the problems with which we are concerned in the following pages.

§ 2.—General Conception of the Quantum Theory

By consideration of Planck's formula $W_0=h\nu$, Einstein was led to interpret phenomena of another type in terms of the quantum theory, thus giving rise to a new conception of this equation which has proved very fruitful. The phenomenon in question is the photoelectric effect. If light of frequency $\tilde{\nu}$ falls on a metallic surface,[4] electrons are set free and it is found that the intensity of the light influences

[1] *Zeitschr. f. Physik*, vol. xxiv, p. 69, 1924; *Phil. Mag.*, vol. xlvii, p. 785, 1924.

[2] W. Bothe and H. Geiger, *Zeitschr. f. Physik*, vol. xxxii, p. 639, 1925.

[3] A. H. Compton and W. Simon, *Phys. Rev.*, vol. xxv, p. 306, 1925.

[4] When the symbols ν and $\tilde{\nu}$ are employed concurrently, $\tilde{\nu}$ always refers to the frequency of the radiation, the symbol ν to a frequency within the atom. (Translator's note.)

the number of electrons emitted but not their velocity. The latter depends entirely on the frequency of the incident light. Einstein suggested that the velocity v of the emitted electrons should be given by the formula

$$\tfrac{1}{2}mv^2 = h\tilde{\nu},$$

which has been verified for high frequencies (X-rays), while for low frequencies the work done in escaping from the surface must be taken into consideration.

We have then an electron, loosely bound in the metal, ejected by the incident light of frequency $\tilde{\nu}$ and receiving the kinetic energy $h\tilde{\nu}$; the atomic process is thus entirely different from that in the case of the resonator, and does not contain a frequency at all. The essential point appears to be, that the alteration in the energy of an atomic system is connected with the frequency of a light-wave by the equation

$$(1) \qquad h\tilde{\nu} = W_1 - W_2,$$

no matter whether the atomic system possesses the same frequency $\tilde{\nu}$ or some other frequency, or indeed has any frequency at all.

Planck's equation

$$W = n \,.\, W_0\,;\ W_0 = h\nu$$

gives a relation between the frequency of oscillation ν of a resonator and its energy in the stationary states, the Einstein equation (1) gives a relation between the change in the energy of an atomic system for a transition from one state to another and the frequency $\tilde{\nu}$ of the monochromatic light with the emission or absorption of which the transition is connected.

Whereas Einstein applied this relation solely to the case of the liberation of electrons by incident light and to the converse process, viz. the production of light (or rather X-rays) by electronic bombardment, Bohr recognised the general significance of this quantum principle for all processes in which systems with stationary states interact with radiation. In fact the meaning of the equation is independent of any special assumptions regarding the atomic system. Since Bohr demonstrated its great fertility in connection with the hydrogen atom, equation (1) has been called Bohr's Frequency condition.

Taking into account the new experiments by Bothe and Geiger, and by Compton and Simon, which have been mentioned above, we have to assume that the frequency $\tilde{\nu}$ is radiated during the transition and the waves carry with them precisely the energy $h\tilde{\nu}$