ATOMIC STRUCTURE

By

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PREFACE

This book has been written to fill a definite classroom need. Unlike many universities in this country, the University of California has a two-year basic sequence in physics required of all its engineers, chemists, and physics majors. This sequence of four one-semester courses of three semester hours each, including laboratory, effectively covers the topics of mechanics, properties of matter and heat, electricity and magnetism, sound and light. There is no time for atomic structure as such in this basic course. Obviously, aspects of atomic structure must enter into any first-class, modern course of physics; the emphasis in these courses, however, is on fundamentals.

For the engineers, the necessary information on atomic structure is being imparted in a course on electronics given in the junior year. For the physics and mathematics majors, chemists, and such engineers as wish a more basic treatment, there is offered a three-unit course in the junior year, entitled "Atomic Structure." This course, given for students who have a working knowledge of the calculus, is considerably above the level of the modern American textbooks of a survey nature covering the same subject. Since it is impossible to teach the subject effectively to classes of seventy and more students on the basis of references to sections of many excellent more specialized textbooks, the present volume has been prepared.

At different times, for many years, the author has been connected with courses of the character outlined. He has been teaching the two-semester-hour forerunner of this course since 1932. He entered the field of physics as a graduate student in 1913, with the introduction of the nuclear atom and the Bohr theory, and has, so to speak, "grown up" with the field of modern atomic structure. It is his firm conviction that it is impossible to introduce the student properly to the subject directly from the rather abstract and modern wave mechanical viewpoint. In order that a student really understand and be able to use the modern developments, he must grow into these, much in the same way as the physicists who developed the field have done.

The subject is thus developed on an essentially experimental and historical basis. Such a procedure is essential, particularly, in this age of wave mechanics, to counteract the otherwise dogmatic and at times seemingly irrelevant empiricism. In fact, it is more important today than ever before in presenting this subject to show the student the fragmentary and incomplete experimental bases of our modern formulations. In view of the fact that we can only observe by experiment *aspects* of the fundamental concepts such as the electron, the photon, and the nucleus, it is especially desirable that the extent and limitations of these experimental observations be repeatedly brought to the student's attention, for it is only from these that he can understand the nature of the more accurate empirical formulations. This then leaves him free to see their faults, to accept changes, and perhaps to add to their reformulation as future discovery demands.

It is the plan of this book to present the early concept of the electron, the positive ray, radioactivity, and x-rays in an experimental and historical fashion. On this basis, one is led to the formulation of the atom of J. J. Thomson, which dominated the scene until the revolutionary discoveries of 1911 to 1913. A treatment of the vital scattering experiments of Rutherford, which led to the nuclear atom, then properly begins the reformulation of ideas necessary for the development of the Bohr theory. A digression, in the form of a special chapter, is introduced at this point for the interested student who wishes more and recent knowledge of the nuclear structure. This follows logically directly after the foundation laid by the scattering experiments. However, it obviously is not vital to the development of the subject.

The story then resumes with Bohr's solution of the dilemma of the nuclear atom by the assumption of stationary non-radiating orbits. These assumptions are justified by the introduction of the de Broglie phase wave, and the *apparent* contradiction with classical electrodynamics in *non-radiating orbits* is clarified. Similar procedures are resorted to, wherever necessary, to resolve conflicts and for clarification in dealing with the classical quantum theory.

After the necessary classical quantum theoretical conclusions have been drawn from the simple model of the H atom, the student is then introduced to the formal general classical procedure of quantization. On the basis of this it is possible to quantize the ellipse and the elliptical orbits in space. From this point on, one encounters the difficulty of the different assignment of quantum numbers characteristic of the period between the Bohr-Sommerfeld theory and the vector model and wave mechanics. This problem is treated by introducing the diverse studies, the "anomalous" Zeeman effect, the gyromagnetic experiments, the Stern-Gerlach experiment, etc., which bear upon electron spin, and the subject is clarified in a formal way by the assignment of the wave mechanical quantum numbers.

Following this, one is able on the basis of the Bohr and Stoner procedure to give the assignment of electrons to states about a nucleus in a neutral atom. The relation of such states to the periodic table of the elements is then obvious.

With the construction of the atom from the four quantum numbers and the Pauli exclusion principle, one is ready to discuss the electrical and magnetic behavior of an atom. This is introduced by means of the Franck and Hertz experiments and a discussion of ionization and excitation potentials. Then follow a discussion of the vector model of the atom and an analysis of the simple and the anomalous Zeeman effect on the Bohr theory. The anomalous Zeeman effect analysis is carried out for the D lines of Na.

This material lays the foundation for a presentation of the energy level diagrams of the alkali and alkaline-earth atoms.

With this background, it is possible to describe the duration of excitation and emission of lines, metastable states, etc. Then, photoelectric excitation and ionization, and excitation and ionization by electron impact, with their attendant probabilities, are presented. After this, one can proceed to organize atoms into molecules, and a section on atomic structure and chemical combination follows. Together with a discussion of polar molecules, a section is devoted to the Debye treatment of the dielectric constant. From the discussion of molecular structure, one naturally goes to molecular behavior. This leads to the energy level diagram of a molecule and a brief discussion of the salient characteristics of the band spectrum. The measurement of temperature by means of rotational line intensities is included, as is a discussion of dissociation and excitation on the Franck-Condon principle. After a brief presentation of kinetic theory as needed in applications to electronic gas reactions, this section concludes with a summary of the basic electronic reactions in equation form.

In view of the fact that there is no modern intermediate source of information on the electron theory of metals, a final section dealing with this subject is included. The first part again introduces the subject from the purely classical viewpoint of Lorentz. It is followed by a brief presentation of the modern wave mechanical theory of the metallic state.

It is believed that, if a student masters the material contained in this book, he is in a position to use it for the following purposes. For the physicist and chemist, it furnishes the basis for further study of atomic structure. It lays the physical basis for an elementary course in wave mechanics and a more advanced course on modern atomic theory. It should prepare the engineer for work in the field of electronics and discharge in gases. Finally, it is hoped that it will interest, stimulate, and inspire students to further study in the fascinating field of atomic structure for its own sake.

In writing the first part of the book, the writer has followed his own experience in "growing up" with the subject. The sections dealing with orbit theory and quantization have drawn their inspiration largely from the fifth edition of Sommerfeld's classic "Atombau und Spektrallinien." The modern spectroscopic terminology and the treatment of the vector model have benefited greatly through the excellent text of H. E. White, "Introduction to Atomic Spectra," while the treatment of the metallic state owes a great deal to Fröhlich's "Elektronen Theorie der Metalle."

It has been the author's aim throughout to present the subjects in as clear and as simple a fashion as possible. However, at no point does he hesitate to use the calculus where it is necessary, for neither physicist, chemist, nor engineer can go far unless he can effectively use this most valuable tool, the calculus.

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The author wishes to express his thanks to Professor Arnold Sommerfeld for permission to include a very free translation of a few sections of his classical *Atombau und Spektrallinien* in the classical quantum presentation in this book. It would be impossible to improve on the clarity and brevity of these presentations, and both were needed. The author is also greatly indebted to Professor H. Fröhlich for the guidance and clarification made possible in the presentation of the electron theory of metals as a result of the use of Fröhlich's excellent monograph, *Die Elektronentheorie der Metalle.* He is also indebted to Professor Fröhlich and his publishers for the right to copy certain figures from that text. To his colleague, Professor H. E. White, and to the McGraw-Hill Book Company, the writer is indebted for permission to publish a number of energy level and charge density distribution diagrams. He wishes to acknowledge his appreciation to Professor G. W. C. Kaye and his publishers for permission to reproduce a few figures dealing with the early history of X-rays, to be found in his book on X-rays, published in 1917. He is also indebted to the Royal Society for permission to reproduce some of the pictures of C. T. R. Wilson cloud tracks. The author is deeply indebted to Mr. Arthur F. Kip for his valuable assistance in revising portions of the manuscript and assisting in the preparation of galley proof, page proof, and index.

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INTRODUCTION

We stand today and glance over a most astounding and revolutionary period in the development of physical thought, and yet a period extending over scarcely more than thirty years. The period began with the chance discovery of x-rays in 1895, at the close of an era of great theoretical development, and culminated in the evolution of the wave mechanics in the period of 1925–1927, another great mathematical-physical systematization.

Physical science began its history proper with Galileo, as a new method, controlled quantitative investigation. Following the rapid accumulation of experimental facts gleaned by this most fruitful method, the need for generalized laws to relate the rather widely separated fields of quantitative investigation was acute. Thus, for instance, static and current electricity, heat and work, light and electricity, could not be properly correlated until some relations having factors expressible in terms of both sets of phenomena could be found. The advance came through the three laws of Newton defining force and giving it a measure. By this means electrical, mechanical, thermal, and luminous phenomena could all be related in terms of comparable forces and the resultant of force actions such as work or energy. Consequently all known physical phenomena of nature were unified, in the short span of a hundred and fifty years, into a coherent system through descriptions of the quantitative relations in the common language of Newtonian mechanics. Thus by 1885 there was a world picture painted in Newtonian mechanical terms. The one hundred and fifty years perhaps should have been subdivided into three general subperiods. The first was devoted to acquiring those data essential to formulating nature in mechanical terms; the second, to correlating the results in different fields; and the last, to great mathematical-physical generalization. The first period can well be exemplified by Coulomb's investigations of the forces between charges and between magnets (1785); the second, by the study of the relations between heat and work by Joule, (1843), or the many researches relating radiant energy to light; and the last, by the generalizations such as the first and second laws of thermodynamics by Helmholtz and Clausius (1850), and the development of electromagnetic theory (1865) by Maxwell.

Already in 1888 the systematization had proceeded so far that discovery by Hertz of Maxwell's predicted electromagnetic waves left apparently little to be expected in the form of further new first-order discoveries of physical phenomena. All known phenomena had been at least roughly studied and fitted beautifully into the generalized Newtonian mechanical scheme. It is therefore not surprising that on several occasions in the period 1885 to 1895 great physicists stated that the future of physical advance lay in the extension of physical measurements to the fourth significant figure. It is true that such an attack would have brought startling discoveries, for it was just such an investigation which led Planck to the quantum theory (radiation laws) and Einstein to the relativity theory (Michelson-Morley experiment). The denouement came, however, in a much more striking and dramatic fashion than this, and presented the physicist with countless new phenomena which required preliminary investigations in the first order of magnitude only. In fact, it is doubtful whether the quantum theory and relativity would have received the support they did, had not the large vistas of unknown territory displayed by the discovery of x-rays made physicists willing to risk much in the exciting new search for truth.

It was the innocent discovery by W. C. Roentgen that the discharge of an induction coil through an evacuated bulb produced fluorescence in a nearby paper coated with barium platinocyanide, that ended by upsetting our smug confidence in the Newtonian mechanical world and ultimately gave us a much broader and more powerful method of analysis in the modern wave or quantum mechanics. For it was the subsequent study of the conductivity of gases and the nature of the agents causing x-rays that introduced us into the subatomic world of physics to which the simple mechanics of Newton are not applicable.

Such a statement about the inapplicability of Newtonian law does not, however, mean that Newton's laws are incorrect. So far as they are applicable to the gross mechanical world of things about us, from which they were derived, they are quite accurate and most satisfactory. But, as soon as one gets to the very large (masses, distances, and speeds of astronomical magnitude) or the very minute (atomic world) these general laws are no longer strictly true. Phenomena deviate further and further, the smaller the dimensions, until for the electron the mechanical considerations apply in order of magnitude only and in some respects not at all.

After the rapid first-order survey of this new field of investigation from 1895 to 1913, giving the elements of atomic structure, physicists were able again to attempt a unification of the various phenomena in terms of the atomic structure and behavior. In this they were continually thwarted by one persistent inconsistency, namely, that light, in its interactions with matter, behaved at times like an electromagnetic wave motion, but at others, particularly in its interaction with electrons, it behaved like a corpuscle. The general acceptance of the Compton effect as real by 1924 tempted some to abandon completely the wave theory of light, seemingly so firmly established by countless researches, for a corpuscular theory of light. Before this view had gained much ground, largely through the work of L. De Broglie, Heisenberg and Bohr, Schroedinger, and later Dirac, the whole subject, including atomic structure, was clarified by the discovery that, in interactions with matter, light could be treated mathematically either as a corpuscle with certain properties, in which case matter must be treated as particulate; or that light could be considered as a wave motion in which a peculiar wavelike character had to be attributed to matter. This peculiar dual nature of light and matter and the relation between the two methods of regarding them has been successfully developed since 1926 in relation to the structure of the atom. It is in essence what is called the wave mechanics or quantum mechanics, and it enables us to correlate the observations in the subatomic world with marked success. It may be said that the term mechanics, as used in the name, is perhaps incorrect, for as a matter of fact *mechanics* is Newtonian and certainly the wave mechanics is non-Newtonian.

With the wave mechanics, therefore, one is forced to abandon the more definite *mechanical* models of the atom. In place of them one must use much more accurate and general wave mechanical equations. These, however, can convey no precise mechanical picture of what takes place. Thus when a modern physicist is asked what would take place in a given situation, he can calculate the answer with considerable accuracy. He would, however, be completely incapable of telling one by analogy, in gross mechanical terms, how it happened. He could merely point to an equation with the proper terms and say that that equation expresses the behavior of the electron or the atom.

Thus, except for the limited macroscopic world immediately about us, Newtonian mechanics does not suffice to explain nature, and man has once again been put in his place for arrogantly assuming that he had found the universal key to the secrets of nature. Thus, philosophically speaking, man has been forced to give up the deductive view of nature based on a few general laws, and has reverted to the more empirical attitude of the Galilean era in which he observes, measures, infers the laws of a phenomenon, and attempts to relate the phenomenon to others. Today therefore, the aim of the physicist is to investigate, relate in as general a fashion as possible, and perhaps predict, without, however, any preconceived notions about the form of the result or about how nature should work, on the basis of general axioms.

It must be added in passing that, in accepting the modern view of nature, one need not abandon all Newtonian concepts when it comes to atomic structure. In fact, without an extension of these concepts as working hypotheses, physics would be nowhere. Physicists live in a mechanical world, and their physical thinking is in terms of their experience and of the Newtonian physics which they first learned. Especially must the experimentalist in his thinking be guided by such notions; otherwise he could not well proceed. It must not seem unnatural then in an experimental approach to the subject of atomic structure to find that the thinking will be continually guided by Newtonian principles. In fact, with the abstract nature of wave mechanics it would be impossible to introduce students to the subject by such means. The course will accordingly be developed in a historical manner, and the approach will be consistently mechanical and classical. Wherever the classical picture breaks down, this will be clearly indicated, and where possible the wave mechanical extensions will be indicated. It may be added again that although in detail the two viewpoints differ radically, to rough order of magnitude approximations the two treatments bring the same result. Thus, for example, the classical size of the electromagnetic electron and the rough size of the wave-packet electron are of the same order of magnitude. Again, the classically assumed electron shells of the atoms are closely approximated by the true charge density distribution of the wave electrons. With the statement that the approach of this course to the problems of atomic structure must in large measure be classical and that this shortcoming must make one hesitate about applying the pictures too rigorously to real atoms, one can turn to the detailed study of the subject and learn the remarkable achievement of thirty short years of physical investigation in one small domain, the structure of the atom.

PART I

EARLY DISCOVERIES AND THE PRENUCLEAR ATOM

CHAPTER I

THE ELECTRON

1. THE DISCOVERY OF THE ELECTRON AND THE MEASUREMENT OF e/m

When static electricity was discovered as consisting of two kinds, vitreous and resinous, and when its ability to move over conductors was observed physics was in the stage of development where such properties were associated with the idea of invisible weightless fluids. In the case of electricity this concept carried over well into the period where the particulate structure of matter was being discussed. In the early eighteenth century the fluid concept of electricity had been set forth from two different viewpoints. Du Fay assumed a vitreous fluid and a resinous fluid which in neutral bodies were present in equal amounts (a two-fluid theory). Benjamin Franklin assumed a single electrical fluid called positive electricity and associated with vitreous substances rubbed with silk. A neutral body (i.e., an unelectrified body) had just enough of this to be neutral. An excess of the fluid charged the body positively; a deficiency gave it a negative or resinous charge. This one-fluid theory was after many years adopted as correct, and our conventions of electrical current flow are all expressed in terms of this theory today. The choice before 1895 was not a reasoned one but really an arbitrary choice based on no real knowledge. It was therefore not surprising that such a viewpoint was at variance with the real mechanism of conduction. The old convention, however, is satisfactory for most purposes of description and will doubtless be retained.

In 1867 at the memorial services on the death of Faraday, Helmholtz gave his famous Faraday Lecture before the Royal Society. In this lecture he pointed out that if one accepted the atomic theory of matter Faraday's laws of electrolysis pointed definitely to the particulate or atomic nature of electricity as contrasted with a fluid concept.

This idea was, in the main, ignored, but certain persons continued a speculative interest in the subject. Among these was Johnston Stoney, who insisted on a negative atom of electricity which he called the electron. However, there was no proof of its existence.

Roentgen's discovery of peculiar radiations coming from an induction-coil discharge through a highly evacuated discharge tube started the investigations which led to the discovery of the electron. The rays were quickly found not only to make the barium platinocyanide glow, but also to affect a photographic plate and to render the air through which they passed electrically conducting. These rays traveled in straight lines, penetrated matter ordinarily opaque to light, e.g., wood, and cast shadows due to differential absorption. They were not affected by electrical or magnetic fields. The rays were called x-rays by Roentgen because of their unknown nature. While these rays of themselves occupied the attention of many investigators, the conditions in the discharge tube emitting them led to further studies.

2. CATHODE RAYS

It was observed that the x-rays appeared whenever the glass walls opposite the cathode or negative electrode became fluorescent and that the causative agent for this fluorescence was some bluish streamers emanating from the cathode. These cathode rays appeared to travel from the cathode in straight lines and cast shadows of objects in their path on the walls. They carried a negative charge of electricity to whatever they impinged on. It was found that they were deflected in a magnetic field as if they were a stream or current of positive particles flowing towards the cathode, or a beam of negative electricity flowing away from the cathode. This indicated that the cathode rays might be streams of negatively charged particles of high velocity and at least atomic mass projected from the cathode. Where they impinged on matter, the matter emitted x-rays. It was at once argued that, if negative particles, they should be deflected towards the positive electrode by an electrical field. Early attempts to deflect them proved futile as the electrodes were placed *outside* of the tube. The reason is obvious today, for the residual gas in the tube was conducting, and positive and negative charges from the gas were drawn to the inside of the glass walls opposite the electrodes, neutralizing the field in the space where the cathode rays passed. This was overcome by J. J. Thomson, who placed his electrodes *inside* the glass. By using a strong source of current the ions drawn to the electrodes inside did not change the field between the electrodes, and the cathode rays were drawn or deflected towards the positive plate as one would expect a beam of negative particles to be deflected. The decision that cathode rays were rapidly moving electrical particles, and not light waves as some had supposed, as a result of the failure of the external electrodes to deflect the rays, was therefore quite definitely established.

This decision at once enabled further progress to be made, for if these rays were particles, there were suggested certain questions which require immediate answer. These were: what is the mass, m, of these particles; what is their charge, e (in e.s.u. or e.m.u.); and what is their velocity, v? There were, therefore, three unknown quantities associated with cathode rays to determine. The problem was to devise a means for measuring e, m, and v. To measure e, m, and v separately, there had to be three experimental relations involving these quantities from which to solve for the unknowns. J. J. Thomson at once saw that the electrical and magnetic deflections would give two relations involving e, m, and v from which two quantities could be derived. He decided to use these equations to measure v and the ratio e/m. The reason for this lay in the fact that v might be variable but e/m, if constant, would enable one to infer a great deal about cathode rays, even though it did not give e and m separately. An elementary analysis of the deflection experiments will at once show how these quantities can be measured.

Let us consider the magnetic case. Assume a uniform magnetic field H. If the charged particles have a constant velocity v, perpendicular to H, these rays have a force acting on them due to H at right angles to the field H. Thus they will be bent into a circular orbit or path of radius ρ as long as H acts on them. If ρ can be measured, we can get an equation between e/m, v, H, and ρ. A current i of length l in a field H experiences a force $F_H = Hil$ at right angles to itself. A particle of charge e and velocity v centimeters per second is equivalent to a charge e going a distance x centimeters in a time t, where $x/t = v$. But $e/t = i$ and x is a length equivalent to l. Hence $Hil \equiv Hev$. Thus $F_H = Hil = Hev$. Now a particle forced into a circular path ρ with a velocity v has a centrifugal force mv^2/ρ which must just equal F_H as the particle is constrained by the field to a path ρ. Hence we can write

$$Hev = \frac{mv^2}{\rho} \quad \text{or} \quad \frac{e}{m} = \frac{v}{H\rho}. \tag{1}$$

Thus we have an important equation between e/m, v, and an experimental constant $H\rho$.

In a uniform electrical field of strength X, a particle of charge e moving with a velocity v perpendicular to X experiences a force in the