QUANTUM THEORY OF ATOMIC STRUCTURE

VOLUME I

JOHN C. SLATER

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Volume I

QUANTUM THEORY OF ATOMIC STRUCTURE

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The late F. K. Richtmyer was Consulting Editor of the series from its inception in 1929 to his death in 1939. Lee A. DuBridge was Consulting Editor from 1939 to 1946; and G. P. Harnwell from 1947 to 1954.

Preface

This two-volume work is the first of a series of books which I hope to write, covering the field of the application of quantum mechanics to the structure of atoms, molecules, and solids and to the theory of the physical and chemical properties of matter. Ever since the development of wave mechanics in 1926, it has been clear that we had the theoretical basis for the study of matter; but the theory has been difficult enough so that progress in working it out has been slow. Nevertheless, even in the first ten years following 1926, the general outlines of the theory began to be clear, and by now a great many of the details have been worked out, though there is still a great deal to be done. The subject has grown enormously and is constantly developing. This expansion, in a sense, is mirrored in a sequence of books which I have already written. In 1933 Professor Frank and I, in "Introduction to Theoretical Physics," included about 200 pages on the quantum theory and its applications to the study of matter. In 1951, in "Quantum Theory of Matter," I enlarged this material to a full-length book of some 500 pages. Now I am taking two volumes to go over the material on atoms which is treated in the first 200 pages of "Quantum Theory of Matter." And I hope that there are a number of volumes still to come.

I have here followed the same general plan which was used in those two earlier books; that is, to start with the principles of wave mechanics, then to use these to discuss the hydrogen atom, the central-field problem, and more complicated atoms. Since some of the same ground was covered in the earlier books, I have not hesitated to use material from them when it seemed appropriate, and the reader will find that in the first volume of the present work, essentially all the topics are covered which are taken up in the first seven chapters of "Quantum Theory of Matter." But it is obvious, from the increased length, that there is much more besides, and I hope that the presentation is significantly improved. The second volume of the present work is almost entirely new material, which was not covered at all in either of the earlier books.

It has been my aim to write the two volumes of the present work on rather different levels of difficulty. The first volume starts with the beginning of wave mechanics, and I believe that it can well be used as an introductory text in quantum mechanics, as well as in atomic structure. It uses only the more elementary methods to discuss the structure of atoms and yet gets far enough so that the two final chapters of the volume give a rather complete survey of present work on the structure of some of the more important of the atoms. It is my view that everything in this volume is really needed by anyone who expects to go on to the study of quantum chemistry, or the theory of solids, or any aspect of the theory of matter. With the needs of the fairly elementary student in mind (that is, of perhaps a first-year graduate student) I have included problems, appendixes covering such topics as the parts of classical mechanics needed to discuss quantum mechanics, and enough references to enable the student to get started studying the literature.

The second volume, on the other hand, is on a level which will probably make it mostly used as a reference work in the more advanced aspects of the theory of atomic structure. In its appendixes it includes considerable tabular material which would be valuable to the professional student of atomic theory. It contains a rather full bibliography of the major papers relating to the development both of wave mechanics and of atomic structure. Many of the topics taken up in this second volume are as essential as those in the first volume for those going on with chemical or solid-state theory; some other parts, such as Racah's methods, for example, have so far found fewer applications outside the field of atomic structure but are likely to prove more useful in the future, and I believe it very desirable for the student to have them available, even though he may not study them in his graduate work. This second volume carries the subject in most respects as far as the excellent and well-known work of Condon and Shortley, "Theory of Atomic Spectra" (Cambridge University Press, 1935), and in many respects it goes further, since there have been many advances in the field since that book was written. I must acknowledge here my debt to that book and my respect for its pioneering effort in the field.

As I mentioned at the beginning of this Preface, it is my hope to follow this book with further ones, on more or less the same level, treating the theory of molecules and of solids. These later books will make use of the present one to give the fundamental grounding which they require; for practically all the more advanced methods of molecular and solid-state theory are the outgrowths of problems which are already met in the study of atomic structure.

In the present state of science the study of atomic structure is needed by many persons other than the theoretical physicist. The chemist, the metallurgist, the electrical engineer, all are meeting problems of the application of quantum theory to the study of matter as very essential parts of their subjects. Often these other workers have not had as thorough a grounding in quantum mechanics and its applications as they need to handle their subjects properly. I have had them in mind, just as much as the professional physicist, in writing this book and shall continue to keep them in mind in the further books in this series. I believe that it is a mistake to think that a chemist or an engineer who wishes to study the application of quantum mechanics to his field can be satisfied with a more superficial treatment than a physicist can. In other words, I do not think that the present two volumes go too far for these workers. But since they often have a restricted background in theoretical physics, I have tried to make this book as complete as possible, so that it can be read without the need of consulting other texts, aside from those on mathematics, with which in these days most engineers are well acquainted.

There is one other comment which I might make concerning the theoretical physicist. In these days physics has become divided very sharply into two categories: nuclear and nonnuclear physics, the latter including the topics taken up in the present series of books. The training of nuclear physicists is often deficient in the study of chemical and solid-state physics. I hope that the present series of books may help remedy this deficiency. I feel, specifically, that there is nothing in the present two volumes which is not as essential to a nuclear physicist as to a chemical or solid-state physicist. Many of the topics coming into nuclear theory, such as multiplet theory, vector coupling, and so on, are taken over rather directly from ordinary atomic theory. It may well be that the present work will prove to be a useful introduction to these topics, for nuclear physicists.

Finally I should like to acknowledge the great stimulation, in the writing of this book and of the others which I hope will follow it, of the members of the Solid-State and Molecular Theory Group at the Massachusetts Institute of Technology, and in particular of Professor G. F. Koster of that group. The chance of talking over the various problems of the quantum theory of matter with the members of the group, over the past eight years or more, has been as helpful to me as I hope it has been to the members of the group. I should also like to acknowledge the helpfulness of the Office of Naval Research, and of the Lincoln Laboratory, in extending the financial support which has made that group possible.

John C. Slater

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The Historical Development of Modern Physics, from 1900 to Bohr's Theory

1-1. Introduction. The first half of the present century has been one of the most fruitful periods in the development of physics. It has seen the theory of relativity, the quantum theory, and modern ideas of the structure of atoms, molecules, and solids come into existence. There have been several other very exciting times in the history of physics. One came with the development of classical mechanics, by Galileo, Huygens, Kepler, and Newton, in the seventeenth century. Another was the development of the wave theory of light, by Young and Fresnel, at the beginning of the nineteenth century. Still another was the development of our ideas of electromagnetism, starting with Oersted, Faraday, and others, and culminating in the theoretical work of Maxwell, showing that electromagnetic waves and light were identical; this was a product of the middle of the nineteenth century. A later nineteenth-century development was the theory of heat, leading to the kinetic theory of gases and the theory of statistical mechanics, by Clausius, Boltzmann, and Gibbs. All these great advances in the science were essentially complete by 1900, and the stage was set for another and different development, along atomic lines. The present century has seen this development, and it deserves to rank with the others in importance, if it does not in fact overshadow them. Perhaps the leading names to be attached to these twentieth-century discoveries are Planck,[1] Einstein,[2] Rutherford,[3] Bohr,[4] Heisenberg,[5] and Schrödinger.[6] They rank with the great physicists of history.

[1] M. Planck, *Ann. Physik,* **4**:553 (1901).
[2] A. Einstein, *Ann. Physik,* **17**:891 (1905); **18**:639 (1905).
[3] E. Rutherford, *Phil. Mag.,* **21**:669 (1911).
[4] N. Bohr, *Phil. Mag.,* **26**(1):476 (1913).
[5] W. Heisenberg, *Z. Physik,* **33**:879 (1925).
[6] E. Schrödinger, *Ann. Physik,* **79**:361, 489, 734; **80**:437, **81**:109 (1926).

The layman has become better acquainted with the name of Einstein and his theory of relativity than with any of the other results of twentieth-century physics. His famous equation $E = mc^2$, where m is a mass, c the velocity of light, and where the equation states that this mass is equivalent to an energy E, is familiar to everyone, along with its application to nuclear physics and the development of nuclear energy. In contrast, Rutherford, who made the discovery of the nuclear atom, and Planck, Bohr, Heisenberg, and Schrödinger, who developed the quantum theory and its application to atomic structure, are less well known. The physicist ranks them as equally significant, however. They will concern us in our work more than Einstein and the theory of relativity. That theory is particularly important when we are dealing with very high energies, very great velocities approaching the velocity of light. Such questions concern us when we are dealing with the atomic nucleus. But one of the facts emerging from our present knowledge of the atom is that there is a very clear-cut distinction between the phenomena of the atomic nucleus and those of the outer part of the atom. All ordinary effects of heat, light, electricity and magnetism, chemistry, metallurgy, and so on, arise entirely from the outer part of the atom. They are not concerned with very great energies; and, for them, relativity plays the part of a minor correction to classical mechanics. On the contrary, it is for just such problems relating to very small systems, on an atomic scale, that the quantum theory is needed. Our task in this volume will be to review the present theory of these phenomena which arise from the outer parts of atoms; we shall omit the nuclear phenomena, not because they are not important but because to include them would make an impracticably large book. Hence we shall use relativity only incidentally, but the quantum theory must be our principal topic.

The development of the quantum theory stretched over 25 years, and there are three vital dates to remember in connection with it, at the beginning, the middle, and the end of the period. In 1901 Planck made the first suggestion of the quantum theory. In 1913 Bohr found how to apply it to the theory of the hydrogen atom, making the first real advance in our understanding of the dynamics of the particles in the atom. And in 1926 Schrödinger discovered the equation which bears his name, which furnished the real mathematical basis of the theory, a basis which was partly foreshadowed in the preceding year, 1925, in a different but equivalent form, by Heisenberg. Since 1926, we have been engaged in working out the consequences of Schrödinger's formulation of the theory, which is known as wave mechanics, and in applying it to the many problems of atomic, molecular, and solid-state structure. We feel that the theory, as now formulated, provides the precise mathematical foundation for all these phenomena, just as Newton's laws provide the foundation for classical mechanics and Maxwell's equations that for electromagnetism. Unfortunately, wave mechanics is a much more difficult branch of mathematics than either of these others, and we are still far from having worked out all the consequences of the theoretical discoveries made in 1926. But the progress has been great, and we can now give a very convincing picture of the structure of atoms and of their behavior under all sorts of external conditions. This is the topic of our book.

In the major part of the present work, we shall assume the principles of wave mechanics as the foundation of our treatment, just as a text on classical mechanics assumes Newton's law or one on electromagnetism assumes Maxwell's equations, and we shall proceed from these principles in a deductive way, to try to explain the behavior of matter. But the reader will not appreciate the subject properly if he is not familiar with the processes of discovery which had to be passed through in the period from 1901 to 1926, to develop these laws. Such an inductive period in science is in some ways more stimulating than a deductive period, in which one is merely working out the consequences of principles which everyone admits are true. To give the reader a little of this appreciation, we present in the first two chapters a short sketch of the historical development of physics, during the momentous quarter century from 1901 to 1926.

1-2. The Electron and the Nuclear Atom. A number of observations during the nineteenth century had indicated that atoms had some sort of internal structure, of an electrical nature. One type of information came from Faraday's experiments on electrolysis. Faraday found that, when electric current passed through an ionic solution, material was deposited on the electrodes. But, furthermore, he observed that the amount deposited was always proportional to the amount of charge transferred by the current. It was as if each ion that had passed through the electrolytic tank had carried just so much charge. If there had been a good measurement of the mass of an atom in those days, Faraday from his experiments could have said just how big this charge was. Crude estimates of atomic masses were available, and hence crude guesses as to this charge were possible. We know now that the charge, for a monovalent ion, is just one electronic charge; and, in the way indicated, there were rough estimates of this quantity by the end of the nineteenth century. The name electron, for this unit of charge, was invented by the Englishman Stoney, in the 1880s.

Before the end of the century, the electron had been discovered as an isolated particle. Crookes, J. J. Thomson, and many others had been making experiments on electrical discharges in gases. They found very good evidence that charged particles, carrying both positive and negative charges, existed in these discharges. They deflected those particles in electric and magnetic fields, just about at the close of the century, and from their dynamics made estimates of the ratio of their charge to mass. From this information it was found that some of the negatively charged particles had a mass small compared with an atomic mass; it was assumed that these particles were the electrons themselves. The positively charged particles, however, called ions, proved to have masses of atomic size.

There was evidence that atoms contained not only electrons but building blocks of other types as well. One could not fail to observe, as Prout had noticed fairly early in the nineteenth century, that the atomic weights of many of the elements proved to be surprisingly close to integers; and Prout had suggested that they were made out of fundamental particles, perhaps hydrogen atoms, all alike. This hypothesis of course came up against the obvious obstacle that some of the atomic weights were very far from integers, and it remained for the discovery of isotopes in the present century to remove this difficulty and show that Prout's hypothesis really had foundation.

Finally, during the last years of the century, two new discoveries greatly excited the physicists. Röntgen, in 1895, discovered the X rays, or roentgen rays. These rays, capable of passing through matter, were completely different from anything observed before. Their discovery was followed almost immediately by Becquerel's discovery of radioactivity, from the observation that uranium emitted rays which, like the X rays, could pass through matter and in fact could blacken a photographic plate even if it were wrapped up in an opaque covering. It was discovered that in radioactive disintegrations several types of radiation were emitted, and by 1900 J. J. Thomson, the Curies, Crookes, Rutherford, and Soddy were all working actively on the problem of finding what they were. Soon, also, the chemical separation of radium from uranium by the Curies, and other similar experiments, had shown that a number of elements were radioactive.

It did not take long to establish the nature of the types of radiation emitted by radioactive atoms, which Rutherford called alpha, beta, and gamma radiation. It was shown that the alpha and beta rays were deflected by electric and magnetic fields, so that they consisted of streams of charged particles, while the gamma rays were not deflected. By experiments on the deflection, it was shown that the beta rays were electrons, with the same ratio e/m, or ratio of charge to mass, which the electrons had already been found to have by J. J. Thomson. The alpha particles, however, were found to be positively charged, rather than negatively as the electrons were, and to have a value of e/m indicating that their mass was in the neighborhood of atomic masses, much greater than the electronic mass. By comparison with e/m experiments on other positive ions, it appeared that they were helium ions with a charge equal to twice the electronic charge. As for the gamma rays, which could not be deflected, it was soon shown that they were identical in nature with X rays, which had been shown to be electromagnetic waves like light; the X rays, however, had wavelengths much shorter than ordinary light, and the gamma rays had still shorter wavelengths.

The next question which arose was: How did these radiations come to be emitted from the radioactive atoms? This question was closely connected with another one, which at first seemed very puzzling: when a sample of radioactive material was examined, its properties often changed with time, in complicated ways, as if its composition were not staying constant. Rutherford and Soddy, in 1903, proposed an explanation which has proved to be correct and which tied together all the known facts about radioactivity. This explanation suggested that radioactive atoms could spontaneously explode, transforming themselves into other atoms, and that such explosions were going on all the time, so that in a given time interval a certain fraction of the atoms would blow up, quite independent of outside influences. If we have a number of atoms of which a fixed fraction is destroyed per second, this means that the number remaining at any time will decrease exponentially with the time (provided there are no new atoms being produced), and the length of time required for the number to be reduced to half its original value is called the half-life. Rutherford and Soddy found elements with all sorts of half-lives, from short ones of a few minutes to long ones of thousands or millions or billions of years.

The theory of Rutherford and Soddy went much further than this simple hypothesis of explosion, for they also were able to find out what were the products of one of the explosions. If an atom when it explodes transforms itself into another, then the number of atoms of this other type will gradually increase with time, unless an equilibrium is established by a subsequent explosion of the new type of atoms. By an elaborate series of tests, Rutherford and Soddy were able to show which atoms were transformed radioactively into which others, with the half-lives of each type. They were able to set up simultaneous differential equations for the numbers of atoms of the various types as functions of time, to solve these equations, and to show that they gave a complete explanation of the complicated effects which they had observed as to the time dependence of radioactivity. The case they made out for the transformation hypothesis was so convincing that it has never been questioned.

They found extremely interesting correlations between the chemical properties of the various radioactive elements which they discovered and the types of radiations which they emitted. They found that, when an atom emitted an alpha particle, the resulting atomic species showed