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ATOMIC PHYSICS

An Atomic Description of Physical Phenomena

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PREFACE

The text that follows represents an effort to present to students in their first year of graduate study the essential physical ideas upon which the current atomic theory of matter rests. It has evolved during the period from 1947 to 1954 in connection with the course given by the authors at the University of Pennsylvania. The students entering their first year of graduate work, during which this course is commonly taken, have all nominally had undergraduate courses in general and atomic physics, and also in mechanics and electricity and magnetism. However, their backgrounds and the quality of their preparation are generally very diverse, and, as indicated by the material in the first chapter, several weeks are given to a general summary of those aspects of classical physics which are essential to the concepts upon which atomic theory is based and to those fields of classical experimentation from which the techniques of atomic investigations have evolved. As the students are most commonly familiar with classical physics in terms of the absolute practical, or mks, system of units, this system of units has been used in the course and adopted in the text, though somewhat of a break with precedent in the field of atomic physics is thereby involved.

Atomic physics has acquired such an extensive history and so vast a literature during the first half of the twentieth century that it is no longer feasible to adopt a strictly historical type of approach to a one-year course, much less to make any pretense at completeness of coverage. The early forms of the quantum theory and the early work on gas discharges, X rays, etc., receive but cursory mention except as background against which the atomic concepts took form. Also the more peripheral areas which are covered by special courses such as quantum mechanics, complex spectra, polyatomic molecules, crystallography, nuclear structure, etc., are touched on very lightly if at all because of both lack of space and lack of any special competence on the part of the authors. The emphasis of the book is upon the extension of the basic classical concepts of physics into the realm of atomic phenomena and on the evolution of those particularly central and elemental quantum concepts, having no classical counterpart, which uniquely characterize the physics of elementary particles.

The last two chapters are then concerned with the statistical description of these particles and their aggregates; in particular those properties of gases, liquids, and solids with which the current theory is adequate to deal on an elementary mathematical level. Throughout the book an attempt is made to focus on the physics involved rather than upon the mathematical apparatus and techniques. The authors are well aware that they have fallen somewhat short of their objectives in this regard and have probably erred in some places by being too detailed and explicit and in others by being too brief or scanty. The general tenor of the presentation will probably be found more congenial to those experimentally minded physicists who, like the authors, admire mathematical elegance but are unable to practice it themselves.

The authors are greatly indebted to their colleagues at the University of Pennsylvania for their continued interest, their helpful suggestions and advice, and their constructive criticism of many sections. They are particularly indebted to Professors Herbert Callen, Sherman Frankel, Vernon Hughes, Peter Landsberg, Enos Witmer, and Paul Yergin for their assistance in the final stages of preparing this manuscript for the printers.

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CHAPTER 1

CLASSICAL FOUNDATIONS OF ATOMIC THEORY

1.1. Scope and Methods of Physical Science. The study of physical science is a variety of intellectual exploration. Of necessity one progresses from the known to the unknown erecting a framework of theory within which quantitative observations form an ordered pattern. This process is accomplished in terms of mental concepts brought to the task, and these are themselves derived from earlier and simpler sensory experiences. Of course many of the primary facts of observation are of great interest in themselves. But to a still greater degree their interrelationships and their implications contribute to our intellectual grasp of the totality of phenomena that constitutes our environment. The objective of the process in which our mental abilities are employed to digest the vast diversity of our observations is the formulation in words or other symbols of an adequate and ordered description of all physical phenomena in terms simple enough for us to grasp. Such a description is called a scientific theory. The word "understanding" is generally used in connection with observed phenomena in the sense of the achievement of an adequate description or the formulation of a satisfactory theory. Understanding is also used in reference to those irreducible concepts in terms of which a theory is formulated, as indicating a mental comprehension or intuitive grasp of these concepts and their relationships with one another.

A description or theory is considered adequate to the extent that it provides a universal, precise, and simple account of observation. Present theories are all inadequate in one or more of these respects, and they do not provide a simple ordering of all of the essential aspects of observation. The objective of science is to extend our observations and to improve the theories that order them. A theory is conceived and evolves by the interplay of inductive and deductive processes. Initial simple observations and imaginative triumphs of conception suggest hypotheses. Further observation and conceptual syntheses contradict, confirm, modify, or extend these hypotheses. Additional concepts are evolved, and relationships and suggestive analogies are noted which indicate profitable directions for further observation. Simplification and unification are striven for, and irrelevancies and errors are sought out and eliminated. The raw data of sensory perception are thus eventually ordered by the resulting description. Our understanding deepens through a simplification of the elementary essential concepts that remain. Uniqueness can hardly be considered as an objective for there are no adequate criteria with which to assess the possibility of constructing alternative explanations or descriptions. But as a theory develops the breadth to account for a wide diversity of observations and as the concepts it employs become reduced to the simplest and most elemental terms, the possibility of formulating completely different alternative descriptions appears to become more and more remote.

A scientific theory resembles a fabric in that its strength and acceptability come from the manifold of separate interwoven threads of connection between observations of different types. The greater the intimacy and extent of relatedness provided by a theory between the phenomena of observation, the more significant and important does the theory become. A description that brings together but a few phenomena in terms of simpler common concepts is a suggestive beginning warranting further exploration, but it is a web of only a few strands upon which little reliance is placed. As the number and variety of observations compatible with the initial small number of hypotheses are extended, the theory takes on generality, it represents a more obvious economy of thought, and it eventually appears actually to provide in some sense an intellectual grasp of a whole aggregate of separate observations and phenomena. The interlacing of the strands of connection between observations is so compact that additional confirming observations are immediately suggested, and the pattern that is finally presented takes on a significance of its own, transcending the sum of the individual observations from which it has been developed. Certain portions of this fabric even tend to take on a rigidity which conditions our acceptance of new phenomena. Thus the basic position of the conservation laws, such as those of mass, energy, and momentum, in dynamical theory imposes certain habits of thought in terms of which the phenomena presented by new elementary particles, such as the varieties of mesons currently being observed, are interpreted. The present difficulties which are being encountered in achieving a consistent theory of these particles may necessitate a restatement of fundamental laws in broader terms than are known at present.

The science of physics relates primarily to the basic phenomena which are associated with the central concepts of mass, charge, motion, and energy. In the previous century physics was considered to represent a more or less unrelated group of fields such as mechanics, properties of matter, heat, sound, light, electricity, and magnetism. The atomic concept of matter and the observed interactions of matter and radiation supplied a common basis for unification of these separate fields and also led to a great expansion of the phenomena included within the field of physics. The experimental observations and the theory which unites them are in a continuous state of flux and growth. The present concepts do not appear to be altogether adequate for the construction of a completely satisfactory physical theory, and in spite of the great progress that has been made our understanding of elementary particles is but fragmentary and imperfect. Much of a very fundamental nature remains to be done, and, in consequence, a grasp of the general methodology and of the criteria for the attainment of the objectives of science is particularly important.

1.2. Evolution of Atomic Concepts. The growth of physical theory is a cumulative process which takes place by painstaking accretion with occasional brilliant flashes of insight, proceeding essentially from the known to the unknown. The concepts and methods of thought that have gone into the construction of atomic theory are those which were current in classical physics together with those drawn from fields of mathematics and certain other quite novel concepts that have been slowly and painfully evolved in the course of recent physical research. Classical physics dealt almost exclusively with objects of simple sensory perception. It was concerned with "man-sized" objects and "man-sized" forces. Color, sound, taste, smell, and surface texture were significant attributes of the objects of observation. Concepts of wave motion came from observing taut strings and the transient conformation of a liquid surface. The apparent permanence of most material objects suggested the reasonableness of conservation laws. The first notions of force and weight and the properties of fluids came from muscular and tactile sensations. These types of qualitative observation were very important in the development of the background of mental images in terms of which descriptions could be formulated and diverse observations related to one another.

Physics, however, is characterized by its emphasis on quantitative relationships. Careful observations led to a knowledge of the existence of such relationships, and mathematics provided a simple and unambiguous method of stating them. The type of sensory data which could yield precise quantitative information assumed the major rôle in contributing to the development of the science. The comparison of lengths, the recording of pointer readings of clocks and balances, and the use of spring-type standards of forces and torques which produced other pointer readings led to the primary reliance on this simple use of the sense of sight as the chief source of quantitative information. The emphasis on numerical description and accuracy tended to sharpen the basic concepts and to reduce the importance of those which could not be stated with precision. The mathematical techniques which were used to express the relationships between concepts were found to be applicable widely throughout the classical subfields of physics and in fact formed the principal unifying link between them. The ideas of coordinate systems and their transformations, vectors, tensors, invariants, and many other concepts from the field of pure mathematics contributed immeasurably to the evolution of simple, precise formalisms in terms of which phenomena could be described and theories expressed.

As the concept of the atomicity of matter evolved from the first simple chemical and physical observations it became clear that the ultimate particles were much smaller than the samples of matter previously dealt with. If these ultimate particles are too small to be seen or felt, localization can only be inferred. Hearing is of no use as a sense for direct perception, and color also ceases to be a significant attribute. Thus it is seen that only certain of the concepts of classical physics, primarily those of a precisely defined and quantitative character, are capable of meaningful extension down to these minute dimensions and hence likely to be of use in the characterization of atoms. The common impressionistic descriptions of everyday objects and occurrences in terms of shape, color, size, texture, and sound find no application in atomic descriptions. Ordinary language largely fails as a method of precise characterization; few common adjectives and but a handful of verbs remain useful. Of course the language of common communication is used to delineate those concepts which are found capable of meaningful extension into the atomic domain, but the precise statements that are made regarding their relationships must be couched in mathematical terms. The field is one of stark utilitarian simplicity; atoms and their constituents have few properties, so there is little variety in what can be said about them. Nevertheless, the statements that can be made are highly precise and carry as their implications all the more complex descriptions of large-scale phenomena.

The attributes with which present theories endow atomic particles may well be only the simplest of those which they will eventually be found to possess. Already, novel concepts such as *parity* and *spin*, which have no direct large-scale classical analogues, have had to be devised. Others may yet be required as the theory evolves. The relationship between direct experiment and ultimate theory in atomic physics is a more difficult and derivative one than in the case of gross or large-scale classical physics. Individual atomic events are not observed directly, though their consequences may be, and hence greater reliance must be placed on logical inference and methodology than in most other branches of science. The relation between an atomic property and an observational test is often a complex one and requires considerable intervening logical connection. This restricts the use of simple, direct inference, and the results of many lines of inquiry are frequently required to establish conclusively the existence of an atomic characteristic.

The concepts of atomic physics are drawn from classical physics, and the instruments used in atomic research are those which were evolved from classical laboratory techniques. Thus an intimate knowledge of the fields of mechanics and electricity is essential to an understanding of atomic theory. Many of the experimental verifications of atomic properties depend on observations of the properties of matter on a large scale. Thus the study of thermodynamics and the statistical behavior of large numbers of atoms, which provides a connection between atomic attributes and the gross properties of matter, is very important. A knowledge of the basic principles in these classical fields and a familiarity with mathematical techniques concerned with them are necessary before undertaking the study of atoms, their elementary constituents, and their combinations in molecules and crystals. The extensive success that has been achieved in accounting for the properties of atoms and atomic systems constitutes strong evidence for the general adequacy of present concepts and theories. The concepts and the theory are basically simple, though somewhat unfamiliar, and with a remarkable elegance and economy of hypotheses they account for a vast diversity of phenomena throughout all of physical observation.

The theory, however, is by no means perfect, and its further development constitutes one of the most absorbingly interesting fields of scientific activity today. One class of current problems centers on the technical difficulties surrounding the mathematical description of complex atoms and molecules involving many electrons and nuclei. Here the laws and concepts appear to be sufficiently well understood to assure a detailed and satisfactory account if the complicated mathematical expressions could be handled. The second and more intriguing class of problems is that in which ideological difficulties are clearly fundamental. These involve the nature of elementary particles which are found to be either permanently or transiently associated with nuclear and high-energy processes. Here present concepts may well be inadequate for construction of a satisfactory theory; certainly more extensive experimental and intellectual investigation will be necessary before the interaction between elemental entities can be understood. These are the frontiers of atomic physics which are now the focus of research effort.

The sections which follow in this chapter summarize those classical concepts and procedures which are basic to the formulation of the atomic theory developed in subsequent chapters. The purpose is merely to organize and recall those fields of mechanics, thermodynamics, and electricity which are assumed to be familiar from courses in these subjects.

The discussion of electromagnetic dipole radiation is somewhat more extended, as this matter is frequently not treated in elementary courses in electricity. More complete accounts of these subjects are to be found in the general references listed at the end of this chapter.

1.3. Newtonian Mechanics. Newtonian mechanics deals with the commonly encountered motion of material objects. A description of this motion involves a statement of the positions of the objects as functions of time, and for this purpose coordinate systems and standards of *length* and *time* are the first requirements. The position of a point relative to an origin may be given in terms of a cartesian coordinate system and a unit of length. The variation in position of a point or a series of points forming an extended body requires for its quantitative description the introduction of a unit of time. The definition of units is always quite arbitrary, and here the so-called *mks* system will be adopted. In this system the unit of length is the meter, which is the interval between two marks on an arbitrarily chosen metal bar, and the unit of time is the second, which is an arbitrarily chosen fraction of the mean solar day. Though the choice of units is inherently arbitrary and quite without effect on the content of physical laws, the constancy of the velocity of light and the characteristic frequencies of the electromagnetic radiation emitted by atoms suggest the choice of certain other standards of length and time as having a more natural relationship to invariant quantities of observation. Thus the wavelength of a line in the red portion of the cadmium spectrum or a spectrum line observed to be emitted from a mercury glow discharge when the mercury consists of a single isotope is more readily reproducible than the arbitrary meter and can be defined and compared with a precision equal to or even greater than that with which meter sticks can be compared. Similarly, the reciprocal of natural atomic or molecular frequencies can be used as standards of time in "atomic clocks" such as those of the U.S. National Bureau of Standards or the British National Physical Laboratory. Such standards appear to be as reliable, reproducible, and convenient as the one derived from astronomical observation, and very high accuracies of comparison can be achieved with ease.

The initial and final data in a mechanical problem, which is the prototype of any set of quantitative observations, are the positions of objects at the initial and final times. To describe the phenomena that are observed, additional concepts are convenient. Two of these are the derived kinematic concepts of *velocity* and *acceleration*, which are the rate of change of position and rate of change of velocity, respectively. The laws of classical, or Newtonian, mechanics relate the motion of bodies or certain readily identifiable quantities of matter to what are called *forces*. The concept of force is one of which we have an immediate, though of course only qualitative, kinesthetic appreciation. The phrase "quantity of matter" is made precise by introducing the concept of *mass*. The mass of a body is a quantity that can be measured, most commonly by the use of a gravity balance. The unit of mass in the system here adopted is the kilogram, which is the mass of an arbitrarily chosen block of platinum approximately equivalent in mass to a cube of water a tenth of a meter on a side. It is permanent and reproducible and can be compared with other masses to about the same accuracy as for the other two basic units. Here again an atomic standard may eventually offer certain advantages, but presently available techniques for comparing atomic masses with gross masses do not as yet offer acceptable precision.

The laws of mechanics can be stated most generally and conveniently in terms of the concept of *momentum*, which is defined as the product of mass and velocity. Mass is a scalar quantity, generally designated by the letter m, and velocity (like position relative to an origin) is a vector quantity having both magnitude and direction, generally designated by the letter $\mathbf{v}$. Thus the momentum $\mathbf{p}$ is defined as $\mathbf{p} = m\mathbf{v}$. The fundamental equation of mechanics which relates mass, motion, and force is the following:

$$\mathbf{F} = \frac{d\mathbf{p}}{dt} \tag{1.1}$$

The quantity on the right is the rate at which momentum changes with time, and this equation defines the mechanical concept of force. It also defines the unit of force in the system of units used for measuring momentum and time. In the mks system the unit of force which causes a change of momentum at the rate of one kilogram meter per second per second is called the newton. Equation (1.1) is a vector relation illustrated in Fig. 1.1. There are three analogous equations between the vector components of the forces and rates at which the vector components of the momentum change. This definition of force is observed to be in general qualitative concordance with our kinesthetic understanding of the term.

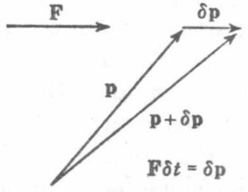

FIG. 1.1. Fundamental law of mechanics.

Through this equation, physics deals with forces of all types which are thought of in various connections as having different natures or origins. Classical mechanics is concerned to a great extent with contact forces such as those involved when one pushes against an object or when two pieces of matter collide. In the description of such events surfaces and areas of contact are involved, but such concepts are found to be of little use in increasing our understanding of forces on an atomic scale. Mechanics is not concerned with the nature of the forces involved since these do not appear in the final answer to a problem. The initial data are the positions of certain objects at certain times, and the predictions of mechanics relate to their positions at later times. Forces are eliminated from the final result by the intervening calculations. Physics as a whole, however, is concerned with the nature of the forces that are observed to bring about changes in momenta, and to the extent that the concept of force is utilized the objective is to account for the presence of forces in terms of simpler and more fundamental relationships between interacting particles.

Historically, the first reduction of a force into more elemental terms was the formulation of the universal law of gravitation by Newton. This law states that a property of a mass is that it exerts on all other masses an attractive force which is proportional to the masses involved and inversely proportional to the square of their separations. This may be expressed quantitatively in terms of kilograms and meters by

$$\mathbf{F}_{m_1} = G\frac{m_1 m_2}{r^2}\mathbf{r}_{12} \tag{1.2}$$

where $\mathbf{F}_{m_1}$ is the force in newtons on the mass m_1 exerted by the mass m_2 at a distance r, $\mathbf{r}_{12}$ is a unit vector from m_1 toward m_2, and G is the gravitational constant determined experimentally to be $(6.670 \pm 0.005) \times 10^{-11}$ newton-m^2 kg^{-2}. The equivalence between inertial mass, which is the m of the equation $\mathbf{p} = m\mathbf{v}$, and gravitational mass, which is the m of Eq. (1.2), is shown by the concordance of Eqs. (1.1) and (1.2) with experimental observation. A second elemental source of force, which is particularly important in atomic physics, is that which is identified with electric charges. Mechanics per se, however, is not concerned with these matters but rather with the motion of particles when subjected to forces of whatever type.

Equation (1.1) is incomplete as a statement of the principles of mechanics since forces do not appear in the final answer to a mechanical problem. An observation, also due to Newton, relating the forces between two interacting bodies must also be included. This can be stated as follows: The force exerted by one body on another is equal in magnitude and opposite in direction to that exerted by the second body on the first. Alternatively, this may be stated as the *conservation of momentum* by saying that the total momentum of a closed system of particles subject only to forces between them and not to forces of external origin is constant. The equivalence of these statements can be seen by the use of Eq. (1.1). If, within a large group of interacting particles, $\mathbf{F}_{ij}$ is the force exerted by particle i on particle j at the time t and $\mathbf{p}_j$ is the momentum of the jth particle, Eq. (1.1) for all the particles may be added together to yield

$$\sum_i \sum_j \mathbf{F}_{ij} = \frac{d}{dt} \sum_j \mathbf{p}_j \qquad (i \neq j)$$

If $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$, which states the equality of action and reaction, the sum on the left cancels in pairs and the rate of change of $\sum_j \mathbf{p}_j$ is zero, or $\sum_j \mathbf{p}_j$ is a constant. The law of conservation of momentum is a most fundamental one and is applicable in this form to all simple mechanical phenomena. In the case of electromagnetic phenomena all the forces acting between the elementary constituent particles are not of such a type that their directions coincide with the lines of centers and the mechanical momentum is not conserved. However, following the mechanical tradition, it has been found possible to formulate the theory of electromagnetic phenomena in such a way that an analogous generalization emerges, and what may be considered as the sum of the mechanical and electromagnetic momenta of a complete system of interacting particles is an invariant quantity.

Considering only the equal-and-opposite line-of-center type of force, a quantity known as the *angular momentum*, defined as the vector product of the vector representing distance from some arbitrary point of origin and the vector momentum, displays a conservation property. The total angular momentum $\mathbf{L}$ of a large group of particles is given by the vector sum of the angular momenta of the individual particles,

$$\mathbf{L} = \sum_i \mathbf{l}_i = \sum_i m_i \mathbf{r}_i \times \dot{\mathbf{r}}_i$$

Taking the derivative of $\mathbf{L}$ with respect to the time,

$$\frac{d\mathbf{L}}{dt} = \sum_i m_i \dot{\mathbf{r}}_i \times \dot{\mathbf{r}}_i + \sum_i m_i \mathbf{r}_i \times \ddot{\mathbf{r}}_i$$

The vector product of $\dot{\mathbf{r}}_i$ with itself vanishes, and by Eq. (1.1) $m_i \ddot{\mathbf{r}}_i$ can be written as $\mathbf{F}_i + \sum_j \mathbf{F}_{ji}$, where $\mathbf{F}_i$ is any external force acting on particle i and $\mathbf{F}_{ji}$ is the force exerted on particle i by particle j. Thus

$$\frac{d\mathbf{L}}{dt} = \sum_i \mathbf{r}_i \times \mathbf{F}_i + \sum_i \sum_j \mathbf{r}_i \times \mathbf{F}_{ji} \qquad (i \neq j)$$

Since $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$ the double sum can be written in pairs as

$$\tfrac{1}{2} \sum_j \sum_i (\mathbf{r}_j - \mathbf{r}_i) \times \mathbf{F}_{ji}$$

If $(\mathbf{r}_j - \mathbf{r}_i)$, which is the vector from i to j (see Fig. 1.2), is collinear with $\mathbf{F}_{ij}$, this sum vanishes and the internal forces make no change in total angular momentum of the system of particles. The sum $\sum_i \mathbf{r}_i \times \mathbf{F}_i$ is defined as the total torque $\mathbf{T}$, and the equation of rotational motion is

$$\mathbf{T} = \frac{d\mathbf{L}}{dt} \tag{1.3}$$

If there are no external forces, $\mathbf{F}_i = 0$; hence $\mathbf{T} = 0$, and $\mathbf{L}$ does not change with time. Thus the angular momentum is said to be conserved. The principle of conservation of angular momentum appears to be as fundamental and capable of as deep extension into the realm of atomic physics as the conservation of linear momentum.

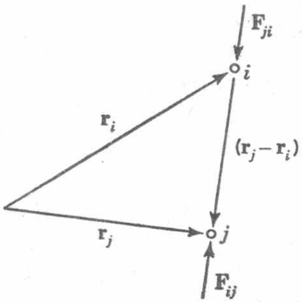

FIG. 1.2. Forces collinear with vector separations.

The concept of *energy*, which evolved from that of work, is also of primary importance in atomic theory. Muscular sensations and the relation of human effort to the accomplishment of alterations in the positions of bodies of matter led to the concept of work, and in general conformity with these ideas work is quantitatively defined for physical purposes as the integral of the scalar product of the force and the displacement which describes the resulting motion. The energy concept has been greatly extended from the form in which it initially appeared in the subject of mechanics, and it is very largely through this extension of the concept of energy that the prevailing unification has been brought about in the subfields of classical physics. The adoption of the principle of the conservation of energy, which survived the extensions and inclusions unifying the classical fields of physics, has had a profound effect upon the concepts of atomic physics and the theory that interrelates these concepts. To kinetic energy and the various forms of potential energy of gravitation, hydrodynamics, and elasticity was added the concept of heat as a form of energy about 100 years ago. The concept of mass as a form of energy introduced at the beginning of this century was a great advance which followed closely on the application of the energy concept to electric, magnetic, and electromagnetic phenomena. More recently, still further extensions are involved in the so-called *exchange energy* of quantum mechanics and the nuclear binding energy.

A mechanical example provides the simplest illustration of the energy concept. If the vector force $\mathbf{F}$ of Eq. (1.1) is multiplied scalarly by the infinitesimal vector $d\mathbf{r}$ and the product integrated from some arbitrary