INTRODUCTION TO ATOMIC PHYSICS

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Preface

This book is part of a series of four separate texts covering the most important areas of modern physics. The other three volumes are: H. A. Enge, ***Introduction to Nuclear Physics***, Addison-Wesley, 1966, D. H. Perkins, ***Introduction to High-Energy Physics***, Addison-Wesley (in press), and a text, ***Introduction to Solid-State Physics***, to be published later.

The present text covers basically the area of atomic physics with wave mechanics, but it also has chapters on solid-state physics and nuclear physics. The book is suitable for a one-semester or two-trimester course in modern physics. The complete series of four books or any combination starting with the present volume can be used for a series of courses in modern physics.

The material covered in this book is arranged roughly in chronological order, not because the historical sense is so important, but because it has proved to be pedagogically advantageous. However, subjects, such as x-rays and nuclear physics, which developed parallel to the basic understanding of the atom and were parts of it, are treated in late chapters.

Chapters 1 through 5 and Chapter 10 are revised and "upgraded" chapters from Wehr and Richards' *Physics of the Atom*. Most of the rest of the material has been written by H. A. Enge, and both the "upgrading" and the new chapters are based on a course taught for a number of years at the Massachusetts Institute of Technology. This one-semester course covered atomic physics with quantum mechanics and was followed by a second-semester course in nuclear physics.

It is unavoidable in any modern physics text that a significant step-up in the level of difficulty occurs at the point where wave mechanics is introduced. The theory of wave mechanics is considerably more abstract than anything the average student has encountered at this point in his study of science. There is no way to soften the blow, although the science libraries are full of attempts. It is my experience that attempts to make wave mechanics look plausible by half-hearted "derivations" are misleading and leave the students frustrated because they are (of course) missing something in the derivations. I have therefore introduced wave mechanics as a series of postulates and justify the theory by the agreement between predicted and measured behaviors of atomic systems.

Prerequisites for a full understanding of the material covered here are courses in mechanics, electricity and magnetism, and differential equations. A few simple matrix multiplications are used, and a short appendix on matrix mechanics is included for those students who have not covered this subject.

It is a pleasure to acknowledge the cooperation, help, and advice of M. R. Wehr and J. A. Richards, Jr., particularly with respect to the upgrading of the material from their earlier book. This is also the place to acknowledge the fact that the atomic physics course referred to above was first developed at M. I. T. by W. W. Buechner, from whom I took it over. The organization of the material in this book is basically as it was presented by Buechner. Many details of presentation and many problems have also been retained. My sincere thanks go to Mrs. Mary E. White who typed the manuscript, corrected the English, and otherwise helped in many ways.

December 1971 H.A.E.

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CHAPTER 1

The Atomic View of Matter

1–1 INTRODUCTION

Atomic Physics is a relatively young science, having been developed mostly in this century. However, the idea that matter is built up of atoms (particles) is a very old one. The Greek philospher Democritus (c. 460–370 B.C.), for example, theorized that not only matter but also the human soul consists of particles. Democritus had one very essential characteristic needed by every student of science, the *inquisitive mind*. He lacked the scientific method (Galileo Galilei, 1564–1642) and, of course, the technology needed to get any further.

Because atomic physics deals with objects (atoms) and events that are not *directly* observable with man's senses, its development often leads along paths which run counter to common sense. As we consider things and events that are orders of magnitude removed from everyday experience, the difficulty of understanding their nature increases. Our common sense enables us to understand the relationship between a brick and a house. Conceiving of the earth as round may involve a little uncommon sense, but for most people it presents no great difficulty. However, the relationship between water and a water molecule is more difficult. While we can see the earth, whether flat or round, we cannot see a water molecule even with the best of instruments. All of our information about single water molecules is of an indirect kind, yet it is a very unsophisticated chemist for whom the concept of a single water molecule is not a part of his common sense. As a man's knowledge expands, more and more facts assume the aspect of "common sense." Certain velocity relationships are common sense. To an observer in a moving car, the velocity of another moving car appears different than to an observer standing beside the highway. In fact, a very young child once observed when the car in which he was traveling was passed by another, "We are backing up from the car ahead." However, the statement made by Albert Einstein that the velocity of light is the same for all observers regardless of their own velocities is initially very uncommon sense.

In Appendix 3 we attempt to show that his statement is reasonable and can appropriately be incorporated into our common sense. The conflict between the earth's actual roundness and its apparent flatness is resolved conceptually, i.e., by imaginative understanding, with the realization that the earth is a very big sphere. Somewhat similarly, the apparent conflict between our statements about relative velocities is resolved conceptually with the realization that the velocity of light is a very large velocity. Democritus, who could propose an atomic theory in about 400 B.C., would have the courage and imagination to face the ideas that lie before us.

It is the business of philosophers to discuss the nature of reality. It is the business of physicists (once called natural philosophers) to discuss the nature of physical reality. Philosophy, therefore, includes all of physics and a lot more besides. It is natural, then, that physics should have a continuing influence on philosophy. As physical discovery is quickly put into engineering practice and made to bear on man's physical environment, so it also affects the formulation of philosophical theory and bears directly on man's outlook and interpretation of life.

The old or classical physics of Newton was extraordinarily successful in dealing with events observed in his day. Using methods he developed, it is simple to equate the earth's gravitational force on the moon to the centripetal force and obtain verifiable relationships about the behavior of the moon. The same methods can be extended to orbits which cannot be regarded as circular. In fact, three observations of a new comet enable astronomers to foretell with great accuracy the entire future behavior of the comet. Given a certain amount of specific data known as initial or boundary conditions, classical Newtonian mechanics enables us to determine future events in a large number of situations. It is easy to move a step further and argue that what Newton has demonstrated to be true often, is true always, and that given sufficient initial data and boundary conditions, laws may be found which show every future event to be determined. The motion of a falling leaf or the fluctuations in the price of peaches may be very complex phenomena. It may require tremendous amounts of data and the application of very complicated laws which we do not yet understand to be able to make predictions in these cases. The important philosophical consequence of classical mechanics was not that every problem had been solved, but that a point of view had been established. It was felt that each new discovery would fall into the Newtonian mechanistic framework. Philosophical questions like the following became more pressing. Do we humans make decisions which alter the course of our lives or are we, like the bodies of the solar system, acting according to a set of inflexible laws and in accordance with a set of boundary conditions? Are we free or is our apparent ability to make decisions an illusion? Is everything we do beyond our responsibility, having been determined at the time of creation? Although mechanistic philosophy is rather repulsive when applied to ourselves, we nevertheless lean heavily upon it in interpreting things that go on about us. Indeed, the whole argument over whether human behavior is influenced more by heredity or environment is based on the assumption that human behavior is determined by some combination of the two.

To the extent that this mechanistic philosophy is based on classical physics, it is due for revision. Upon examination of events that are either very large or very small, we find that classical physics begins to fail. When a new theory or a modified theory has had to be applied in order to describe experimental observations, it has often resulted that the new theory is very different from classical physics. The method of attack, the mathematical techniques, and the form of the solution are often quite different. At one point we shall show that the observations of natural phenomena are inherently *uncertain*. It becomes evident, then, that if some circumstance had led to the development of atomic physics before classical physics, the influence of atomic physics on philosophy would have been against mechanism rather than for it.

Atomic physics has given us electronics and all that that word implies, including radio, radar, television, computers, etc. Atomic physics has given us nuclear energy. The new physics is as successful with submicroscopic events as classical physics was with large-scale events. But it may be that the most important benefits that can result from the study of atomic physics are philosophical rather than technical.

1-2 CHEMICAL EVIDENCE FOR THE ATOMIC VIEW OF MATTER

The speculations of Democritus and of the Epicurean school, whose philosophy was based on atomism, were not the generally accepted views of matter during the Middle Ages and the Renaissance. The prevailing concepts were those of Aristotle and the Stoic philosophers, who held that space, matter, and so on were continuous, and that all matter was one primordial stuff which was the habitat of four elementary principles—hotness, coldness, dryness, and wetness. Different materials differed in the degree of content of these principles. The hope of changing the amount of these principles in the various kinds of matter was the basis of alchemy. Not until the development of quantitative chemistry in the last half of the eighteenth century did the experimental evidence needed for evaluating the conflicting speculations about the constitution of matter begin to appear.

Antoine Lavoisier of France was outstanding among the early chemists. He evolved the present concept of a chemical element as "the last point which analysis is capable of reaching"; and he concluded from his observations on combustion that matter was conserved in chemical reactions.

In 1799 the French chemist J. L. Proust stated the law of definite or constant proportions, which summed up the results of his studies of the substances formed when pairs of elements are combined. The law is: *in every sample of any compound substance, formed or decomposed, the proportions by weight of the* *constituent elements are always the same.* This statement actually defines chemical compounds, because it differentiates them from solutions, alloys, and other materials which do not have definite composition.

The principal credit for founding the modern atomic theory of matter goes to John Dalton, a teacher in Manchester, England. His concern with atoms seems to have originated with his speculations about the solubilities of gases in water and with his interest in meteorology, which led him to try to explain the fact that the atmosphere is a homogeneous mixture of gases. Eventually, he believed that an element is composed of atoms that are both *physically* and *chemically* identical, and that the atoms of different elements differ from one another. In a paper he read at a meeting of the Manchester Literary and Philosophical Society in 1803, Dalton gave the first indication of the quantitative aspect of his atomic theory. He said, "An enquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new: I have lately been prosecuting this enquiry with remarkable success." This was followed by his work on the composition of such gases as methane (CH_4), ethylene (C_2H_4), carbon monoxide (CO), carbon dioxide (CO_2), and others which led him to propose the law of multiple proportions in 1804. This law states: *if substance A combines with substance B in two or more ways, forming substances C and D, then if mass A is held constant, the masses of B in the various products will be related in proportions which are the ratios of small integers.* The only plausible interpretation of this law is that when elementary substances combine, they do so as discrete entities or atoms. Dalton emphasized the importance of relative masses of atoms to serve as a guide in obtaining the composition of other substances, and stressed that a chemical symbol means not only the element but also a fixed mass of that element. The introduction of the concept of atomic masses* was Dalton's greatest contribution to the theory of chemistry, because it gave a precise quantitative basis to the older vague idea of atoms. This concept directed the attention of quantitative chemistry to the determination of the relative masses of atoms.

An important law pertaining to volumes of gases was announced by Gay-Lussac in 1808. He said that *if gas A combines with gas B to form gas C, all at the same temperature and pressure, then the ratios of the volumes of A, B, and C will all be ratios of simple integers.* Two examples of this law are (a) the combining of two volumes of hydrogen and one volume of oxygen to form two volumes of water vapor, and (b) the union of one volume of nitrogen and three volumes of hydrogen to produce two volumes of ammonia. The following are symbolic forms of these reactions:

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* It has been customary, particularly among chemists, to talk about atomic *weights.* This may be because chemists can determine relative atomic masses by weighing macroscopic samples of matter. To a physicist, the *mass* of an atom is much more meaningful than the weight. In these days of space travel, weightlessness is commonplace, but a substance never loses its mass.

$$\overset{\text{Hydrogen gas}}{\boxed{1\text{ vol}}\ \boxed{1\text{ vol}}} + \overset{\text{Oxygen gas}}{\boxed{1\text{ vol}}} \longrightarrow \overset{\text{Water vapor}}{\boxed{1\text{ vol}}\ \boxed{1\text{ vol}}}$$

$$\overset{\text{Nitrogen gas}}{\boxed{1\text{ vol}}} + \overset{\text{Hydrogen gas}}{\boxed{1\text{ vol}}\ \boxed{1\text{ vol}}\ \boxed{1\text{ vol}}} \longrightarrow \overset{\text{Ammonia gas}}{\boxed{1\text{ vol}}\ \boxed{1\text{ vol}}}$$

It is obvious that Gay-Lussac's law, like the law of multiple proportions, implies that the substances which participate in these reactions participate in discrete or corpuscular amounts. The ratio between the number of shoes worn to the number of people wearing them is almost an exact integer, namely two, showing that both people and shoes are discrete entities. The ratio of the number of tomatoes used per serving of tomato soup is quite a different kind of situation, and if the ratio is integral it is only by coincidence.

Gay-Lussac's law supported the work of Dalton, but it also raised difficult questions about the composition of an element in the gaseous state. In the case of the first reaction given, does each atom in the given oxygen gas divide to spread through the two volumes of water vapor? If so, the indivisibility of atoms must be abandoned. Or does each entity in the oxygen gas consist of a multiplicity of atoms? If so, how many atoms are grouped together? Similar questions can be raised about each of the gases in the two reactions given. It is evident that the numerical values of the relative masses of the atoms determined from these reactions will depend upon the answers to these questions.

In 1811, Avogadro, an Italian physicist, proposed the existence of different orders of small particles for the purpose of correlating the works of Dalton and Gay-Lussac. He postulated the existence of "elementary molecules" (atoms) as the smallest particles that can combine to form compounds, and the existence of "constituent molecules" (molecules of an element) and "integral molecules" (molecules of a compound) as the smallest particles of a body that can exist in the free state. He went on to state (without proof) a very important generalization, known as Avogadro's law, that *at the same temperature and pressure equal volumes of all gases contain the same number of molecules*. From this law and his concepts of atoms and molecules, Avogadro showed that the ammonia-producing reaction required that nitrogen gas consist of diatomic molecules and that oxygen must also be diatomic to account for the water-vapor reaction. He further concluded that water must consist of a union of two atoms of hydrogen and one atom of oxygen.

Unfortunately, the ideas advocated by Avogadro received little notice even when revived by Ampere in 1814. The notion that hydrogen and other gases were composed of diatomic molecules was ridiculed by Dalton and others, who would not conceive of a combination of atoms of the same kind. They asked, "If two hydrogen atoms in a container filled with this gas can cling together, why do not all cling together and condense to a liquid?" This is indeed a very good question. Science was not able to give a satisfactory answer until over a century later. (See the discussion of the covalent bond in Section 11-2.)

In the next two sections in this chapter we will describe some of the methods which were and still are used to determine the relative masses of atoms. The results obtained by the analytical chemists using these several methods during the first half of the nineteenth century were often contradictory. They frequently obtained different values for the atomic mass of the same element. By the 1850's inconsistencies were so numerous that many felt that the atomic theory of matter would have to be discarded. However, the contradictions were resolved in 1858 by the Italian chemist Cannizzaro, who had an intimate knowledge of the then known methods for determining atomic masses and a broad grasp of the whole field of chemistry. He showed that Avogadro really had provided a rational basis for finding atomic masses, and that the inconsistent results obtained by various experimenters resulted from a lack of clear distinction between atomic masses, equivalent masses, and molecular masses. The views of Cannizzaro received the approval of the scientific world when they were adopted by the international conference on atomic masses which met in Karlsruhe, Germany, in 1869. This, then, is the year in which the fundamental ideas of modern chemistry were widely accepted.

1-3 MOLECULAR MASSES

After Cannizzaro had clarified and established some of the basic definitions in chemistry, Avogadro's law opened the door to one of the methods for determining molecular masses. No one had any idea of what the mass of a single molecule was, but once there was a way of isolating equal numbers of different kinds of molecules, the relative masses could be determined. The hydrogen molecule was found to be the lightest molecule, and the hydrogen atom proved to be the lightest atom. In 1815 Proust had proposed that the relative atomic mass of hydrogen be arbitrarily taken as one. On this basis most other light atoms and molecules had relative masses which were nearly integers. But, for reasons to be discussed later, it turned out that the atomic masses of many of the heavier atoms were not very nearly integers. Hydrogen appeared to be a poor basis for the system, and more nearly integral atomic masses for all atoms could be obtained by making a heavier atom the basis of the system.

For many years physicists and chemists used two different systems, both based on the mass of oxygen. On the physics scale, the mass of the isotope (Section 2-7) of oxygen having 8 protons and 8 neutrons in the nucleus was set at 16. On the chemistry scale the natural mixture of oxygen isotopes was given an average mass value of 16. In 1961 the two scales were replaced by a common atomic-mass scale, in which the mass of the carbon isotope ^{12}C (6 protons and

6 neutrons) is set to 12. On this scale, the atomic mass of hydrogen is not exactly unity, although it is nearly so.

These relative molecular and atomic masses are all dimensionless ratios. If about four parts by weight of hydrogen were combined with 32 parts by weight of oxygen, about 36 parts by weight of water vapor can be formed, according to the familiar equation, $2H_2 + O_2 = 2H_2O$.

Chemists as well as physicists measure amounts of material in grams or in moles. A *mole* is defined as the amount of a given substance containing the same number of molecules as the number of atoms in 12 grams of ^{12}C. One mole of ^{12}C is 12 grams, one mole of carbon in its natural mixture of isotopes is 12.01115 grams, one mole of H_2O is 18.0153 grams, etc. The number of atoms in 12 grams of ^{12}C (number of molecules in a mole) is called Avogadro's number or the *Avogadro constant*, N_A, and it is of basic importance in physics and physical chemistry. (Note that the mole and the Avogadro constant have been defined in terms of 12 grams of ^{12}C. This is the modern practice. However, these definitions do not always conform to the MKSA system of units.* Therefore, we will on occasion use the kilomole, kmole, which is 1000 moles. Obviously a kilomole of carbon 12 has a mass of 12 kilograms.)

The value of the Avogadro constant was of relatively minor importance to chemistry in the early nineteenth century and its magnitude was not even estimated until Loschmidt did so in 1865. We will discuss Perrin's method of determining it later in this chapter. Here is an interesting case where knowing the existence of a number was more important than knowing its magnitude as, for example, in determining the relative masses of the atoms involved in the ammonia-producing hydrogen-nitrogen reaction previously described. The value of the Avogadro constant is by modern measurements

$$N_A = (6.02217 \pm 0.00004) \times 10^{23}$$

particles per mole. Only after the magnitude of the Avogadro constant was known could the absolute mass of an atomic particle be computed. Since N_A ^{12}C atoms of 12 u (mass units) is 12 grams, the mass (in grams) of one unit is clearly

$$1\ \text{u} = 1/N_A = (1.66054 \pm 0.00001) \times 10^{-24}\ \text{g}.$$

It follows from Avogadro's law that the volume of a mole of a gas is the same for all gases. The normal volume of a perfect gas or the standard molar

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* For students not familiar with the MKSA system, a brief review is given in Appendix 1.