

SERIES I

THE STRUCTURE OF THE ATOM

LECTURE 1

Comparison between the classical continuum theory and the quantum theory — Chief experimental results on the structure of the atom — General principles of the quantum theory — Examples.

Physics today is everywhere based on the theory of atoms. Through experimental and theoretical researches we have reached the conviction that matter is not infinitely divisible, but that there exist ultimate units of matter which cannot be further divided. However, it is not the atoms of the chemists that we feel authorized in calling "indivisible"; on the contrary they are very complicated structures composed of smaller elements. These are, from the point of view of recent investigations, the atoms of electricity, the (negative) electrons and the (positive) protons. It is conceivable that at a later epoch science will change its point of view and penetrate to still smaller elements; in this case the philosophical significance of atomistics could no longer be valued as highly. The last units would not be anything absolute, but only a measure of the present status of science. But I do not think that is so; I believe that we can hope that we have not to do with an endless chain of divisions, but that we are near the end of a finite chain, perhaps we have even attained it. The reasons that can be given for this optimism lie less in the experimental evidence for the reality of atoms, protons and electrons, which the new physics has furnished, than in the special character of the laws which govern the interactions of elementary electric particles. These laws have indeed properties which permit us to conclude that we are near their final formulation.

Such an assertion may seem too bold, because all philosophies of all ages have taught that human knowledge is incomplete, that each goal of knowledge is attained only at the cost of new puzzles. Up to the present, in physics as in other sciences, every result that our age has proclaimed as absolute has had to fall after a few years, decades or centuries, because new investigations have brought new knowledge and we have become used to consider the true laws of nature as unattainable ideals to which the so-called laws of physics are only successive approximations. Now, when I say that certain formulations of the laws of the atomistics of today have a character which is in a certain sense final, this does not fit in with our scheme of successive approximations and it becomes necessary that I offer an explanation. This special character that the atom possesses is the appearance of *whole numbers*. We pretend not only that in any body, for instance a piece of metal, there exist a certain finite number of atoms or electrons, but further that the properties of a single atom and the processes which occur during the interaction of several atoms are capable of being described by whole numbers. This is the substance of the *quantum theory*, the fundamental significance of which is based not only in its practical application but above all in its philosophical consequences considered here. To illustrate this idea we consider a small body free to move in a straight line. According to the usual ideas it can be at any time at any point. To fix this point we give the coördinate x measured from a point 0.

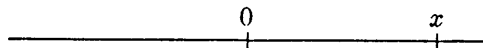


FIG. 1

But the accuracy of this indication depends entirely on experimental means of observation. If x can vary continuously, a more exact measurement may give us another decimal. For the processes in the atom, however, conditions seem to be different. We may compare them with the behavior of this body if we consider it infinitely small and allow it to occupy only certain discrete points which we shall number 1, 2, 3, The coördinate x can therefore only take the values 1, 2, 3, . . . but not, for instance, $\frac{1}{2}$ or 3.7. This is in fact the behavior of

the so-called quantum numbers by means of which we describe today the state of atoms. Should this process be always satisfactory we evidently stand before a new state of our knowledge. If the value of x should be exactly a whole number, then a determination of such a number once made could not be altered. If it had been determined that x is certainly not equal to 1, nor to 3 or 4, nor to any greater number, then there remains for x only the value 2, and a more accurate measurement cannot change anything. We have therefore definite elements in the statements of laws, and there seems to exist a tendency that laws obtain this essential final character when expressed as relations between whole numbers. I therefore do not exaggerate when I say that the year 1900, when Planck first stated his theory of quanta, marked the beginning of an entirely new conception of nature.

The theory of matter, as treated up to the present, still falls very short of this extreme view. To emphasize this standpoint, we consider again the body in the straight line with the coordinate x . Then the usual quantum theory corresponds somewhat to the condition that x be allowed to take all possible continuous values, but that then the integral values of x should be selected as stationary states through the so-called quantum conditions. This conception is altogether too unsatisfactory. For this reason we have sought at Göttingen to find a new formulation of the quantum theory in which only these integral values of x occur and intermediate fractional values have no meaning. This theory has been verified in the sense that certain fundamental difficulties that existed in the old quantum theory are not encountered in the new. On the other hand, calculations are rather complicated. Therefore I shall not begin my course of lectures with this new theory, but start with a short survey of the old theory. Let me remind you of the most important experimental investigations of the structure of atoms.

The first of these is the conception developed by Lenard and Rutherford, that the atom is composed of a positive *nucleus* surrounded by negative *electrons*. The simplest atom, that of hydrogen, consists of one electron revolving around the

simplest nucleus, a *proton*, each having the same charge $e = 4.77 \times 10^{-10}$ e.s.u., but different masses, the ratio of the masses being 1 : 1830. The nuclei of the other atoms are complex structures built up of protons and electrons, as shown by radioactive phenomena, but in these lectures we shall not discuss the structure of these nuclei, but treat them as mass-points with a charge which is an integral multiple Z of the charge e given above. This number Z is known as the atomic number and determines the position of the element in the periodic system. In the neutral atoms the number of electrons is also Z ; in negative ions the number of electrons is greater than Z , in positive ions it is less.

The forces binding the electrons to the nucleus are certainly of electrical nature. This has been proved by the experiments of Lenard on the scattering of cathode rays and the experiments of Rutherford and his students on the scattering of α -rays, in which it was shown that Coulomb's law of force holds for distances of the order of magnitude involved in this theory.

But the supposition of purely electrical forces leads to difficulties. There is a mathematical theorem which states that a system of electric charges cannot be in stable equilibrium; therefore Rutherford was compelled to assume that the electrons move around the nucleus in such a way that the centrifugal force balances the resultant of the electrical forces. But if electromagnetic laws can be applied to such a system, it must radiate energy until the electrons fall into the nucleus. A second difficulty arises from the kinetic theory of gases. We know that every molecule or atom of a gas under normal conditions collides with other molecules or atoms about 100,000,000 times per second. If the ordinary laws of mechanics held, there would be expected a slight change of the electron orbits at each collision and these changes would accumulate so that after one second the system would be materially altered. But we know that every molecule has a definite set of properties. It is therefore necessary to find a principle of stability which evidently cannot be derived from the ordinary laws of mechanics.

Niels Bohr has given this principle by applying the rules of quantum theory to atomic systems. These rules were devel-

oped by Max Planck in the study of the laws of heat radiation. He proved that it is impossible to explain the spectral distribution of the energy radiated by a black body if we make the ordinary assumption that energy can be divided into infinitely small parts; but it may be explained if we assume that the energy exists in quanta of finite size, $h\nu$, where ν is the frequency of the radiation and h is a constant, $h = 6.54 \times 10^{-27}$ erg. sec. This remarkable idea has been of the greatest fruitfulness in the development of physics, for it has been shown that the constant h and the quantum $h\nu$ play important rôles in many phenomena. In the photoelectric effect the kinetic energy of the photoelectron is given by $mv^2/2 = h\nu$, where ν is the frequency of the incident radiation. This equation, proposed by Einstein, was proved experimentally by Millikan and others and gave the first direct evidence of the existence of the quantum. It was followed by many other experiments of a similar kind of which I will mention only one group: that investigating the relation between the kinetic energy of an electron and the frequency of the light emitted as the result of the collision between this electron and an atom, first tested by Franck and Hertz and later developed by Compton, Foote, Mohler and many other American physicists.

All these experiments show that the production of radiation of a certain frequency requires a certain amount of kinetic energy. Niels Bohr has made the assumption that this law holds not only between kinetic energy and radiation, but between all kinds of energy and radiation. In this way he found a very simple interpretation of the fact that isolated atoms, as in a rarefied gas, emit a line spectrum, that is, a set of monochromatic light waves. He assumes that Einstein's law can be applied to the emission of a line in the spectrum in such a way that while the system loses a finite amount of internal energy $W_1 - W_2$, the frequency ν of the emitted light is connected with this loss of energy by the equation

$$W_1 - W_2 = h\nu. \quad (1)$$

To explain the whole system of lines of the atom Bohr postulated the existence of a system of so-called "stationary states"

in which the atom can exist without loss of energy by radiation, while keeping its total energy contents $W_1, W_2 \dots$. The frequency of every spectral line appears now as the difference of two terms W_1/h and W_2/h , in perfect agreement with the well-known optical fact formulated in the Ritz combination principle. At the same time this hypothesis solves the difficulty previously mentioned concerning the stability of atomic systems, for the energy necessary to change an atom from one stationary state to another is large, larger than that available at ordinary temperatures as a consequence of thermal agitation, therefore the atom remains unaltered.

These assumptions are in direct contradiction to classical dynamics, but lacking any knowledge of the exact laws of the new theory we use the classical laws as far as possible and then seek to alter them, when they lead nowhere. The chief problem becomes the determination of the stationary states and their energies; but first we show, after Einstein, that Bohr's principle suffices to give a very simple derivation of Planck's formula for *black-body radiation*.

Consider two stationary states W_1 and W_2 ($W_1 > W_2$). In statistical equilibrium they may exist in the amounts N_1 and N_2 . Then by Boltzmann's principle

$$\frac{N_2}{N_1} = \frac{e^{-W_2/kT}}{e^{-W_1/kT}} = e^{\frac{W_1 - W_2}{kT}}$$

and using Bohr's frequency condition (1):

$$\frac{N_2}{N_1} = e^{\frac{h\nu}{kT}}$$

In the classical theory, the interaction of atomic systems and radiation is made up of three processes:

1. If the atom is in a state of higher energy it loses energy spontaneously by outward radiation.
2. The external radiation field adds or subtracts energy to or from the atom depending on the phase and amplitude of the waves of which it consists. We call these processes:

- (a) positive absorption if the atom gains energy,
 (b) negative absorption if the atom loses energy through the action of the external field.

In the last two cases the contribution of these processes to the change of energy is proportional to the energy density ρ_ν .

In analogy to these we assume for the quantic interaction three corresponding processes. The following transitions occur between the two energy levels W_1 and W_2 :

1. Spontaneous decrease in energy through changes from W_1 to W_2 . The frequency with which these transitions occur is proportional to the number of systems, N_1 , which are in the initial state W_1 and is also dependent on the final state. For the number of these transitions we therefore write,

$$A_{12}N_1.$$

2a. Increases in energy due to the radiation field (transitions from W_2 to W_1). We place, likewise, for the number of such transitions

$$B_{21}N_2\rho_\nu.$$

2b. Decreases in energy due to the radiation field (transitions from W_1 to W_2). The number of such transitions is

$$B_{12}N_1\rho_\nu.$$

For statistical equilibrium between the states W_1 and W_2 it is required that

$$A_{12}N_1 = (B_{21}N_2 - B_{12}N_1)\rho_\nu,$$

from which

$$\rho_\nu = \frac{A_{12}}{B_{21}\frac{N_2}{N_1} - B_{12}} = \frac{A_{12}}{B_{21}e^{\frac{h\nu}{kT}} - B_{12}}. \quad (2)$$

It is natural to suppose that the classical laws are limiting cases of the quantum laws. Here the limiting case is that of high temperatures, where $h\nu$ is small compared with kT . Under

such conditions Equation (2) should go over into the classical law of Rayleigh and Jeans,

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

For large values of T (2) has the form

$$\rho_\nu = \frac{A_{12}}{B_{21} - B_{12} + B_{21} \frac{h\nu}{kT} + \dots}.$$

These two expressions become identical if

$$B_{12} = B_{21},$$

and

$$\frac{A_{12}}{B_{12}} = \frac{8\pi}{c^3} \nu^3 h.$$

Inserting these values in (2) we obtain Planck's radiation formula

$$\rho_\nu = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/kT} - 1}.$$

We see that the validity of Planck's formula is quite independent of the determination of the stationary states.

We shall now consider the problem of the *determination of the stationary states*. The simplest model of a radiating system is the *harmonic oscillator*, the equation of motion of which is

$$m\ddot{q} + \kappa q = 0$$

where q is the distance of the moving point from the position of equilibrium, m its mass, and κ a constant which is connected with the natural frequency ν_0 by the relation

$$\kappa = m(2\pi\nu_0)^2.$$

The motion of a point obeying this equation is very closely related to the motion of the field vector in a monochromatic light wave. An immediate assumption is that the frequency of such a linear oscillator is the same as the frequency of the emitted light; then it follows from Bohr's frequency condition (1) that the energies of the stationary states of the oscillator

must differ by $h\nu_0$, that is they are, for an appropriate choice of additive constants,

$$W_0 = 0, \quad W_1 = h\nu_0, \quad W_2 = 2h\nu_0 \dots, \quad W_n = nh\nu_0 \dots$$

In the case of one degree of freedom the motion is completely determined by the energy, so in this simple example the stationary states are completely known,

$$q = \sqrt{\frac{W}{2\pi m\nu_0^2}} \cos(2\pi\nu_0 t + \delta).$$

From the system of energy levels it is possible to derive the complete system of spectral lines by taking all possible differences,

$$\nu = \frac{1}{h}(nh\nu_0 - kh\nu_0) = \nu_0(n - k).$$

We see that Bohr's principle gives for the frequency of the emitted light not only the fundamental frequency, ν_0 , as in the classical theory, but also the overtones $\nu_0(n - k)$. But in this simple case of the linear oscillator we should expect that both theories give exactly the same result; therefore we need a new principle to eliminate superfluous overtones. Bohr has supplied this under the name of the *Principle of Correspondence*. He makes the assumption we have already used once, that the quantum laws must go over into the classical laws in the limiting case. If the oscillator has a very large amount of energy, that is if n is large, the difference between two neighboring energy-levels is small compared with their absolute values, and approximately the series of values of W_n may be looked upon as varying continuously, as in the classical theory. Therefore Bohr assumes that the classical theory remains approximately valid in this limiting case. Then the emitted light may be calculated classically, and the light vector is proportional to the electric moment of the vibrating system. In the case of one coördinate q , this moment is eq , where e is the charge of the moving point, and for the oscillator we have,

$$eq = e\sqrt{\frac{W}{2\pi m\nu_0^2}} \cos(2\pi\nu_0 t + \delta).$$

In the general case the electric moment is a Fourier series with an infinite number of terms of the same form. The squares of the coefficients of the terms of the series will be a measure of the intensity of light emitted at the corresponding frequency of the overtone; this measure must also hold approximately in the quantum theory. In this way we get a rough estimate of the intensities of spectral lines even for small quantum numbers. But in one case we may expect this rule to give the exact results, namely, when one Fourier coefficient is identically zero. Then we may assume that the corresponding frequency is not emitted at all and that the corresponding transition does not occur. In our case we see that the Fourier series has only one term, corresponding to the transition $n - k = 1$. In this way Bohr's correspondence principle reduces the number of frequencies to that of the classical theory. It seems quite trivial in this example, but we shall see that in other cases it gives valuable information concerning possible transitions.

We go over now to more complicated systems, at first those of one degree of freedom but of any energy-function. In a system of this kind we have in general, if we exclude orbits which go to infinity, periodic motions, so that the coördinate q can be expanded in a Fourier series of the time t . It might be thought that it would be possible to determine the stationary states, as in the case of the oscillator, by making the energies integral multiples of $h\nu$, where $T = 1/\nu$ is the period of the motion, i.e., the time of a complete revolution. We shall see that this is not possible on account of another principle, the last to be mentioned in this introduction: the *adiabatic hypothesis* of Ehrenfest.

We consider the action of an external force on the atomic system. There are two limiting cases: constant forces and oscillating forces of high frequency. We know that in the second case classical mechanics cannot be applied, for the action of light consists in the production of transitions or quantum jumps which cannot be described by classical theory. But suppose that we investigate the action of a force changing slowly relatively to the inner motions. From the assumption of stationary states it follows that this force can have either no

effect or a finite effect resulting in a quantum jump; it is natural to suppose that the latter case will be more and more improbable as the rate of change of the force diminishes. So we see that quantities which are suitable for fixing the stationary states must have the property of not being altered by slowly changing forces. Ehrenfest calls them "adiabatic invariants," from analogy to similar quantities in thermodynamics. The question is whether such quantities can be found at all in classical mechanics. In the case of a linear oscillator it is not the energy which has this property, because the frequency ν is not constant under the influence of slowly changing forces, but it can be proved that the quotient W/ν is an adiabatic invariant. Indeed our fixation of the stationary states of the oscillator can be formulated by giving to this quotient the discrete values $0 h, 1 h, 2 h \dots$ etc. One of the aims of these lectures will be to find adiabatic invariants for every atomic system; we shall show that they exist not only for simple periodic systems, but also for the larger class of so-called multiple-periodic systems.

Periodic properties are closely connected with the laws of the quantum theory. A process which can be resolved into rotations and oscillations falls in its domain. Therefore, it will be our first problem to study systematically the most general systems having periodic properties.