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Let us now look more closely at Bohr's contributions. The year 1913 was a crucial one in the history of atomic theory, and in our understanding of the structure of the atom and of matter; in July of that year one of the greatest of all scientific papers appeared in the *Philosophical Magazine* of London, Edinburgh, and Dublin under the authorship of N. Bohr. The title of this paper, "On the Constitution of Atoms and Molecules," indicated that it might contain some interesting ideas, but hardly heralded the shattering impact its contents were to have on future concepts of atomic structure.

Before this paper on the structure of the hydrogen atom appeared, two important discoveries had been made: one dealing with the properties of radiation and the other with the interaction of atoms with charged particles, that is, with ions. Although at first sight these two developments do not appear to be directly related, they were really the key to Bohr's revolutionary theory of the atom.

We recall that Planck introduced the concept of the quantum of energy and the quantum of action to derive the correct formula for black-body radiation. But except for Einstein's extension of this idea, which led him to introduce the photon and to apply it to the explanation of the photoelectric effect and the specific heats of solids, no one else had applied Planck's quantum concept to anything but the behavior of radiation. The next great step was to be taken by Bohr, who saw quite clearly that Planck's discovery of the quantum of action and Einstein's concept of the photon could be combined with Rutherford's discovery of how α particles are scattered by atomic nuclei to derive a self-consistent planetary (that is, nuclear) atomic model.

Bohr saw that without introducing Planck's ideas into the theory of atomic structure, there was no way to obtain a stable planetary atom. On the other hand, he saw that introducing the Planck constant of action would do two things: lead to a description of stable electronic orbits and demonstrate the kind of discrete line spectrum that is observed.

Let us now see why Rutherford's discovery required a drastic departure from the laws of classical electrodynamics. We saw that to account for the scattering of α particles Rutherford found it necessary to introduce a model of the atom in which the positive charge is concentrated in a nucleus at the center. But, as we noted, the ideas of Rutherford were still somewhat tentative since he only hinted at a planetary model; he dealt only with the nucleus of the atom. In any case, the arrangement of the electrons in precise orbits was not clearly postulated, and the whole question of the stability of an atom constructed according to such a model presented what appeared to be insurmountable difficulties. An electron can be in stable equilibrium with a central positive nucleus only if the electron revolves around the nucleus in a closed orbit (circle or ellipse), for only then is the electrical force of attraction balanced by the centrifugal force acting outwardly on the electron. But, as we have already noted, an electron moving in this way must, according to classical electrodynamical theory, lose energy by radiating, so that it must ultimately spiral into the nucleus.

We see that we can overcome this difficulty if we introduce the kind of discontinuity into atomic processes that Planck introduced in analyzing the emission and absorption of radiation by the walls (actually, the atoms in the walls) of the container housing the radiation. The spiraling of an electron into the nucleus of an atom is clearly a consequence of the continuous change in its motion, as permitted by the classical laws of dynamics. These laws allow an accelerated electron to lose energy continuously by radiation so that there is no way, in terms of classical electrodynamics, for the electron to remain in any one orbit. The slightest change in its state of motion can, according to such a picture, cause it to gain or lose a slight amount of energy, and vice versa.

But if the electron can change its state of motion only discontinuously, that is, in discrete steps, it must then stay in a particular orbit until it emits or absorbs enough energy in one single process to go from one orbit to another. This then leads to discrete orbits, and transitions from one such orbit to another give rise to a discrete spectrum.

Niels Bohr was aware of this when he began his historic work. He was in his early twenties when Rutherford published his paper on the scattering of α particles by heavy nuclei. Bohr was then working in theoretical physics at the Manchester Laboratory under Rutherford and was greatly stimulated by the Rutherford nuclear model and its implications for the quantum theory. Realizing its importance, he set out to see if he could solve the problem of stability by introducing the new quantum concepts. As he states in the paper reprinted here, he recognized that the Rutherford model would "meet with difficulties of a serious nature arising from the apparent instability of the system of electrons: difficulties purposely avoided in atom models previously considered, for example, in the one proposed by Sir J. J. Thomson." And yet he felt sure that the difficulty present in the Rutherford model could be eliminated by introducing a quantity involving the dimension of length.

His reasoning went somewhat as follows: With the Thomson model of an atom one automatically obtains a fundamental length about equal in magnitude to the size of the atom, because this is the diameter of the positive sphere of electricity in which the electrons are supposed to be embedded. The appearance of such a length in the Thomson theory of the atom means that this kind of atom cannot collapse to a dimension less than this and therefore is stable. Bohr notes in the present paper that "such a length does not appear among the quantities characterizing the second [that is, the Rutherford] atom, viz. the charges and masses of the electrons and the positive nucleus; nor can it be determined solely by help of the latter quantities." He means that no quantity having the dimensions of a length can be constructed from the charge and masses and be numerically of the right size for an atom. All such lengths would be much too small.

But here Bohr experiences one of those miraculous insights that so often occur to the creative mind. In looking around for some way to introduce a length of atomic dimensions into the Rutherford model of the atom as naturally as possible, he observed that a new quantity had been introduced into physics seven years previously by Max Planck—Planck's constant, or, as it often is called, "the elementary quantum of action." By the introduction of this quantity, the question of the stable configuration of the electrons in the atoms is essentially changed, as this constant is of such dimensions and of such a magnitude that it, together with the mass and charge of the particles, can determine a length of the order of magnitude required. If Planck's constant is squared and the result divided by the product of the mass of the electron and the square of its charge, the number thus obtained is 10^{-8} cm, which is the size of an atom.

This type of general reasoning used by Bohr to obtain a correct theory is characteristic of all of his work. Einstein, Fermi, Lorentz, and the other outstanding figures of this anthology had the same ability to arrive at an important result without complex mathematical analysis and involved physical arguments. Bohr did not have to analyze all the aspects of the Rutherford model of the atom before discovering what is needed to make it work. His observation that in the Rutherford theory, as it stood, no quantity of the nature of a length and of the right order of magnitude was present, showed him what was wrong and where he would have to look to find the missing length. He was further strengthened in his beliefs by the ease with which the Planck theory of radiation had cleared up many difficulties that had bothered physicists for years; in Bohr's words, the elementary quantum of action had previously demonstrated "the inadequacy of classical electrodynamics in describing the behavior of systems of atomic size." Since the instability of the Rutherford atom was associated with the classical theory of the radiation of electrons moving in closed orbits, why could not the Planck theory straighten things out in this respect as well? Bohr was convinced that it could.

Using elementary algebra, the simple concepts of classical electrostatics, and the Newtonian laws of motion, Bohr derived a simple expression for the frequency of an electron moving in a circular orbit; he noted that according to classical theory, this electron would have to sink into the nucleus because it would lose energy continuously. Then he introduced Planck's constant, imposing the condition that the electron must not radiate continuously but rather in the form of "distinctly separated emissions." The amount of energy radiated during such emissions must be some integral value of Planck's constant multiplied by the frequency of the atom in its orbit. Thus Bohr introduces Planck's constant into the Rutherford model of the atom and at the same time shows that the stability of, and the radiation by, the atom depend in some way upon the integers. The presence of these integers in conjunction with Planck's constant shows the departure of the theory from classical dynamics and electrodynamics.

We briefly note here Bohr's procedure; the details are contained in his famous paper, which we have included in this volume. His procedure is also outlined somewhat more simply in an address on the spectrum of hydrogen delivered in 1913 before the Physical Society in Copenhagen. This address is particularly interesting because it clearly indicates the tentativeness of the quantum theory at the time and the incompleteness of its acceptance. Even Bohr, who was to put the Planck theory to its most important use, stated in this address,

> In formal respects Planck's theory leaves much to be desired; in certain calculations the ordinary electrodynamics is used, while in others assumptions distinctly at variance with it are introduced without any attempt being made to show that it is possible to give a consistent explanation of the procedure used.[10]

Nevertheless, Bohr clearly recognized that "energy quanta" had come to stay and summed up his feelings as follows:

> It is therefore hardly too early to express the opinion that, whatever the final explanation will be, the discovery of "energy quanta" must be considered as one of the most important results arrived at in physics, and must be taken into consideration in investigations of the properties of atoms and particularly in connection with any explanation of the spectral laws in which such phenomena as the emission and absorption of electromagnetic radiation are concerned.[11]

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[10] Bohr, "On the Spectrum of Hydrogen," address before Physical Society, Copenhagen, 1913, p. 6.

[11] *Ibid.*, p. 7.

After a brief survey of the laws of radiation and Planck's contribution to these, Bohr proposes to combine these ideas with the results of Rutherford's α-particle scattering experiments and in this way derive a formula for the frequencies of the spectral lines of hydrogen. He chose hydrogen to work with because he asssumed it to be (and correctly so) the simplest atomic structure, having just one electron revolving around a single proton. Moreover, the spectrum of hydrogen had been studied more thoroughly than that of any other atom and the numerical simplicity of Balmer's formula for the spectral lines suggested that a simple algebraic analysis might solve the problem.

Bohr began, then, by picturing an electron as revolving around a proton according to the classical laws of Newtonian mechanics, the centrifugal force on it, resulting from its orbital motion, being balanced by the electrostatic pull of the proton. This leads to the same kind of orbit for the electron around the proton as the planets have around the sun: elliptical orbits, first discovered by Kepler.

But here a difficulty is encountered because a charged particle behaves quite differently from a planet; it would, according to Maxwell's electrodynamics theory, lose energy continuously by radiation, causing the electron's orbit to become smaller and smaller, finally shrinking to the size of the proton. Bohr recognized this and introduced the Planck concept of the quantum to prevent this catastrophe.

Bohr now pictures the electron as being capable of moving in only a discrete set of orbits; while the electron is in any of these orbits, it does not radiate energy, even though classical electrodynamics demands that it must. This use of discrete, nonradiating orbits accomplishes two things: on the one hand, it leads to a set of distinct spectral lines, since a discrete set of frequencies is associated with the discrete orbital motions of the electron; discrete, non-radiating orbits lead to a stable nuclear atom, since one must then have the lowest orbit which is, then, the closest the electron can get to the nucleus. Moreover, discrete orbits can immediately be correlated to a quantum picture of nature, since changes in the atom can only occur in discontinuous steps, the electron changing from one fixed orbit to another; this must therefore involve discrete changes in the energy of the atom or in the action of the electron in the emission or absorption of a quantum.

To account numerically for the actually observed spectral lines, Bohr proceeds as follows: He first notes that in the hydrogen atom the energy of an electron moving around the proton in a Keplerian orbit depends only on the size of the orbit (that is, upon the semimajor axis of the ellipse in which the electron is moving); this is in accordance with the Newtonian laws of motion. We may think of this energy as the negative of the work that would have to be done to tear the electron completely out of this orbit and bring it to a very great distance from the proton, as occurs in ionization. A discrete set of orbits of different sizes thus means a discrete set of energy states for the electron (or for the atom), since the energy of the electron depends on the size of the orbit.

Bohr now introduces a crucial step in his argument. He postulates that the radiation or the absorption of energy occurs only when the atomic system passes from one energy state to another and that each such change in the energy state means the emission or absorption of a quantum of energy $h\nu$, where h is Planck's constant of action and ν is the frequency of the emitted radiation. Since one can assign a definite amount of energy to the electron in any orbit, according to the laws of classical mechanics (just as this can be done for each planet in the solar system), one can calculate all possible energy changes and hence obtain the frequencies of all possible quanta. These should then correspond to the observed spectral lines.

Bohr describes these ideas in a general way in his essay on the spectrum of hydrogen, where he introduces the concept of "stationary states" to describe the discrete orbits:

> During the emission of the radiation the system may be regarded as passing from one state to another; in order to introduce a name for these states, we shall call them "stationary" states, simply indicating thereby that they form some kind of waiting places between which occurs the emission of the energy corresponding to the various spectral lines. As previously mentioned the spectrum of an element consists of a series of lines whose wave lengths may be expressed by the formula (2). By comparing this expression with the relation given above it is seen that—since $\nu = \frac{c}{\lambda}$, where c is the velocity of light—each of the spectral lines may be regarded as being emitted by the transition of a system between two stationary states in which the energy apart from an additive arbitrary constant is given by $chF_r(n_1)$ and $chF_s(n_2)$ respectively. Using this interpretation the combination principle asserts that a series of stationary states exists for the given system, and that it can pass from one to any other of these states with the emission of a monochromatic radiation. We see, therefore, that with a simple extension of our first assumption it is possible to give a formal explanation of the most general law of line spectra.[12]

From this description we note a very important point: each spectral line involves two orbits and hence two different frequencies or two energies, not one as we would have in classical physics.

To complete his derivation of the Balmer formula for the hydrogen spectral lines, Bohr still had to introduce a scheme for picking out among

[12] *Ibid.*, p. 11.

all possible orbits the particular discrete set associated with the hydrogen atom. Why should the electron be limited to just these orbits and no others? What magical property do these orbits have that gives them their preferred character? To understand this and to follow Bohr's reasoning we note first that Kepler's third law of planetary motion also applies to the motion of the electron: it can be derived by equating the Coulomb electrostatic pull of the proton on the electron to the centrifugal force on the electron. According to this law, the square of the period of the electron (the period is time in fractions of a second taken to go once around the orbit) is proportional to the cube of the radius of the orbit. This means that the square of the frequency of the electron (frequency being the number of orbital trips made in one second and hence the reciprocal of the period) depends on the cube of the energy, since the energy is related to the size of the orbit. Thus frequency is related to energy.

But from classical physics one can also show that the period of an electron or its frequency and the size of its orbit can be related to its angular momentum. The angular momentum of a particle is a quantity that is obtained by multiplying the radius of the orbit of the particle and its momentum. Since Planck's constant h is in the nature of an angular momentum, Bohr simply assumed that the angular momentum of an electron in an orbit can only equal $\frac{h}{2\pi}$, or $\frac{2h}{2\pi}$, or $\frac{3h}{2\pi}$, etc., since $\frac{h}{2\pi}$ is an indivisible unit of angular momentum. In this way Bohr related the sizes of his discrete orbits to integers and to Planck's constant. From this he then obtained a formula, in terms of Planck's constant and the integer assigned to an orbit, for the energy of the electron.

As Bohr notes in the paper that follows, the theory as he developed it is pretty much of a hybrid, for the dynamic equilibrium of the electron in one of its orbits (Bohr's "stationary states") is treated by means of ordinary classical mechanics and electrostatics, whereas the quantum theory is used to describe what happens when the electron jumps from one stationary state to the other, which is accompanied either by the emission or absorption of a single quantum of *homogeneous* radiation (radiation of a definite frequency).

By using these simple though revolutionary ideas Bohr eliminated the difficulties that plagued all previous theories. In particular, he refers to the work of Nicholson, who had worked extensively on a model of the atom similar to the Bohr model. Nicholson had attempted to obtain the Rydberg-Ritz formula for the hydrogen spectrum, but had failed because, as Bohr points out, "The frequency of lines in a line spectrum is identified with the frequency of vibration of a mechanical system in a distinctly indicated state of equilibrium." And, as Bohr goes on to say, although Nicholson did relate the radiation from his atom to the Planck theory, it could not be a correct picture because such systems are incapable of emitting homogeneous radiation in discrete quantities.

By means of simple algebra and elementary physical concepts, Bohr obtains the correct expression for the frequencies of the spectral lines in the Balmer series in the spectrum of hydrogen. In addition, he shows that his formulas contain the frequencies of the other series in the hydrogen spectra, such as the Paschen and Lyman series. Bohr also shows in this paper that certain series of lines that were thought to be due to hydrogen must, indeed, be due to helium, and he obtains a simple formula for the helium spectrum, which is algebraically similar to the formula for the hydrogen spectrum, differing from it only because the charge on the nucleus of helium is twice the elementary electron charge itself (the charge on the hydrogen nucleus, the proton).

After Bohr obtains the correct formula for the frequencies of the spectral lines, he gives a critical analysis of the assumptions that he made to obtain the formula. He is particularly concerned with the assumptions that different stationary states correspond to the emission of different numbers of energy quanta or photons, and that the frequency of the radiation emitted by an electron that falls from a state of rest at a great distance from the nucleus to a nearer orbit is equal to half the frequency of the motion of the electron in this final stationary state.

He first points out that the assumption of the emission of different numbers of quanta in association with different stationary states is not really necessary for a correct application of the theory; the assumption that one quantum corresponds to each transition of an electron is all that one requires. Here he uses what has since been called the "correspondence principle," for he considers how the electron would behave in passing into an orbit where it moves very slowly. Under these conditions he can compare the results of his theory with the results obtained from the classical electrodynamics, since for very small frequencies the classical picture is correct, and the Planck theory of radiation passes over to the Maxwellian picture.

By using the correspondence principle, Bohr shows that one may correctly assume that only one quantum of energy is emitted, regardless of which orbit the electron moves into. He also uses this principle to validate the assumption that the frequency of the emitted radiation is half the frequency of the motion in the final orbit. One other important point comes out of these considerations. As Bohr points out, and as we have already noted, one can show that the result of the calculation in this paper may be "expressed by the simple condition that the angular momentum of the electron around the nucleus [on the assumption that the orbits are circular] in a stationary state of the system is equal to an entire multiple of a universal value, independent of the charge on the nucleus." This is a statement of a very important principle later generalized by Wilson and Sommerfeld, and contains within it the germs of Heisenberg's principle of indeterminacy.

It is interesting to note in connection with this paper how close Nicholson had come to discovering these results. As Bohr points out: "The possible importance of angular momentum in the discussion of atomic systems in relation to Planck's theory is emphasized by Nicholson." There can be no doubt that Bohr was influenced by and owed a good deal to Nicholson.

Bohr was greatly influenced and encouraged by Rutherford, who thought very highly of him and his work. They spent many hours together in 1912, and, in a letter dated July 24, 1912, Bohr thanked Rutherford for "your suggestions and criticisms [which] have made so many questions so real for me, and I am looking forward so very much to try to work upon them in the following years." While Bohr was preparing his paper, Rutherford advised that Bohr be as brief as possible, consistent with clarity, for as he said: "long papers have a way of frightening readers. It is the custom in England to put things very shortly and tersely in contrast to the Germanic method, where it supposed to be a virtue to be as long winded as possible." On March 6, 1913, Bohr sent what he called "the first chapter" of his paper to Rutherford with the request that the latter communicate it to the *Philosophical Magazine*. Bohr was quite concerned about his use of both classical mechanics and the quantum theory to obtain his results and hoped "that [Rutherford] will find that I have taken a reasonable point of view as to the delicate question of the old mechanics and of the new assumptions introduced by Planck's theory of radiation."

Rutherford recognized the great importance of Bohr's paper and immediately sent it on for publication, but he had many questions about the basic ideas. Thus, in a letter to Bohr on March 20, 1913, he stated, after praising Bohr's ingenious derivation of the hydrogen spectral lines, that "the mixture of Planck's ideas with the old mechanics makes it very difficult to form a physical idea of what is the basis of it all." He then goes on to point out that he considers a "grave difficulty in [Bohr's] hypothesis. . . . How does an electron decide what frequency it is going to vibrate at when it passes from one stationary state to the other? It seems to me that you would have to assume that the electron knows beforehand where it is going to stop."

That it took great courage to publish such a revolutionary theory at that period is clear from a letter that G. Von Hevesy, an outstanding Hungarian chemist working on relativity, wrote to Rutherford in the fall of 1913. He describes his meeting with Einstein at a science congress a few months earlier, shortly after the publication of Bohr's paper, and states that Einstein "told me that he had once had similar ideas but he did not dare to publish them." Einstein considered Bohr's paper to be "of the greatest importance" and "one of the greatest discoveries."

In the last few paragraphs of his paper, Bohr reaches an important conclusion, which was not verified until a number of years later, that indicated that the quantum would have to be extended to processes outside the atom. He notes that in a gaseous mixture of free electrons and electrons bound inside atoms, the bound electrons do not have the same energy that the free electrons have on the average, as determined by the temperature of the gas. Bohr correctly points out that this is so because the bound electrons cannot absorb energy continuously but only in discrete quanta. Hence, collisions between free and bound electrons lead to a new exchange of energy.

Like most of Bohr's important contributions this paper is marked by very little formal mathematics, but by very penetrating physical arguments and bold assumptions of a revolutionary nature. Its important contribution lies in its unification of atomic theory with the Planck theory of radiation.

BOHR

On the Constitution of Atoms and Molecules[13]

INTRODUCTION

IN ORDER TO EXPLAIN THE results of experiments on scattering of α rays by matter Prof. Rutherford has given a theory of the structure of atoms. According to this theory, the atoms consist of a positively charged nucleus surrounded by a system of electrons kept together by attractive forces from the nucleus; the total negative charge of the electrons is equal to the positive charge of the nucleus. Further, the nucleus is assumed to be the seat of the essential part of the mass of the atom, and to have linear dimensions exceedingly small compared with the linear dimensions of the whole atom. The number of electrons in an atom is deduced to be approximately equal to half the atomic weight. Great interest is to be attributed to this atom-model; for, as Rutherford has shown. the assumption of the existence of nuclei, as those in question, seems to

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[13] Niels Bohr, *Philosophical Magazine,* 26 (1913), 1–19.