

very act, the magnitudes belonging to the other picture more and more vague. Together, the two sets of concepts give a full description of all we know now about the material universe; separately, each can represent only one aspect of it.

There are eminent scientists who are dissatisfied with this dual picture, which implies renunciation of strict causal interpretation of the behavior of elementary particles, replacing it by statistical laws of probability determined by the propagation of the correlated waves. But the majority believe that this duality is not a temporary weakness of theory, but represents the ultimate realization of the capacity to understand the material world possible for man as a sensing organism. They consider the dualistic picture created by Bohr's complementarity principle and Heisenberg's uncertainty relation as logically satisfactory. The apparent contradiction of the wave and the particle pictures is, in their eyes, only a weakness of traditional ways of thinking, based on observations of macroscopic objects.

I believe that acceptance of the legitimate existence of two physical pictures—incompatible on the surface but never contradictory in predicting future observations—implies a major revolution in man's concept of the world. It offers a glimpse of how the apparent contradiction between the material and the spiritual elements in human existence could be ultimately resolved.

There is obviously no simple analogy between the particle and the wave aspects

of the material world and the spiritual and the material aspects of human existence, but it suggests that the modes of interaction between man and the world around him may, by their very nature, make it impossible to form a unified picture, and requires "coexistence" of two (or perhaps more) independent systems of concepts and relations. If the analogy holds, the two systems can become contradictory only if one of them is applied to the types of observations which rightfully belong to the other.

The spiritual aspect of the world is, then, not contradictory to and not separable from its material aspect; it is complementary to it. The existence of spiritual forces cannot reveal itself, as many believe, in occasional violations of the laws which govern the material world. Rather, the whole world confronted by man has its spiritual and its material aspects. The material aspects reveal themselves to man through his sense organs, refined by instruments. These organs or instruments could not reveal the existence and operation of the spiritual forces even if each event in the world has its physical as well as its spiritual aspects, because by the very process of observation of material parameters, the spiritual ones are made diffuse and escape observation.

The more we will learn about the physical aspects of the physiological processes which accompany man's thoughts and emotions, the vaguer will become their spiritual content. We may be able to induce emotions and visions by drugs; but this only illustrates the coupling of physicochemical and spiritual experience, and does not make the one "explain" the other.

CHAPTER 6 ATOMS AND RADIATION

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6.1

The Roots of Atomic Science

Werner Heisenberg

The concept of the atom goes back much further than the beginning of modern science in the seventeenth century; it has its origin in ancient Greek philosophy and was in that early period the central concept of materialism taught by Leucippus and Democritus. On the other hand, the modern interpretation of atomic events has very little resemblance to genuine materialistic philosophy; in fact, one may say that atomic physics has turned science away from the materialistic trend it had during the nineteenth century. It is therefore interesting to compare the development of Greek philosophy toward the concept of the atom with the present position of this concept in modern physics.

In the philosophy of Democritus the atoms are eternal and indestructible units of matter, they can never be transformed into each other. With regard to this question modern physics takes a definite stand against the materialism of Democritus and for Plato and the Pythagoreans. The elementary particles are certainly not eternal and indestructible units of matter, they can actually be

transformed into each other. As a matter of fact, if two such particles, moving through space with a very high kinetic energy, collide, then many new elementary particles may be created from the available energy and the old particles may have disappeared in the collision. Such events have been frequently observed and offer the best proof that all particles are made of the same substance: energy. But the resemblance of the modern views to those of Plato and the Pythagoreans can be carried somewhat further. The elementary particles in Plato's *Timaeus* are finally not substance but mathematical forms. "All things are numbers" is a sentence attributed to Pythagoras. The only mathematical forms available at that time were such geometric forms as the regular solids or the triangles which form their surface.

In modern quantum theory there can be no doubt that the elementary particles will finally also be mathematical forms, but of a much more complicated nature. The Greek philosophers thought of static forms and found them in the regular solids. Modern science, however, has from its beginning in the sixteenth and seventeenth centuries started from the dynamic problem. The

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constant element in physics since Newton is not a configuration or a geometrical form, but a dynamic law. The equation of motion holds at all times, it is in this sense eternal, whereas the geometrical forms, like the orbits, are changing. Therefore, the mathematical forms that represent the elementary particles will be solutions of some eternal law of motion for matter. Actually this is a problem which has not yet been solved. The fundamental law of motion for matter is not yet known and therefore it is not yet possible to derive mathematically the properties of the elementary particles from such a law. But theoretical physics in its present state seems to be not very far from this goal...

If we follow the Pythagorean line of thought we may hope that the fundamental law of motion will turn out as a mathematically simple law, even if its evaluation... may be very complicated. It is difficult to give any good argument for this hope for simplicity—except the fact that it has hitherto always been possible to write the fundamental equations in physics in simple mathematical forms. This fact fits in with the Pythagorean religion, and many physicists share their belief in this respect, but no convincing argument has yet been given to show that it must be so.

It may seem at first sight that the Greek philosophers have by some kind of ingenious intuition come to the same or very similar conclusions as we have in modern times only after several centuries of hard labor with experiments and mathematics. This interpretation of our comparison would, however, be a complete misunderstanding. There is an enormous difference between modern science and Greek philosophy, and that is just the empiristic attitude of modern science. Since the time of Galileo and Newton, modern science has been based upon a detailed study of nature and upon the postulate

that only such statements should be made, as have been verified or at least can be verified by experiment. The idea that one could single out some events from nature by an experiment, in order to study the details and to find out what is the constant law in the continuous change, did not occur to the Greek philosophers. Therefore, modern science has from its beginning stood upon a much more modest, but at the same time much firmer, basis than ancient philosophy. Therefore, the statements of modern physics are in some way meant much more seriously than the statements of Greek philosophy. When Plato says, for instance, that the smallest particles of fire are tetrahedrons, it is not quite easy to see what he really means. Is the form of the tetrahedron only symbolically attached to the element fire, or do the smallest particles of fire mechanically act as rigid tetrahedrons or as elastic tetrahedrons, and by what force could they be separated into the equilateral triangles, etc.? Modern science would finally always ask: How can one decide experimentally that the atoms of fire are tetrahedrons and not perhaps cubes? Therefore, when modern science states that the proton is a certain solution of a fundamental equation of matter it means that we can from this solution deduce mathematically all possible properties of the proton and can check the correctness of the solution by experiments in every detail. This possibility of checking the correctness of a statement experimentally with very high precision and in any number of details gives an enormous weight to the statement that could not be attached to the statements of early Greek philosophy.

All the same, some statements of ancient philosophy are rather near to those of modern science. This simply shows how far one can get by combining the ordinary experience of nature that we have without doing experiments with the untiring effort to get some logical order into this experience to understand it from general principles.

6.2

*Note on the Spectral Lines of Hydrogen**Johann Jacob Balmer*

Using measurements by H. W. Vogel and by Huggins of the ultraviolet lines of the hydrogen spectrum I have tried to derive a formula which will represent the wavelengths of the different lines in a satisfactory manner. I was encouraged to take up this work by Professor E. Hagenbach. Ångström's very exact measurements of the four hydrogen lines enable one to determine a common factor for their wavelengths which is in as simple a numerical relation as possible to these wavelengths. I gradually arrived at a formula which, at least for these four lines, expresses a law by which their wavelengths can be represented with striking precision. The common factor in this formula, as it has been deduced from Ångström's measurements, is $b = 3645.6 \text{ cm}/10^8$.

We may call this number the fundamental number of hydrogen; and if corresponding fundamental numbers can be found for the spectral lines of other elements, we may accept the hypothesis that relations which can be expressed by some function exist be-

do not form a regular series; but if we multiply the numerators in the second and the fourth terms by 4 a consistent regularity is evident and the coefficients have for numerators the numbers $3^2, 4^2, 5^2, 6^2$ and for denominators a number that is less by 4.

For several reasons it seems to me probable that the four coefficients which have just been given belong to two series, so that the second series includes the terms of the first series; hence I have finally arrived at the present formula for the coefficients in the more general form: $m^2 / (m^2 - n^2)$ in which m and n are whole numbers.

For $n = 1$ we obtain the series $4/3, 9/8, 16/15, 25/24$, and so on for $n = 2$ the series $9/5, 16/12, 25/21, 36/32, 49/45, 64/60, 81/77, 100/96$, and so on. In this second series the second term is already in the first series but in a reduced form.

If we carry out the calculation of the wavelengths with these coefficients and the fundamental number 3645.6 , we obtain the following numbers in 10^{-8} cm .

TABLE 6.2-1

According to the formula	Ångström gives	Difference
$H\alpha$ (C-line) = $\frac{3}{2}b$ = 6562.08	6562.10	+0.02
$H\beta$ (F-line) = $\frac{4}{3}b$ = 4860.8	4860.74	-0.06
$H\gamma$ (near G) = $\frac{5}{2}b$ = 4340	4340.1	+0.1
$H\delta$ (h-line) = $\frac{7}{2}b$ = 4101.3	4101.2	-0.1

tween these fundamental numbers and the corresponding atomic weights.

The wavelengths of the first four hydrogen lines are obtained by multiplying the fundamental number $b = 3645.6$ in succession by the coefficients $9/5, 4/3, 25/21$; and $9/8$. At first it appears that these four coefficients

The deviations of the formula from Ångström's measurements amount in the most unfavorable case to not more than $1/40,000$ of a wavelength, a deviation which very likely is within the limits of the possible errors of observation and is really striking evidence for the great scientific skill and

care with which Ångström must have worked.

From the formula we obtained for a fifth hydrogen line $49/45 \times 3645.6 = 3969.65 \times 10^{-8}$ cm. I knew nothing of such a fifth line, which must lie within the visible part of the spectrum just before H_γ (which according to Ångström has a wavelength 3968.1); and I had to assume that either the temperature relations were not favorable for the emission of this line or that the formula was not generally applicable.

On communicating this to Professor Hagenbach he informed me that many more hydrogen lines are known, which have been measured by Vogel and by Huggins in the violet and the ultraviolet parts of the hydrogen spectrum and in the spectrum of the white stars; he was kind enough himself to compare the wavelengths thus determined with my formula and to send me the result.

While the formula in general gives somewhat larger numbers than those contained in the published lists of Vogel and of Huggins, the difference between the calculated and the observed wavelengths is so small that the agreement is striking in the highest degree. Comparisons of wavelengths measured by different investigators show in general no exact agreement; and yet the observations of one man may be made to agree with those of another by a slight reduction in an entirely satisfactory way.

[Here Balmer compares the wavelengths calculated from his formula with the measurements of several observers—Ed.]

These comparisons show that the formula holds also for the fifth hydrogen line, which lies just before the first Fraunhofer H-line (which belongs to calcium). It also appears that Vogel's hydrogen lines and the corresponding Huggins lines of the white stars can be represented by the formula very satisfactorily. We may almost certainly assume that the other lines of the white stars which Huggins found farther on in the ultraviolet part of the spectrum will be expressed by the formula. I lack knowledge of the wavelengths. Using the fundamental number 3645.6 we obtain according to the formula

for the ninth and the following hydrogen lines up to the fifteenth:

$$\begin{array}{ll} \frac{144}{11}b = 3770.24 & \frac{225}{11}b = 3711.58 \\ \frac{144}{9}b = 3749.76 & \frac{225}{9}b = 3703.46 \\ \frac{144}{8}b = 3733.98 & \frac{225}{8}b = 3696.76 \\ \frac{144}{7}b = 3721.55 & \end{array}$$

Whether the hydrogen lines of the white stars agree with the formula to this point or whether other numerical relations gradually replace it can only be determined by observation.

I add to what I have said a few questions and conclusions.

Does the above formula hold only for the single chemical element hydrogen, and will not other fundamental numbers in the spectral lines of other elements be found which are peculiar to those elements? If not, we may perhaps assume that the formula that holds for hydrogen is a special case of a more general formula which under certain conditions goes over into the formula for the hydrogen lines.

None of the hydrogen lines which correspond to the formula when $n = 3, 4,$ and so on, and which may be called lines of the third or fourth order, is found in any spectrum as yet known; they must be emitted under entirely new relations of temperature and pressure if they are to become perceptible.

If the formula holds for all the principal lines of the hydrogen spectrum with $n = 2,$ it follows that these spectral lines on the ultraviolet side approach the wavelength 3645.6 in a more closely packed series, but they can never pass this limiting value, while the C-line also is the extreme line on the red side. Only if lines of higher orders are present can lines be found on the infrared side.

The formula has no relation, so far as can be shown, with the very numerous lines of the second hydrogen spectrum which Haselberg has published in the *Mémoires de l'Académie des Sciences de St. Petersburg*, 1882. For certain values of pressure and temperature hydrogen may easily change in such a way that the law of formation of its spectral lines becomes entirely different.

There are great difficulties in the way of finding the fundamental numbers for other chemical elements, such as oxygen or carbon, by means of which their principal spectral lines can be determined from the formula. Only extremely exact determinations of wavelengths of the most prominent lines of

an element can give a common base for these wavelengths, and without such a base it seems as if all trials and guesses will be in vain. Perhaps by using a different graphical construction of the spectrum a way will be found to make progress in such investigations.

6.3

On the Constitution of Atoms and Molecules

Niels Bohr

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 be necessary in order to account for the results of the experiments on large angle scattering of the α rays.

In an attempt to explain some of the properties of matter on the basis of this atom-model we meet, however, 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 instance, in the one proposed by Sir J. J. Thomson. According to the theory of the latter the atom consists of a sphere of uniform positive

electrification, inside which the electrons move in circular orbits.

The principal difference between the atom-models proposed by Thomson and Rutherford consists in the circumstance that the forces acting on the electrons in the atom-model of Thomson allow of certain configurations and motions of the electrons for which the system is in a stable equilibrium; such configurations, however, apparently do not exist for the second atom-model. The nature of the difference in question will perhaps be most clearly seen by noticing that among the quantities characterizing the first atom a quantity appears—the radius of the positive sphere—of dimensions of a length and of the same order of magnitude as the linear extension of the atom, while such a length does not appear among the quantities characterizing the second 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.

The way of considering a problem of this kind has, however, undergone essential alterations in recent years owing to the development of the theory of the energy radiation, and the direct affirmation of the new assumptions introduced in this theory, found by experiments on very different phenomena such as specific heats, photoelectric effect, Röntgen-rays, etc. The result of the discussion of these questions seems to be a general

acknowledgment of the inadequacy of the classical electrodynamics in describing the behavior of systems of atomic size. Whatever the alteration in the laws of motion of the electrons may be, it seems necessary to introduce in the laws in question a quantity foreign to the classical electrodynamics, *i.e.* 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 magnitude that it, together with the mass and charge of the particles, can determine a length of the order of magnitude required.

This paper is an attempt to show that the application of the above ideas to Rutherford's atom-model affords a basis for a theory of the constitution of atoms. It will further be shown that from this theory we are led to a theory of the constitution of molecules.

In the present first part of the paper the mechanism of the binding of electrons by a positive nucleus is discussed in relation to Planck's theory. It will be shown that it is possible from the point of view taken to account in a simple way for the law of the line spectrum of hydrogen. Further, reasons are given for a principal hypothesis on which the considerations contained in the following parts are based.

I wish here to express my thanks to Prof. Rutherford for his kind and encouraging interest in this work.

BINDING OF ELECTRONS BY POSITIVE NUCLEI¹

General Considerations. The inadequacy of the classical electrodynamics in accounting for the properties of atoms from an atom-model as Rutherford's, will appear very clearly if we consider a simple system consisting of a positively charged nucleus of very small dimensions and an electron describing closed orbits around it. For simplic-

ity, let us assume that the mass of the electron is negligibly small in comparison with that of the nucleus, and further, that the velocity of the electron is small compared with that of light.

Let us at first assume that there is no energy radiation. In this case the electron will describe stationary elliptical orbits. The frequency of revolution ω and the major-axis of the orbit $2a$ will depend on the amount of energy W which must be transferred to the system in order to remove the electron to an infinitely great distance apart from the nucleus. Denoting the charge of the electron and of the nucleus by $-e$ and Ze , respectively, and the mass of the electron by m , we thus get

$$\omega = \frac{\sqrt{2} W^{3/2}}{\pi Ze^2 \sqrt{m}}, \quad 2a = \frac{Ze^2}{W} \quad (1)$$

Further, it can easily be shown that the mean value of the kinetic energy of the electron taken for a whole revolution is equal to W . We see that if the value of W is not given, there will be no values of ω and a characteristic for the system in question.

Let us now, however, take the effect of the energy radiation into account, calculated in the ordinary way from the acceleration of the electron. In this case the electron will no longer describe stationary orbits. " W " will continuously increase, and the electron will approach the nucleus describing orbits of smaller and smaller dimensions, and with greater and greater frequency; the electron on the average gaining in kinetic energy at the same time as the whole system loses energy. This process will go on until the dimensions of the orbit are of the same order of magnitude as the dimensions of the electron or those of the nucleus. A simple calculation shows that the energy radiated out during the process considered will be enormously great compared with that radiated out by ordinary molecular processes.

It is obvious that the behavior of such a system will be very different from that of

an atomic system occurring in nature. In the first place, the actual atoms in their permanent state seem to have absolutely fixed dimensions and frequencies. Further, if we consider any molecular process, the result seems always to be that after a certain amount of energy characteristic for the systems in question is radiated out, the systems will again settle down in a stable state of equilibrium, in which the distances apart of the particles are of the same order of magnitude as before the process.

Now the essential point in Planck's theory of radiation is that the energy radiation from an atomic system does not take place in the continuous way assumed in the ordinary electrodynamics, but that it, on the contrary, takes place in distinctly separated emissions, the amount of energy radiated out from an atomic vibrator of frequency ν in a single emission being equal to $n h \nu$, where n is an integer number, and h is a universal constant.

Returning to the simple case of an electron and a positive nucleus considered above, let us assume that the electron at the beginning of the interaction with the nucleus was at a great distance apart from the nucleus, and had no sensible velocity relative to the latter. Let us further assume that the electron after the interaction has taken place has settled down in a stationary orbit around the nucleus. We shall, for reasons referred to later, assume that the orbit in question is circular; this assumption will, however, make no alteration in the calculations for systems containing only a single electron.

Let us now assume that, during the binding of the electron, a homogeneous radiation is emitted of a frequency ν equal to half the frequency of revolution of the electron in its final orbit; then, from Planck's theory, we might expect that the amount of energy emitted by the process considered is equal to $n h \nu$, where h is Planck's constant and n an integer number. If we assume that the radiation emitted is homogeneous, the second assumption concerning the frequency of the radiation suggests itself, since the frequency of revolution of the electron at the beginning of the emission is 0. . . . The question, how-

ever, of the rigorous validity of both assumptions, and also of the application made of Planck's theory, will be more closely discussed in [the section entitled "General Considerations Continued."]

Putting

$$W = n h \frac{\omega}{2}, \quad (2)$$

we get by help of the formula (1)

$$W = \frac{2\pi^2 m Z^2 e^4}{n h^2},$$

$$\omega = \frac{4\pi^2 m Z^2 e^4}{n^3 h^3}, \quad (3)$$

$$2a = \frac{n^2 h^2}{2\pi^2 m Z e^2}$$

If in these expressions we give n different values, we get a series of values for W , ω and a corresponding to a series of configurations of the system. According to the above considerations, we are led to assume that these configurations will correspond to states of the system in which there is no radiation of energy; states which consequently will be stationary as long as the system is not disturbed from outside. We see that the value of W is greatest if n has its smallest value 1. This case will therefore correspond to the most stable state of the system, *i.e.* will correspond to the binding of the electron for the breaking up of which the greatest amount of energy is required.

Putting in the above expressions $n = 1$ and $Z = 1$, and introducing the experimental values

$$e = 4.7 \times 10^{-10} \text{ statcoul},$$

$$\frac{e}{m} = 5.31 \times 10^{17} \text{ statcoul/g},$$

$$h = 6.5 \times 10^{-27} \text{ erg-sec},$$

we get

$$2a = 1.1 \times 10^{-8} \text{ cm},$$

$$\omega = 6.2 \times 10^{15} \text{ sec}^{-1},$$

$$W = 13 \text{ eV}.$$

We see that these values are of the same

¹Some of the notation in this section has been changed to conform with modern practice. [Ed.]

order of magnitude as the linear dimensions of the atoms, the optical frequencies, and the ionization energies.

The general importance of Planck's theory for the discussion of the behavior of atomic systems was originally pointed out by Einstein. The considerations of Einstein have been developed and applied on a number of different phenomena, especially by Stark, Nernst, and Sommerfeld. The agreement as to the order of magnitude between values observed for the frequencies and dimensions of the atoms, and values for these quantities calculated by considerations similar to those given above, has been the subject of much discussion. It was first pointed out by Haas, in an attempt to explain the meaning and the value of Planck's constant on the basis of J. J. Thomson's atom-model, by help of the linear dimensions and frequency of an hydrogen atom.

Systems of the kind considered in this paper, in which the forces between the particles vary inversely as the square of the distance, are discussed in relation to Planck's theory by J. W. Nicholson. In a series of papers this author has shown that it seems to be possible to account for lines of hitherto unknown origin in the spectra of the stellar nebulae and that of the solar corona, by assuming the presence in these bodies of certain hypothetical elements of exactly indicated constitution. The atoms of these elements are supposed to consist simply of a ring of a few electrons surrounding a positive nucleus of negligibly small dimensions. The ratios between the frequencies corresponding to the lines in question are compared with the ratios between the frequencies corresponding to different modes of vibration of the ring of electrons. Nicholson has obtained a relation to Planck's theory showing that the ratios between the wave length of different sets of lines of the coronal spectrum can be accounted for with great accuracy by assuming that the ratio between the energy of the system and the frequency of rotation of the ring is equal to an integer multiple of Planck's constant. The quantity Nicholson refers to as the

energy is equal to twice the quantity which we have denoted above by W . In the latest paper cited Nicholson has found it necessary to give the theory a more complicated form, still however, representing the ratio of energy to frequency by a simple function of whole numbers.

The excellent agreement between the calculated and observed values of the ratios between the wave lengths in question seems a strong argument in favor of the validity of the foundation of Nicholson's calculations. Serious objections, however, may be raised against the theory. These objections are intimately connected with the problem of the homogeneity of the radiation emitted. In Nicholson's calculations 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. As a relation from Planck's theory is used, we might expect that the radiation is sent out in quanta; but systems like those considered, in which the frequency is a function of the energy, cannot emit a finite amount of a homogeneous radiation; for, as soon as the emission of radiation is started, the energy and also the frequency of the system are altered. Further, according to the calculation of Nicholson, the systems are unstable for some modes of vibration. Apart from such objections—which may be only formal—it must be remarked, that the theory in the form given does not seem to be able to account for the well-known laws of Balmer and Rydberg connecting the frequencies of the lines in the line-spectra of the ordinary elements.

It will now be attempted to show that the difficulties in question disappear if we consider the problems from the point of view taken in this paper. Before proceeding it may be useful to restate briefly the ideas characterizing the calculations [following formulas (2) and (3)]. The principal assumptions used are:

(1) That the dynamical equilibrium of the systems in the stationary states can be discussed by help of the ordinary mechanics,

while the passing of the systems between different stationary states cannot be treated on that basis.

(2) That the latter process is followed by the emission of a *homogeneous* radiation, for which the relation between the frequency and the amount of energy emitted is the one given by Planck's theory.

The first assumption seems to present itself; for it is known that the ordinary mechanics cannot have an absolute validity, but will only hold in calculations of certain mean values of the motion of the electrons. On the other hand, in the calculations of the dynamical equilibrium in a stationary state in which there is no relative displacement of the particles, we need not distinguish between the actual motions and their mean values. The second assumption is in obvious contrast to the ordinary ideas of electro-dynamics, but appears to be necessary in order to account for experimental facts.

In the calculations [just referred to] we have further made use of the more special assumptions, viz. that the different stationary states correspond to the emission of a different number of Planck's energy quanta, and that the frequency of the radiation emitted during the passing of the system from a state in which no energy is yet radiated out to one of the stationary states, is equal to half the frequency of revolution of the electron in the latter state. We can, however, also arrive at the expressions (3) for the stationary states by using assumptions of somewhat different form. We shall, therefore, postpone the discussion of the special assumptions, and first show how by the help of the above principal assumptions, and of the expressions (3) for the stationary states, we can account for the line-spectrum of hydrogen.

Emission of Line-Spectra. SPECTRUM OF HYDROGEN. General evidence indicates that an atom of hydrogen consists simply of a single electron rotating round a positive nucleus of charge e . The re-formation of a hydrogen atom, when the electron has been removed to great distances away from the nucleus—*e.g.* by the effect of electrical dis-

charge in a vacuum tube—will accordingly correspond to the binding of an electron by a positive nucleus considered [earlier]. In (3) we put $Z = 1$, we get for the total amount of energy radiated out by the formation of one of the stationary states,

$$W_n = \frac{2\pi^2 me^4}{h^2 n^2}$$

The amount of energy emitted by the passing of a system from a state corresponding to $n = n_1$ to one corresponding to $n = n_2$, is consequently

$$W_{n_1} - W_{n_2} = \frac{2\pi^2 me^4}{h^2} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right).$$

If now we suppose that the radiation in question is homogeneous, and that the amount of energy emitted is equal to $h\nu$, where ν is the frequency of the radiation, we get

$$W_{n_1} - W_{n_2} = h\nu,$$

and from this

$$\nu = \frac{2\pi^2 me^4}{h^3} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right). \quad (4)$$

We see that this expression accounts for the law connecting the lines in the spectrum of hydrogen. If we put $n_2 = 2$ and let n_1 vary, we get the ordinary Balmer series. If we put $n_2 = 3$, we get the series in the infra-red observed by Paschen and previously suspected by Ritz. If we put $n_2 = 1$ and $n_1 = 4, 5, \dots$, we get series respectively in the extreme ultra-violet and the extreme infra-red, which are not observed, but the existence of which may be expected.

The agreement in question is quantitative as well as qualitative. Putting

$$e = 4.7 \times 10^{-10} \text{ statcoul},$$

$$\frac{e}{m} = 5.31 \times 10^{17} \text{ statcoul/g},$$

$$\text{and } h = 6.5 \times 10^{-27} \text{ erg-sec},$$

we get

$$\frac{2\pi^2 me^4}{h^3} = 3.1 \times 10^{15} \text{ sec}^{-1}.$$

The observer value for the factor outside

the bracket in the formula (4) is

$$3.290 \times 10^{15} \text{ sec.}^{-1}.$$

The agreement between the theoretical and observed values is inside the uncertainty due to experimental errors in the constants entering in the expression for the theoretical value. We shall return to consider the possible importance of the agreement in question.

It may be remarked that the fact, that it has not been possible to observe more than 12 lines of the Balmer series in experiments with vacuum tubes, while 33 lines are observed in the spectra of some celestial bodies, is just what we should expect from the above theory. According to the equation (3) the diameter of the orbit of the electron in the different stationary states is proportional to n^2 . For $n = 12$ the diameter is equal to 1.6×10^{-6} cm, or equal to the mean distance between the molecules in a gas at a pressure of about 7 mm mercury; for $n = 33$ the diameter is equal to 1.2×10^{-3} cm, corresponding to the mean distance of the molecules at a pressure of about 0.02 mm mercury. According to the theory the necessary condition for the appearance of a great number of lines is therefore a very small density of the gas; for simultaneously to obtain an intensity sufficient for observation the space filled with the gas must be very great. If the theory is right, we may therefore never expect to be able in experiments with vacuum tubes to observe the lines corresponding to high numbers of the Balmer series of the emission spectrum of hydrogen; it might, however, be possible to observe the lines by investigation of the absorption spectrum of this gas [see section entitled "Absorption of Radiation"].

It will be observed that we in the above way do not obtain other series of lines, generally ascribed to hydrogen; for instance, the series first observed by Pickering in the spectrum of the star ζ Puppis, and the set of series recently found by Fowler by experiments with vacuum tubes containing a mixture of hydrogen and helium. We shall, however, see that, by help of the above theory, we can account naturally for these series of lines if we ascribe them to helium.

A neutral atom of the latter element consists, according to Rutherford's theory, of a positive nucleus of charge ze and two electrons. Now considering the binding of a single electron by a helium nucleus, we get, putting $Z = 2$ in the expressions (3), and proceeding in exactly the same way as above,

$$\nu = \frac{8\pi^2 m e^4}{h^3} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) = \frac{32\pi^2 m e^4}{h^3} \left(\frac{1}{\left(\frac{n_2}{2}\right)^2} - \frac{1}{\left(\frac{n_1}{2}\right)^2} \right)$$

If we in this formula put $n_2 = 1$ or $n_2 = 2$, we get series of lines in the extreme ultra-violet. If we put $n_2 = 3$, and let n_1 vary, we get a series which includes 2 of the series observed by Fowler, and denoted by him as the first and second principal series of the hydrogen spectrum. If we put $n_2 = 4$, we get the series observed by Pickering in the spectrum of ζ Puppis. Every second of the lines in this series is identical with a line in the Balmer series of the hydrogen spectrum; the presence of hydrogen in the star in question may therefore account for the fact that these lines are of a greater intensity than the rest of the lines in the series. The series is also observed in the experiments of Fowler, and denoted in his paper as the Sharp series of the hydrogen spectrum. If we finally in the above formula put $n_2 = 5, 6, \dots$, we get series, the strong lines of which are to be expected in the infra-red.

The reason why the spectrum considered is not observed in ordinary helium tubes may be that in such tubes the ionization of helium is not so complete as in the star considered or in the experiments of Fowler, where a strong discharge was sent through a mixture of hydrogen and helium. The condition for the appearance of the spectrum is, according to the above theory, that helium atoms are present in a state in which they have lost both their electrons. Now we must assume that the amount of energy to be used in removing the second electron from a helium atom is much greater than that to be used in removing the first. Further, it is known

from experiments on positive rays, that hydrogen atoms can acquire a negative charge; therefore the presence of hydrogen in the experiments of Fowler may effect that more electrons are removed from some of the helium atoms than would be the case if only helium were present.

General Considerations Continued. . . . The possibility of an emission of a radiation of a frequency $[\nu = n\omega]$ may also be interpreted from analogy with the ordinary electrodynamics, as an electron rotating round a nucleus in an elliptical orbit will emit a radiation which according to Fourier's theorem can be resolved into homogeneous components, the frequencies of which are $n\omega$, if ω is the frequency of revolution of the electron.

We are thus led to assume that the interpretation of the equation (2) is not that the different stationary states correspond to an emission of different numbers of energy-quanta, but that the frequency of the energy emitted during the passing of the system from a state in which no energy is yet radiated out to one of the different stationary states, is equal to different multiples of $\omega/2$, where ω is the frequency of revolution of the electron in the state considered. From this assumption we get exactly the same expressions as before for the stationary states, and from these by help of the principal assumptions [given earlier] the same expression for the law of the hydrogen spectrum. Consequently we may regard our preliminary considerations only as a simple form of representing the results of the theory.

Before we leave the discussion of this question, we shall for a moment return to the question of the significance of the agreement between the observed and calculated values of the constant entering in the expressions (4) for the Balmer series of the hydrogen spectrum. From the above consideration it will follow that, taking the starting-point in the form of the law of the hydrogen spectrum and assuming that the different lines correspond to a homogeneous radiation emitted during the passing between different stationary states, we shall arrive at exactly

the same expression for the constant in question as that given by (4), if we only assume (1) that the radiation is sent out in quanta $h\nu$, and (2) that the frequency of the radiation emitted during the passing of the system between successive stationary states will coincide with the frequency of revolution of the electron in the region of slow vibrations.

As all the assumptions used in this latter way of representing the theory are of what we may call a qualitative character, we are justified in expecting—if the whole way of considering is a sound one—an absolute agreement between the values calculated and observed for the constant in question, and not only an approximate agreement. The formula (4) may therefore be of value in the discussion of the results of experimental determinations of the constants e, m , and h .

While there obviously can be no question of a mechanical foundation of the calculations given in this paper, it is, however, possible to give a very simple interpretation of the result of the calculation [following formulas (2) and (3)] by help of symbols taken from the ordinary mechanics. Denoting the angular momentum of the electron round the nucleus by M , we have immediately for a circular orbit $\pi M = T/\omega$, where ω is the frequency of revolution and T the kinetic energy of the electron; for a circular orbit we further have $T = W$ and from (2), we consequently get

$$M = nh/2\pi = n\hbar$$

where

$$\hbar = 1.04 \times 10^{-27} \text{ erg-sec.}$$

If we therefore assume that the orbit of the electron in the stationary states is circular, the result of the calculation can be expressed by the simple condition: that the angular momentum of the electron round the nucleus in a stationary state of the system is equal to an entire multiple of a universal value, independent of the charge on the nucleus. The possible importance of the angular momentum in the discussion of atomic

systems in relation to Planck's theory is emphasized by Nicholson.

The great number of different stationary states we do not observe except by investigation of the emission and absorption of radiation. In most of the other physical phenomena, however, we only observe the atoms of the matter in a single distinct state, *i.e.* the state of the atoms at low temperature. From the preceding considerations we are immediately led to the assumption that the "permanent" state is the one among the stationary states during the formation of which the greatest amount of energy is emitted. According to the equation (3), this state is the one which corresponds to $n = 1$.

Absorption of Radiation. In order to account for Kirchhoff's law it is necessary to introduce assumptions on the mechanism of absorption of radiation which correspond to those we have used considering the emission. Thus we must assume that a system consisting of a nucleus and an electron rotating round it under certain circumstances can absorb a radiation of a frequency equal to the frequency of the homogeneous radiation emitted during the passing of the system between different stationary states. Let us consider the radiation emitted during the passing of the system between two stationary states A_1 and A_2 corresponding to values for n equal to n_1 and n_2 , $n_1 > n_2$. As the necessary condition for an emission of the radiation in question was the presence of systems in the state A_1 , we must assume that the necessary condition for an absorption of the radiation is the presence of systems in the state A_2 .

These considerations seem to be in conformity with experiments on absorption in gases. In hydrogen gas at ordinary conditions for instance there is no absorption of a radiation of a frequency corresponding to the line-spectrum of this gas; such an absorption is only observed in hydrogen gas in a luminous state. This is what we should expect according to the above. We have assumed that the radiation in question was emitted during the passing of the systems between stationary states corresponding to $n \geq 2$. The state of the atoms in hydrogen gas at ordinary conditions

should, however, correspond to $n = 1$; furthermore, hydrogen atoms at ordinary conditions combine into molecules, *i.e.* into systems in which the electrons have frequencies different from those in the atoms. From the circumstance that certain substances in a non-luminous state, as, for instance, sodium vapor, absorb radiation corresponding to lines in the line-spectra of the substances, we may, on the other hand, conclude that the lines in question are emitted during the passing of the system between two states, one of which is the permanent state.

How much the above considerations differ from an interpretation based on the ordinary electro-dynamics is perhaps most clearly shown by the fact that we have been forced to assume that a system of electrons will absorb a radiation of a frequency different from the frequency of vibration of the electrons calculated in the ordinary way. It may in this connection be of interest to mention a generalization of the considerations to which we are led by experiments on the photo-electric effect, and which may be able to throw some light on the problem in question. Let us consider a state of the system in which the electron is free, *i.e.* in which the electron possesses kinetic energy sufficient to remove to infinite distances from the nucleus. If we assume that the motion of the electron is governed by the ordinary mechanics and that there is no (sensible) energy radiation, the total energy of the system—as in the above considered stationary states—will be constant. Further, there will be perfect continuity between the two kinds of states, as the difference between frequency and dimensions of the systems in successive stationary states will diminish without limit if τ increases. In the following considerations we shall for the sake of brevity refer to the two kinds of states in question as "mechanical" states; by this notation only emphasizing the assumption that the motion of the electron in both cases can be accounted for by the ordinary mechanics.

Tracing the analogy between the two kinds of mechanical states, we might now expect the possibility of an absorption of radiation,

not only corresponding to the passing of the system between two different stationary states, but also corresponding to the passing between one of the stationary states and a state in which the electron is free; and as above, we might expect that the frequency of this radiation was determined by the equation $E = h\nu$, where E is the difference between the total energy of the system in the two states. As it will be seen, such an absorption of radiation is just what is observed in experiments on ionization by ultra-violet light and by Röntgen rays. Obviously, we get in this way the same expression for the kinetic energy of an electron ejected from an atom by photo-electric effect as that deduced by Einstein, *i.e.* $T = h\nu - W$, where T is the kinetic energy of the electron ejected, and W the total amount of energy emitted during the original binding of the electron. . . .

Experiments on the phenomena of X-rays suggest that not only the emission and absorption of radiation cannot be treated by the help of the ordinary electro-dynamics, but not even the result of a collision between two electrons of which the one is bound in an atom. This is perhaps most clearly shown by some very instructive calculations on the energy of β -particles emitted from radioactive substances recently published by Rutherford. These calculations strongly suggest that an electron of great velocity in passing through an atom and colliding with the electrons bound will lose energy in distinct finite quanta. As is immediately seen, this is very different from what we might expect if the result of the collisions was governed by

the usual mechanical laws. The failure of the classical mechanics in such a problem might also be expected beforehand from the absence of anything like equipartition of kinetic energy between free electrons and electrons bound in atoms. From the point of view of the "mechanical" states we see, however, that the following assumption—which is in accord with the above analogy—might be able to account for the result of Rutherford's calculation and for the absence of equipartition of kinetic energy: two colliding electrons, bound or free, will, after the collision as well as before, be in mechanical states. Obviously, the introduction of such an assumption would not make any alteration necessary in the classical treatment of a collision between two free particles. But, considering a collision between a free and a bound electron, it would follow that the bound electron by the collision could not acquire a less amount of energy than the difference in energy corresponding to successive stationary states, and consequently that the free electron which collides with it could not lose a less amount.

The preliminary and hypothetical character of the above considerations needs not to be emphasized. The intention, however, has been to show that the sketched generalization of the theory of the stationary states possibly may afford a simple basis of representing a number of experimental facts which cannot be explained by help of the ordinary electro-dynamics, and that the assumptions used do not seem to be inconsistent with experiments on phenomena for which a satisfactory explanation has been given by the classical dynamics and the wave theory of light.

6.4

The Chance Discovery of X-rays

A. Sutcliffe and A. P. D. Sutcliffe

In the later part of the nineteenth century many scientists were studying the remarkable effects produced when electricity is discharged in a partial vacuum and were greatly

helped in their work by the invention of Crookes's tube in 1879. This is a long cylindrical tube of glass containing two terminals. One is connected through an induction coil