## Some Contemporary Advances in Physics IX The Atom-Model, Second Part<sup>1</sup>

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## G. RECAPITULATION OF THE FACTS TO BE EXPLAINED

 $\mathrm{E}_{\mathrm{view}}^{\mathrm{VERY}}$  atom-model that is worthy of notice was designed in view of a certain limited group of facts. That is to say, every valuable atom-model is the invention of somebody who, being acquainted with certain of the ways in which matter behaves, set himself to the devising of atoms of which an assemblage should behave like matter in those ways. Of course, it would be a most wonderful achievement to conceive atoms, of which assemblages should behave like matter in all ways; but this is too exalted an ambition for this day and generation, no man of science bothers with it. Each atommodel of the present is partially valid, not universally; and nobody can rightly appreciate any one of them, unless he knows the facts for which it was designed. I might add that he should also know the relative importance, in the world and in life, of the facts for which it was designed. But this also is too exalted an ambition: we do not know much, if anything, about the relative importance of facts sub specie aternitatis, and can hardly refrain from regarding with an especial favour the facts which happen to have been successfully explained. At all events it is clear that every account of an atommodel should be preceded by an independent account of the things it is meant to explain. For the favorite atom of these days, the atom of Rutherford and Bohr, I have provided this preliminary account of the facts in the First Part of the article. Let me give a brief outline of the most important among them, before entering upon the task of constructing an atom-model to reproduce them.

First and foremost, the elements are very definite things; each of the ninety of them is distinguishable from the other eighty-nine, not in one respect only but in many, and in many cases the contrasts are very severe. The atom designed for each of them must therefore have definiteness and fixity and a sharply-marked character.

Next: although the atom must be definite, it must not be absolutely immutable; it must be capable, under stress, of assuming various distinct states or forms or configurations or whatever you choose to call them. This is prescribed by that great and essential fact of the Stationary States, to which so much of the First Part of

<sup>1</sup> Devoted to Bohr's atom model for hydrogen and ionized helium. The models for other atoms, as well as some general considerations, are reserved for the Third Part.

this article was devoted. For an atom, when initially in its normal state and properly stimulated, is able to receive energy in certain definite measurable amounts, and to retain it for a while; and this is tantamount to saying that each atom may exist for a while in one or another of certain states distinct from the normal state, in each of which it possesses a certain distinctive amount of extra energy. Thus a helium atom may receive 19.75 equivalent volts of energy from an impinging electron, no less and (within certain limits) no more; and this is tantamount to saying that a helium atom may exist, not only in its normal state but also transiently in an abnormal state in which its energy is greater by 19.75 equivalent volts than in the normal state. The atom-model for each element must therefore be designed to be definite in each of several distinct and interchangeable states, and not in one only.

The energy-values of some few of these stationary states are determinable directly; but most of them (and they are very numerous) are deduced from spectra. The spectrum of an element is the family of radiations of various frequencies which it emits when it is in the gaseous state. These are commonly ascribed to the individual atoms. The first task of the spectroscopist is to measure these frequencies; his second, to classify them. In certain spectra his task of classification is easy, for there is a natural arrangement of the spectrum lines which "leaps to the eye." This is an arrangement of lines in one or several converging series, like those of which there were photographs of the First Part of the article. Let me represent by

$$\nu_1, \nu_2, \nu_3, \ldots, \nu_i, \ldots$$

the frequencies of the consecutive lines of a series, and by  $\nu_{lim}$  the frequency of the series-limit upon which they converge. Now the frequencies of the various lines may be described by a formula

$$\nu_i = \nu_{lim} - f_i \tag{1}$$

in which  $\nu_i$  is expressed as the difference between two *terms*. The term  $f_i$  varies from one line to the next; and in some instances this function  $f_i$  is algebraically of an extreme simplicity, just the sort of a simple elegance which is apt to suggest that the formula has an inward physical meaning. Also one and the same term may figure in the formulae for lines belonging to different series, a fact which enhances the feeling that the terms are physically "real." Thus the spectroscopist seeks "terms" whereby to classify the lines of a spectrum; and the analysis of a spectrum leads to the measurement of a multitude of terms.

Now multiply both sides of equation (1) by Planck's constant h; it becomes

$$h\nu_i = h\nu_{lim} - hf_i. \tag{2}$$

On the left-hand side we have  $h\nu_i$ , a quantity of the dimensions of Now there is much reason to believe that when radiant energy. energy streams out from a substance in the form of radiation of frequency v, it emerges often if not always in parcels or packets or units or quanta, each consisting of an amount of energy equal to  $h\nu$ . Suppose that the radiant energy constituting any line of a series is emitted in quanta such as these: then whenever an atom performs the act of radiating that line, it loses the amount of energy which stands on the left-hand side of Equation (2). The right-hand side represents the same thing, and is itself the difference between two terms which are spectrum-terms multiplied by h; these are themselves the values (reckoned from a suitable zero) of the energy of the atom before and after the radiation occurs, they are the energy-values of the atom in the state before radiating and in the state after radiating. The spectrum-terms, when multiplied by Planck's constant h, are translated into the energy-values of the Stationary States of the atom. When expressed in proper units, terms are energies and energies are terms. In the decades during which the spectroscopists were analyzing linespectra, disentangling line-series-by no means a light labor, for the perspicuity of the series shown in the photographs of the First Part is anything but common-and disengaging terms, they were unknowingly recognizing and locating the Stationary States of the atom. Spectrum analysis culminates in the fixation of the Stationary States. This is the greatest of the ideas for which the world is indebted to Bohr, and eventually through him to Planck.

These Stationary States constitute one of the great systems of facts, which the atom-model of Rutherford and Bohr is designed to interpret. Let me formulate the demands which thus are made upon this atom-model. It must have features to account for these facts: *First*, that there are such things as Stationary States;

Second, that in passing over in a "transition" from one stationary state to another of which the energy is less by  $\Delta U$ , the atom releases the energy  $\Delta U$  in radiation of the one frequency  $\Delta U/h$ ;

Third, that certain transitions do not occur, or occur under abnormal circumstances only, or occur less frequently than others; and

*Fourth*, that the stationary states of each particular kind of atom have the particular numerical energy-values which they are observed to have.

The first three of these demands are of a general and fundamental nature. If someone were to design an atom-model for these phenomena of the Stationary States and these alone, he would probably begin by imagining an atom which would satisfy these general demands; then he would proceed so to specialize it that it would comply also with the fourth. It might have been well, had this happened; the course of history was otherwise. The atom-model of Rutherford was designed originally to interpret phenomena of quite another field, and then Bohr modified it by violence to satisfy the fourth of the foregoing demands.

Of the facts which Rutherford devised his atom-model to interpret, the cardinal one is that the atom contains electrons. The best evidence for this fact is, that electrons can be extracted from atoms.<sup>2</sup> One can even measure the amount of energy required to extract an electron from an atom—in other words, the difference between the energy of an atom in its normal state, and the energy of the same atom in its "ionized" state.<sup>3</sup> This has a direct bearing on the phenomena of the Stationary States; for the spectrum-terms, when they are multiplied by Planck's constant h, yield the energy-values of the corresponding Stationary States, reckoned from the energy-value of the ionized state as zero of energy.

Granted that the atom contains electrons: it must contain positive electricity also, to compensate their negative charge. Now it is easy to imagine the positive electricity so arranged, that the electrons can be fitted into various places within and around it, and remain in equilibrium<sup>4</sup>; it is possible to imagine that the positive electricity acts upon the electrons with a force which is compounded of the familiar inverse-square attraction and a particular sort of a repulsion, so adjusted that the electrons will remain in equilibrium in various positions. It seems as though the Stationary States might be interpreted in this fashion, and several attempts have in fact been made; but they are discouraged by the experiments of Rutherford and his followers on the deflections of alpha-particles and electrons which pass through atoms. For these deflections occur exactly as if the positive electricity were concentrated at a point or "nucleus," and an inverse-square electric field prevailed in the region between this nucleus

<sup>2</sup> This is not quite a proof of the fact. As Aston cleverly remarked, when a pistol is fired, smoke and a bullet come out of it; we are quite justified in inferring that the bullet was originally within the pistol, but not the smoke!

<sup>3</sup> This energy, which I called the energy of the "state of the ionized atom" in the First Part, is truly the energy of the system composed of the atom minus its electron, and the free electron.

<sup>4</sup> Although not in stable equilibrium.

and the electrons.<sup>5</sup> They may be compatible with other atom-models; it is certainly incumbent upon the designer of any other to prove that they are compatible with his. Furthermore these deflections indicate that the positive charge on the nucleus of the atom is just sufficient to compensate the negative charges of a number N of electrons, equal to the "atomic number" Z which is the cardinal number defining the position of the element in the Periodic Table of the Elements. This confirmation of the splendid idea of van den Broek and Moseley is so delightful and so precious, that anyone would hesitate long before rejecting the atom-model whereby it is deduced from Rutherford's experiments.

Yet this nuclear atom-model cannot be accepted, without being instantly modified. A system consisting of a positively-charged nucleus and electrons surrounding it, all acting upon one another with inverse-square forces of attraction between nucleus and electrons and repulsion between one electron and another, is not a stable system: it is a suicidal system, doomed to quick and permanent collapse. If the electrons were initially standing still, they would fall into the nucleus; if the electrons were initially swinging in orbits about the nucleus like planets around the sun, they would steadily radiate their energy into space-not in radiation of one single frequency either, but in a mixture of all possible frequencies-and would wind their ways spirally into the nucleus. Therefore, the nuclear atom-model must be altered; for instance, by adding a proviso, that the electrons shall stand still, and shall not be sucked into the nucleus; or a proviso, that the electrons shall revolve in closed orbits planetwise, without radiating any of their energy<sup>6</sup>, and without gliding by a spiral path into the nucleus.

Suppose then that we decide to make one or the other of these provisos, in order to save the interpretation of Rutherford's experiments. Could we then so shape the proviso, that it would satisfy the four demands which I described as being made upon the atom-

<sup>5</sup> Apart from such deviations in the immediate neighborhood of the nucleus as the most delicate experiments of this sort reveal; which cannot be supposed to extend to the region where the electrons are.

To indicate how much this neglect of the radiation from the revolving electron amounts to, I cite the results of a calculation given by Wien in his lecture Ueber Elektronen, and doubtless elsewhere. Imagine an electron distant by ten Angstrom units from a hydrogen nucleus, and moving with such a velocity that, but for the radiation, it would revolve in a circle about the nucleus. In a single circuit, it should radiate about one ten-millionth part of the kinetic energy it initially possesses. Hence the single circuit will differ very little indeed from a perfect circle; and in this sense, the radiation is truly negligible. But the single circuit is described in less than  $10^{-20}$  second; hence, in any time-interval long enough to be measured by the most delicate of physical apparatus, the dissipation of energy by radiation is far too great to be neglected with impunity. model by the facts of the Stationary States? Could we for instance so shape the first proviso, *could we choose such locations for the electrons assumed stationary*, that the sodium atom (for instance) would display only those energy-values which the spectrum of sodium allows for its Stationary States, and no others?

Undoubtedly we could. The sodium atom is supposed to consist of eleven electrons surrounding a nucleus of charge +11e. If the electrons were all stationary in assigned positions about the nucleus, we could calculate the energy of the arrangement. The energy-values of the various Stationary States being known, it would not be difficult to find, for each one of the Stationary States, at least one arrangement of the eleven electrons identical with it as to energy-value. Having done this, we could lay it down as a law that the electrons shall stand still in each and any one of these arrangements; but not in any other arrangement whatsoever.

But would this be an explanation of the Stationary States? Not, I think, in any significant sense of that valuable word. It could justly be designated as an explanation, as a theory, only if the various arrangements so prescribed for the various Stationary States should turn out to be interrelated according to some law—to be governed by some unifying principle—to display some intrinsic quality of simplicity and elegance and beauty, distinguishing them from all the other and rejected arrangements. This has not been achieved.

Let me now take up the other of the two suggestions which were made above. Suppose that we accepted the nuclear atom-model, with the proviso that the electrons should revolve in closed orbits planetwise, without radiating any of their energy, and without gliding by a spiral path into the nucleus. Could we so shape this second proviso, *could we choose such orbits for the electrons assumed revolving without loss of energy*, that the sodium atom or the hydrogen atom (for instance) would display only those energy-values which the spectrum of sodium or the spectrum of hydrogen prescribes for the Stationary States, and no others?

Again, there is no doubt that we could; but the value of the achievement, again, would depend on whether or not the orbits which we thus selected were interrelated according to some law, or governed by some unifying principle, or distinguished from all the other orbits by something seemingly fundamental. Consider Rutherford's model for the hydrogen atom, which consists of a nucleus and an electron. If we adopt the proviso which was just set forth, and suppose that the electron may revolve around the nucleus in circular orbits without radiating any of its energy, then we can select particular circular orbits, such that when the electron is revolving in one or another of these, the energy of the atom shall have one or another of the values prescribed by the Stationary States. If we arbitrarily say that the electron can revolve only in one or another of these orbits, then we have an atommodel competent to interpret the Stationary States of the hydrogen atom. But is there anything distinctive about these selected orbits, anything peculiar, anything which marks them out and sets them apart from the other, from the discarded orbits? Have they any feature in common, apart from being necessary to give the observed energyvalues of the Stationary States?

It is hardly possible to lay too strong an emphasis upon this requirement; the value of the contemporary atom-model depends upon satisfying it. Let me put the matter another way. From the moment that we imagine that the electrons within the atom are cruising around the nucleus in orbits without radiating energy and without dropping into the nucleus, we are sacrificing the unity and the coherence of the classical theory of electricity. So grave an action is not to be undertaken lightly nor with indifference; it were foolish to make such a sacrifice without recompense; and there is no recompense to be found in merely proving that especial orbits can be so selected as to copy the energy-values of the Stationary States. If one is going to deviate from the rules of the classical theory of electricity, one must deviate by rule. If one is going to disrupt the system which prevails in one great department of theoretical physics, one must systematize another department in exchange. If one proposes to violate some of the principles of modern physics, by asserting that electrons can travel in certain orbits without radiating, he must reconcile the congregation of physicists to his sacrilege by proving that the selected motions are themselves governed by a principle, as imposing as those he lacerated. If the innovator cannot show that his innovations are systematic, he is not likely to prosper; but if his innovations are derived from a principle, it may supersede those which he contradicted.

To discover such a principle is the ambition of, probably, half of the theoretical physicists who are active today.

There are other general statements which might be made at this point; but they will be more intelligible, and so will the foregoing paragraphs be, after I have given an illustration. For this purpose I will describe two models of the hydrogen atom, each of them consisting of a nucleus and a single electron, each capable of being so constrained that its energy-values will copy those of the Stationary States of hydrogen. With one of these, however, the description can be carried no farther. With the other, I shall show—following Bohr—that the orbits in which the electron is constrained to revolve have certain peculiar features, distinguishing them above all other orbits; and these distinctive features may be consequences of the desired and still hidden principle.

# H. FEATURES OF THE NECESSARY ORBITS OF THE HYDROGEN ATOM (QUANTIZATION)

Hydrogen being the first element in the periodic table, Rutherford's atom-model for it consists of a nucleus and one electron. The electron bears (or *is*) a negative charge amounting to -e or  $-4.774.10^{-10}$  electrostatic units, and its mass is approximately  $9.10^{-28}$  grammes. The nucleus bears a positive charge amounting to +e, and its mass is about 1,840 times as great as that of the electron.

The stationary states of the hydrogen atom possess the energyvalues -Rh, -Rh/4, Rh/9, -Rh/16, -Rh/25, and so on; in general, the values  $-Rh/n^2$  (n=1,2,3...). The constant <sup>5</sup> R is equal to  $3.29.10^{15}$ ; the constant h is Planck's constant  $6.56.10^{27}$  erg. sec.

Rutherford's atom-model for the hydrogen atom must now be so modified, that it will admit the energy-values just specified, and no others.

I will begin by doing something which amounts to setting up a straw man, to be knocked down immediately,—but not, I hope, before he dces us some service. Let us suppose that, in spite of all the laws of dynamics, the electron may stand still at a distance r from the nucleus, without starting towards and falling into it. With the electron in such a position, the energy of the atom is  $-e^2/r$ . This is an energyvalue referred, like all energy-values, to a particular zero; in this case, the zero-value of energy corresponds to the condition in which the electron is infinitely far away from the nucleus. We recognize at once the "state of the ionized atom," to which the energy-values of the Stationary States as given by the spectrum-terms are automatically referred. This quantity  $-e^2/r$  must be permitted to assume the successive energy-values of the successive Stationary States, and no others; we must have

 $-e^2/r = -Rh$  for the first (or normal) stationary state

 $-e^2/r = -Rh/4$  for the second stationary state

(3)

 $-e^2/r = -Rh/9$  for the third stationary state; and so forth.

<sup>5</sup> I deviate here from the more frequent usage of defining R from the equation

$$\frac{1}{\lambda} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

for the reciprocals of the wavelengths of the various lines of hydrogen; in which equation R = 109677.69 by measurements of tremendous accuracy, and is to be multiplied by c to get what I have called R.

Now each of these equations defines a value of r; we have

 $r = e^2/Rh$  for the normal state  $r = 4e^2/Rh$  for the second stationary state  $r = 9e^2/Rh$  for the third stationary state; and so on.

Each of these values of r represents the distance at which the electron must stand from the nucleus, that the atom may have the energy-value of the corresponding stationary state. If we say that the electron may stand still at and only at the distances given by

$$r = e^2/Rh, \ 4e^2/Rh, \ 9e^2/Rh, \ \dots \ \dots \ (5)$$

(4)

we thus define an atom-model interpreting the Stationary States. It is scarcely an atom-model to be recommended, and I certainly am not taking the responsibility of recommending it. Nevertheless the reader had best beware of picking out the obvious objections to it, and condemning it because of them. For if he objects that I have given no reason why the electron should stand still at all, nor why it should stand still in these and only in these positions, nor why it should cause radiation of a peculiar and well-defined frequency when it passes from one of these positions to another-if he makes these objections, I can retort that the atom-model favored by Bohr himself suffers from every one of these deficiencies. In fact, the only defects peculiar to this "atom-model of the stationary electron" appear The first is, that the distances specified by (5) do not have to be two. distinctive features such as I shall presently show for the orbits specified for the "atom-model of the revolving electron": and this defect, as I have tried to emphasize, is a grave one. The second is, that an atom in which the charges are stationary is not *ipso facto* magnetic, whereas an atom with revolving electrons is.7

Following Bohr, and practically all the other physicists of today, we now assume that the electron revolves planetwise around the nucleus describing a closed orbit and radiating none of its energy as it revolves. A planet revolves in an elliptical orbit; this elliptical orbit may be a circle, or it may not be; but for the present paragraph we will think of the circles only. Let us suppose, then, that the electron may revolve in a circle about the nucleus, without radiating its energy and spiralling into the nucleus. Designate the radius of the circle by r. With the electron revolving in a circle of radius r, the energy of the atom is  $-e^2/2r$ . This value is obtained by adding together the potential energy of the atom, which is  $-e^2/r$  just as it

<sup>7</sup> If any reader can abolish these defects, a multitude of chemists will be glad to hear from him. Chemists want atom-models with stationary electrons.

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was when we supposed the electron to be standing still, and the kinetic energy of the electron, which is  $\frac{1}{2}mv^2$ . In this last expression, v stands for the speed of the electron in its orbit; now,  $mv^2/r$  is the "centrifugal force" acting upon the electron, which is equal (and opposite) to the attraction exercised by the nucleus upon the electron, which is  $e^2/r^2$ ; so that  $\frac{1}{2}mv^2$  is equal to  $+e^2/2r$ , and the total energy of the atom has the value  $-e^2/2r$ . As before, this is the energy-value referred to the state of the ionized atom.

This quantity  $-e^2/2r$  must be permitted to assume the successive energy-values of the successive Stationary States, and no others; we must have

$$-e^{2}/2r = -Rh/n^{2} (n = 1, 2, 3, 4, \dots)$$
(6)

Each of these equations defines a value of r, as follows:

$$r = n^2 e^2 / 2Rh \ (n = 1, 2, 3, 4, \dots)$$
 (7)

If we say that the electron may revolve in and only in such circles as have the radii given by the equations (7), we thus define an atommodel interpreting the Stationary States. Is this atom-model superior to the tentative one which was described just before it? Not in any way which has yet been brought to notice. No reason is given why the electron should revolve in a circle instead of spiralling into the nucleus, nor why it should revolve in these and only in these circles, nor why it should cause radiation of a peculiar frequency to be emitted when it passes from one of these circles into another. All of the objections which I suggested, a few paragraphs above, that the reader might raise against the then-mentioned atom-model with the stationary electron, may equally well be raised against this atommodel with the revolving electron. Why then should we attach greater importance to this one than to that? Partly, as I said, because this atom possesses intrinsic magnetic properties, while to the other one magnetic qualities would have to be ascribed by an additional assumption; but chiefly because Bohr discovered certain distinctive features of the circular orbits defined by (7), which set them apart from all others. These we now examine.

To understand the first of these features, it is necessary to consider the angular momentum of the atom. Sooner or later we shall have to make a slight alteration in the reasoning indicated in the last paragraphs; it may as well be made now even though it is not yet necessary. Heretofore I have tacitly assumed that the nucleus stands still while the electron revolves around it. As a matter of fact, if the atom may be represented as a solar system in miniature, the nucleus and the electron both revolve about their common centre of mass in ellipses —we will think, as before, only of circles (Figure 1). The radii a and Aof the circular orbits of the nucleus and the electron, being the respective distances of the particles from their centre of mass, stand in the reciprocal ratio of the masses M of the nucleus and m of the electron; and as they describe their orbits in the same period (since the centre



Fig. 1—Diagram to illustrate how the electron and the nucleus revolve around their common centre of mass in synchronous orbits

of gravity is at rest and always between them) their speeds v and V stand in the same ratio:

$$a/A = v/V = M/m. \tag{8}$$

I introduce the symbol  $\mu$  to denote the equal quantities

$$\frac{M}{M+m} = \frac{a}{a+A} = \frac{v}{v+V}.$$
(9)

The potential energy of the atom, reckoned as always from the state in which the nucleus and the electron are infinitely far apart, is obviously  $-e^2/(a+A) = -e^2\mu/a$ . The kinetic energy of the atom is the sum of the portion  $\frac{1}{2}mv^2$  belonging to the electron and the portion  $\frac{1}{2}MV^2$ , belonging to the nucleus. I point out that the "centrifugal force" acting upon the electron is  $mv^2/a$ , and that acting upon the nucleus is  $MV^2/A$ , and each of these separately must be equal to the reciprocal attraction  $e^2/(a+A)^2$  of nucleus and electron; and I leave it to the reader to show by means of these equalities that the kinetic energy amounts to  $\frac{1}{2}e^2\mu/a$ . The total energy of the atom is therefore equal to  $-\frac{1}{2} e^2 \mu/a$ , and this is the quantity to be equated to the observed energy-values of the stationary states; equation (6) is replaced by

$$-e^{2}\mu/2a = -Rh/n^{2}.$$
 (10)

The angular momentum of the electron is mva; the angular momentum of the nucleus is M VA; the angular momentum of the atom, for which I use the symbol p, is the sum of these:

$$p = mva + MVA = mva/\mu. \tag{11}$$

I leave it again to the reader to use the foregoing statements to arrive at the expression

$$p = e\sqrt{ma} \tag{12}$$

and by combining (12) and (10), at the expression

$$p_n = ne^2 \sqrt{m\mu/2Rh} \tag{13}$$

for the value  $p_n$  of the angular momentum of the atom, or rather of our atom-model, in its *n*th stationary state.

Thus the values of the angular momentum of the atom-model, in the various states in which it has the prescribed energy-values -Rh, -Rh/4, and so forth, increase from the first of these states onward in the ratios 1:2:3:4... They are the consecutive integer multiples of a fundamental quantity, the quantity

$$p_1 = e^2 \sqrt{m\mu/2Rn}.\tag{14}$$

Now it happens that this fundamental quantity is equal, within the limits of experimental error, to  $h/2\pi$  to  $1/2\pi$  times that same constant h which has already figured in this discussion:

$$p_1 = h/2\pi; \ p_n = nh/2\pi.$$
 (15)

This occurs because the value of R is equal, within experimental error, to the combination of m, e, and h on the right of this equation:

$$R = 2\pi^2 \mu m e^4 / h^3. \tag{16}$$

The atom-model which I have been describing at some length could therefore be described in a few words by saying that the electron is permitted to revolve only in certain circular orbits, determined by the condition that the angular momentum of the atom shall be equal to an integer multiple of  $h/2\pi$ . This condition is in fact sufficient to impose the values given for the radii of the circular orbits in equations (10) which values in turn entail the desired energy-values for the stationary states. The reader can easily prove this by working backward

through the train of equations; and indeed this is the manner in which the Bohr atom-model is usually presented, so as to arrive finally at the agreement between "theory" and experiment which is expressed in equation (16), and is a most striking climax to the whole exposition. By working through the train of equations in the inverse sense, I have considerably mitigated the effect of the climax; and this procedure seems hardly fair to the author of the theory, but it is not without its merits, for it enables us to see the exact role of equation (15) more clearly than the commoner procedure.

The situation now is this. It is possible to construct, out of a nucleus and an electron, an atom-model possessing stationary states of the energy-values displayed by the hydrogen atom, provided that we assume that the electron may revolve only in circular orbits for which the angular momentum of the atom is an integer multiple of  $h/2\pi$ . There is no known reason why an electron should do a thing like this, there is good reason to suppose that it cannot do anything of the sort, for if it started out to revolve in a circular orbit it would radiate its energy and descend spirally into the nucleus. If nevertheless we assert that the electron does just this sort of thing, we have nothing with which to support the assertion, nothing extrinsic by which to render it plausible; it must stand on its own merits as an independent principle.

These merits, had we no data other than the energy-values of stationary states catalogued in equation (6), would probably be regarded as scanty. After all, the agreement between the constant  $p_1$  and the quantity  $h/2\pi$  might be fortuitous. But there are other stationary states of the hydrogen atom, beyond those listed in (6). For instance there are the stationary states which are evoked by a strong electric field acting upon hydrogen, and there are the stationary states which are called into being by a magnetic field applied to hydrogen, as I related in earlier sections of this article. There is also the fact, that at least one of what I have been calling the stationary states of hydrogen is not a single stationary state at all; there are two states of which the energy-values lie exceedingly close together and to the value -Rh/4, so close that nearly all experiments fail to discriminate them. And there is the great multitude of stationary states exhibited by other elements than hydrogen; but we will not think about these for the time being.

Now the situation is transformed into this. Consider all these additional stationary states, exhibited by the hydrogen atom under unusual or even under usual circumstances. Is it possible to trace, for each one of them, an orbit for the electron, such that while the

electron is describing that orbit, the energy of the atom possesses just the value appropriate to that Stationary State? And granting that this is possible and accomplished; can it be shown that these additional orbits are distinguished by some feature resembling that feature of the circular orbits which is described by equation (15)? Our condition laid upon the circular orbits, that in each of them the angular momentum of the electron is an integer multiple of  $h/2\pi$  this condition valid for the limited case, can it be generalized into a condition governing the Stationary States of the hydrogen atom under all circumstances? Can orbits be described which account for all of the Stationary States of hydrogen under all circumstances, and which are determined by a general condition of which the condition set forth in equation (15) is one particular aspect? If so, that general condition might well be such a Principle as the one towards which, as it was said in the last section, so many physicists aspire. Thus the test to which this condition laid upon the angular momentum must be submitted is this: can it be generalized?

Before trying to generalize it let us examine some other distinctive features of the circular orbits defined in (7)—I will call them henceforth the "permissible" circular orbits, but we should remember that perhaps it is only ourselves who are "permitting" them and forbidding the others, and not Nature at all. Let us calculate the integral I of the doubled kinetic energy 2K of the atom over a complete revolution of the electron (and nucleus):

$$I = \int_0^T 2K dt. \tag{17}$$

It is easy in this case, for K is constant in time, so that I = 2KT. Now K is equal to  $\frac{1}{2}mv^2/\mu$ , and T is equal to  $2\pi a/v = 2\pi^2 ma^2/\mu K$ ; which expression the reader may reduce, by means of that equation  $K = \frac{1}{2}e^2\mu/a$  which he was invited to derive, to

$$T = \pi e^2 \sqrt{m\mu/2K^3} \tag{18}$$

multiplying which by K, and using equation (10), we have

$$I = 2\pi n \cdot e^2 \sqrt{m\mu/Rh}.$$
(19)

The reader will recognize the factor which appeared in (14) and was there stated to be numerically equal, within the error of observation, to  $h/2\pi$ .

Therefore this atom-model could also be described by saying that the electron is permitted to revolve only in certain circular orbits determined by the condition that I shall be equal to an integer multiple of h. For future use I interpolate the remark that the factor n is called the *total* or *principal quantum number*; in German, *Hauptquantenzahl*.

The reader will think that this is not a new condition, but only a futile way of re-stating the condition laid upon the angular momentum. So it might be, in this case. But when we come to the more complex cases, we shall find that the two conditions diverge from one another. Which of the two can be generalized, if either? Only experience can show.

I will describe one more distinctive feature of the permissible orbits; it may seem more impressive than either of the others.

We have seen that the frequency of the radiation emitted, when the hydrogen atom passes from one stationary state to another—say from the state of energy  $-Rh/n'^2$  to that of energy  $-Rh/n''^2$ —is

$$v = \frac{R}{n^{\prime\prime 2}} - \frac{R}{n^{\prime 2}}$$

which may be written

$$\nu = \frac{R}{n'^2 n''^2} (n' - n'') (n' + n'').$$
<sup>(20)</sup>

Suppose that n'-n''=1, that is, that the transition occurs between two adjacent stationary states of the atom; and let n' and n'' increase indefinitely. In the limit we shall have

$$Lim \ \nu = \frac{2R}{n^{\prime 3}}.\tag{21}$$

Accepting the atom-model with the electron revolving in a circular orbit, we take from (18) the value for the period of the revolution, substitute for K by the aid of (10), and arrive at this expression for the frequency of the revolution:

$$\omega' = v/2\pi r = \sqrt{8R^3h^3}/2\pi n'^3 e^2 \sqrt{m\mu}$$
<sup>(22)</sup>

Comparing this expression for  $\omega'$  with the expression for  $\lim \nu$  in (21), we see that they are identical, if

 $R=2\pi^2m\mu e^4/h^3$ 

and this will be recognized as being that very value of R which was given in equation (13), as the value established by experiment. Thus the experimental value of R is such that

$$Lim \ \omega = Lim \ \nu.$$
 (23)

In this equation the symbol  $\omega$  stands for the frequency of revolution of the electron in its orbit, when the energy of the atom is  $-Rh/n^2$ . It therefore stands for the frequency of the radiation which the atom would be expected to emit; for an electrical charge performing a periodic motion should, according to the fundamental doctrines of the electromagnetic theory, be the origin of a stream of radiation with period equal to its own. The symbol  $\nu$  stands for the frequency of the radiation which the atom does emit in passing between two adjacent Stationary States. According to (19), this actual frequency is more nearly equal to the expected frequency, the more remote these two adjacent Stationary States are from the normal State; and in the limit, actual frequency and expected frequency merge into one. The numerical value of the constant R is just such as to bring about this relation.

Here again we have a curious numerical agreement which, like the other correlated fact that the angular momentum of the electron in the *n*th orbit is  $nh/2\pi$ , may by itself be merely a coincidence; but this one has a much greater inherent appeal. We have relinquished the expectation that the electron, cruising around the nucleus in a cyclic path, will send forth radiation of the frequency of its own revolutions, as every inference from the laws of electricity indicates that it should; but here is a case—even if it is only a limiting case in which the frequency emitted from the atom agrees with the one which we should expect. Generally there is discord; but in the limiting case there is consonance. Does this not suggest that the desired Principle may be one which in a limiting case merges with the classical theory of electricity—possibly, indeed, nothing less than the foundation of a general theory of electricity, of which the classical theory expresses only a special case?

Let us review our situation.

Having supposed for hydrogen an atom-model consisting of a nucleus and an electron;

Having supposed that these revolve around their common centre of mass according to the laws of dynamics, but without spending any energy in radiation;

Having supposed in particular that they revolve only in circular orbits, and only in such circular orbits as yield for the atom-model the energy-values  $-Rh/n^2$  measured by experiments upon the Stationary States;

Having traced these "permissible" circular orbits,

We have found that they are distinguished from all the other circular orbits by at least three peculiar features (viz., the features expressed by the equations  $p = nh/2\pi$ , and I = nh, and  $Lim \omega = Lim \nu$ ).

We do not know that there is any revolving electron at all. We know only that if all our suppositions be correct, the consequences

expressed by these three equations are correct also. Are these consequences impressive enough to prove the suppositions true?

The answer to this question depends on our degree of success, or rather on the degree of success attained by Sommerfeld and Bohr and their followers, in generalizing these equations to other and more complex cases. Usually the process of generalizing will involve difficult labours of orbit-tracing. But it is possible to make a significant comparison between the spectra of hydrogen and of ionized helium, without additional studies of orbits.

## I. Relations Between the Spectrum of Hydrogen and the Spectrum of Ionized Helium

To make trial of the validity of the foregoing ideas about the origin of the hydrogen spectrum, one naturally applies them to whatever other spectra may reasonably be ascribed to an atom consisting of a nucleus and a single electron. As according to the view adopted in this article the atom of the nth element in the Periodic Table consists of a nucleus and n electrons, the only way to produce such a spectrum is to produce a sufficient number of atoms of some element or other, each atom lacking all but one of its electrons; helium atoms deprived each of one electron or "once-ionized," lithium atoms deprived each of two or "twice-ionized," beryllium atoms deprived each of three electrons, or in general atoms of the nth element of the Periodic Table divested each of (n-1) electrons. This we should expect to require violent electrical or thermal stimulation of the vapor of the element, more violent the more electrons have to be removed. Hence it is not surprising that the spectrum of onceionized helium is the easiest of these spectra to produce; but it is more than a little strange that this is not merely the easiest but the only spectrum of this kind which has ever been obtained. Even the spectrum of twice-ionized lithium has not been generated, in spite of efforts quite commensurate with the value it would have.8 The spectrum of once-ionized helium remains the only companion of the spectrum of hydrogen; these are the only two known spectra which are ascribed to atoms consisting of a nucleus and a single electron.

We have seen that if we imagine that the electron of the hydrogen atom can revolve, without spending energy by radiation, in and only in those circular orbits for which the angular momentum of the atom is equal to  $h/2\pi$ ,  $2h/2\pi$ ,  $3h/2\pi$ ,  $\ldots$   $nh/2\pi$ ,  $\ldots$ , then the energy of the atom-model can assume only the values -Rh, -Rh/4,

<sup>8</sup> Consult for instance the article by Angerer, ZS. f. Physik, 18, pp. 113 ff.

 $-Rh/9, \ldots -Rh/n^2$ , which are the energy values for the observed stationary states of hydrogen. If this is not an accidental coincidence, then by imagining that the electron of the ionized helium atom likewise can revolve only in orbits for which the angular momentum of the atom is some integer multiple of  $h/2\pi$ , and by calculating the corresponding energy-values for the atom-model, we should arrive at the energy-values of the observed stationary states of ionized helium. Now the charge on the nucleus of the helium atom is 2e, twice the charge of the hydrogen nucleus; the force which it exerts on an electron at distance r is  $2e^2/r^2$ , instead of  $e^2/r^2$ . If the reader will work through the equations of Section H, making this alteration wherever appropriate, he will find for the energy-values of the stationary states the sequence

$$-4Rh, -4Rh/9, -4Rh/16, \ldots -4Rh/n^2, \ldots$$

in which

$$R = \frac{2\pi^2 \mu m e^4}{h^3}$$
(25)

as heretofore. The quantity  $\mu$  will be different from what it was for hydrogen; but the difference will be very slight. Therefore if the condition that the electron may revolve about the nucleus only in circular orbits for which the angular momentum of the atom is  $nh/2\pi$ is an essential condition, and governs the atoms of hydrogen and ionized helium alike, the stationary states of ionized helium correspond one-to-one with those of hydrogen, but with energy-values almost exactly four times as great. So also with the lines of the spectrum; to each line of the hydrogen spectrum should correspond a line of fourfold frequency in the ionized-helium spectrum; the spectrum of ionized helium should be the spectrum of hydrogen on a quadrupled frequency-scale.

This conclusion is verified. The historical sequence of observations and theories is rather interesting. Certain lines of ionized helium were earliest observed in stars; their simple numerical relations with hydrogen lines being noticed, they were naturally ascribed to hydrogen, and when they were generated in mixtures of hydrogen and helium within a laboratory they were still attributed to the firstnamed of these gases. Bohr in his first published paper reasoned in the manner I have followed in this section, and inferred that these lines really belonged to helium; which was shortly afterwards verified by seeking and finding them in the spectrum of helium made as pure as possible. A number of additional lines of the spectrum have since been found, although the lines corresponding to transitions into the normal state (the state of energy -4Rh) are so far out in the ultraviolet region of the spectrum that no one has yet succeeded in detecting them.

We will now take account of the fact that the numerical values of the constant R calculated for hydrogen (equation 16) and for ionized helium (equation 25) are not quite the same; they are in fact proportional to  $\mu$ , the quantity which determines the motion of the nucleus, and which varies from one atom to another. In particular

$$R_{He}/R_H = \mu_{He}/\mu_H = (1 + m/M_H) \ (1 + m/M_{He})$$
(26)

in which the symbols m,  $M_{H}$ ,  $M_{He}$  denote the masses respectively of the electron, the hydrogen nucleus and the helium nucleus, which stand to one another as .000542; 1.000:3.968. Consequently the right-hand member of equation (26) is equal to 1.000403, and the ratio of the frequencies of corresponding lines in the spectra of ionized helium and of hydrogen is

$$4 R_{He}/R_H$$
 calculated = 4.001612 (27)

The values of  $R_{He}$  and  $R_{H}$  deduced from frequency measurements yield the ratio

$$4 R_{He}/R_H \text{ observed} = 4.0016212$$
 (28)

The very-exactly-known observed value lies well within the margin of uncertainty of the calculated value. The calculated value of the ratio depends on otherwise-made measurements of the mutual ratios of the three masses (those of the electron, the hydrogen nucleus, the helium nucleus). These otherwise-made measurements are not of the grade of precision claimed for the measurements of 4  $R_{He}/R_H$  by the observations on the spectra. Hence if we combine the observed value of the ratio  $4R_{He}/R_H$  with (for instance) the ratio  $M_{He}/M_H$ derived from density-measurements upon the two gases, we can calculate a value for the ratio  $M_H/m$  ostensibly much more precise than the amount ascertained by direct measurement. This value is

$$M_H/m = 1847. (29)$$

Let me state briefly what the numerical agreement between the "calculated" and "observed" values of  $4R_{He}/R_H$  specifies. It is a test of this set of assumptions; the hydrogen atom and the ionized helium atom may each be represented by a single electron and a nucleus of charge +e in one case and +2e in the other; each stationary

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state corresponds to a certain circular orbit of the electron; the Angular Momenta of the two atoms are identical when they are in corresponding stationary states. As a test, it is favorable. It does not involve the relation between angular momenta and integer multiples of  $h/2\pi$ which was stressed in the foregoing section. It is independent of that relation, and may fairly be considered as the second numerical agreement offered by this atom-model, if that relation be considered the first. The idea is due to Sommerfeld; the data whereby the test was made were obtained by Paschen, as a by-product of the work cited in footnote 12.

Although the statements in the foregoing paragraphs are literally true, they do not prove that the condition Angular Momentum =  $nh/2\pi$  is the distinctive feature par excellence of the permissible circular orbits. The result would have been exactly the same if I had defined the stationary states of the ionized helium atom as those for which I = nh or as those for which  $Lim \omega = Lim \nu$ .

#### J. TRACING OF ORBITS

We must now seek for opportunities to make and test generalizations of the notions about the hydrogen atom explained in section H.

I began by saying that the electron should be supposed to revolve in the inverse-square electrostatic field of the nucleus, according to the laws of dynamics, without spending energy in radiation; and continued by saying that I should speak of circular orbits only. Now the laws of dynamics prescribe elliptical orbits, of which the circular orbits are but special cases. In fact, for each one of the sequence of energy-values  $-Rh/n^2$  corresponding to the sequence of Stationary States, there is an infinity of elliptical orbits possessing that energyvalue, of which the circle of radius specified by equation (7) is only one. Suppose we should inquire what, if any, are the distinctive features of these elliptical orbits which set them apart from all others?

Again: when radiating hydrogen is exposed to a strong electric field, new stationary states appear, and their energy-values are known. The orbit of an electron, in a field compounded of an inverse-square central field and another field uniform in magnitude and direction, is no longer a circle nor even an ellipse nor even a closed orbit (except in special cases). Could the orbits having energy-values equal to those of the stationary states be identified and traced, and could distinctive features be found which mark them out from among all the others?

Again: when radiating hydrogen is exposed to a strong magnetic

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field, new stationary states appear, and their energy-values are known. Could the orbit of an electron in a field compounded of an inversesquare central electric field and an uniform magnetic field be traced? and could the orbits having energy-values equal to those of the stationary states be identified? and could peculiar features be found which mark them out from all the others?

Or conversely: is it possible to make "trial" generalizations of one or another of the conditions  $p = nh/2\pi$  and I = nh and  $Lim \ \omega = Lim \ \nu$ ? to invent features for the more complex orbits, which sound like reasonable generalizations of these features of the simplest ones? and, having done so, to trace the orbits exhibiting these "trial" features, determine their energy-values, and compare these with the observed energy-values of the stationary states?

Whichever of these two ways is employed to attack the problem, it is necessary to trace orbits more complex, and usually in more complex fields, than the circular orbits imagined for the hydrogen atom. This problem of tracing orbits is the fundamental problem of Celestial Mechanics—the oldest and the most richly developed department of mathematical physics, which in its two centuries and more of history has developed a language and a system of procedures all its own. It is chiefly on that account that many of the recent articles on the atom-model of Bohr are so excessively difficult for any physicist, unless he is of the few who practiced the arts of theoretical astronomy diligently and for a long time before passing over into the field of physics.

In this section I shall quote the equations for the motion of a particle in an ellipse under the influence of an inverse-square central field, and give the derivation with all necessary detail. For the other relevant cases-motion of an electron in a central electric field upon which an uniform electric field, or an uniform magnetic field, or a small central field varying according to some other law of distance than the inverse square, is superposed—I shall give only some of the results, without even attempting the derivation. I shall make no allowance for the motion of the nucleus; the electron will be supposed to revolve around the nucleus considered as fixed. The very small correction required to take account of the motion of the nucleus can easily be applied by the reader, if he so desire. The principal disadvantage involved in neglecting it is, that one too easily thinks of the angular momentum of the electron in its orbit as belonging to the electron alone, whereas it is really the angular momentum of the atom-model. I shall also put Efor the charge on the nucleus; E will be equal to e for the hydrogen

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and to 2e for the ionized-helium atom-model, no other cases matter for the time being.<sup>9</sup>

#### J1. Motion of an Electron in an Inverse-Square Central Field

Most people recognize the equation of the ellipse most easily in the form

$$x^2/a^2 + y^2/b^2 = 1$$

in a coordinate-system of which the origin is at the centre of the ellipse, the x-axis and the y-axis parallel respectively to the major and the minor axes of the ellipse.

The symbol a and b denote the semi-major and semi-minor axes of the ellipse; they are related by

$$b^2 = a^2(1 - \epsilon^2) \tag{30}$$

in which  $\epsilon$  stands for the "eccentricity" of the ellipse. The foci of the ellipse lie on the major axis at distances  $a\epsilon$  to either side of its centre. Transferring the origin to one focus, say the focus at  $x = +a\epsilon$ , and using coordinate-axes parallel to the former ones, we have

$$(\zeta + a\epsilon)^2/a^2 + y^2/b^2 = 1$$

Transforming coordinates again, this time into polar coordinates r and  $\phi$  with the origin at the focus of the ellipse and the direction  $\phi = O$  pointing along the *x*-axis, by means of the substitutions

$$\zeta = r \cos \phi$$
  $y = r \sin \phi$ 

we arrive after somewhat tedious but not difficult algebra<sup>4</sup> at the equation for the ellipse in the form in which we shall use it

$$r = \frac{a(1-\epsilon^2)}{1+\epsilon\,\cos\phi}$$

and at the derivative thereof

$$\left(\frac{dr}{d\phi}\right)^2 = \frac{r^4\epsilon^2 \sin^2\phi}{a^2(1-\epsilon^2)^2} = -\frac{r^4}{a^2(1-\epsilon^2)} + \frac{2r^3}{a(1-\epsilon^2)} - r^2.$$
 (31)

<sup>9</sup> The allowance to be made for the motion of the nucleus never differs perceptibly from that already made by introducing  $\mu$  into equation (16), and the magnetic fields arising from the motions of the electron and of the nucleus are without perceptible effect (C. G. Darwin, *Phil. Mag. 39*, pp. 537-551; 1920). The correction which would be required if the nucleus or the electron were oddly shaped, if the nucleus were a magnet, or if there were entrainment of the potential energy of the system by the moving electron, have been evaluated by various people; consult A. E. Ruark, Astroph. Jl., 58, pp. 46-58 (1923).

<sup>4</sup> The ambiguity of sign which arises in the course of the development may be resolved by thinking of the limiting case of the circle ( $\epsilon = O$ ).

All this is geometry. We must now prove that a particle moving under the influence of an inverse-square attraction, drawing it towards a fixed point, will describe an ellipse with that fixed point in one of its foci—will describe, otherwise expressed, a curve defined by equation (31).

As the particle is an electron, and the fixed point is occupied by a nucleus of charge E, the mutual attraction is  $eE/r^2$  when their dis-



Fig. 2-Diagram to illustrate the notation used in describing elliptical orbits

tance apart is r. Equating this attraction to the product of the mass of the electron into the sum of its accelerations, linear and "centrifugal," we have

$$eE/r^2 = -m\frac{d^2r}{dt^2} + mr\left(\frac{d\phi}{dt}\right)^2 \tag{32}$$

It is necessary to assume the law of conservation of angular momentum; the angular momentum of the electron  $mr^2 d\phi/dt$  about the centre of attraction remains constant in time:

$$mr^2 \frac{d\phi}{dt} = p, \tag{33}$$

inserting which into (32) we have

$$eE/r^2 = -m\frac{d^2r}{dt^2} + p^2/mr^3$$
(34)

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This is to be integrated in the usual way, by multiplying each term with 2(dr/dt); the result is

$$\left(\frac{dr}{dt}\right)^2 = -p^2/m^2r^2 + 2eE/mr - C,$$
 (35)

the last symbol standing for a constant of integration. Finally,

$$(dr/d\phi)^2 = (dr/dt)^2 / (d\phi/dt)^2 = (dr/dt)^2 (m^2 r^4 / p^2) = - Cmr^4 / p^2 + 2eEmr^3 / p^2 - r^2.$$
 (36)

We recognize at once the identical form of this equation for the path in which the attracted particle moves and the equation (31) for the ellipse drawn about the centre of attraction as focus.

It remains only to identify the constants. Equating the coefficients of  $r^3$  in the two equations, we have

$$p^2 = eEma \ (1 - \epsilon^2). \tag{37}$$

This is the equation giving the angular momentum of the electron in terms of the major axis and the eccentricity of the orbit. Equating the coefficients of  $r^4$  in (31) and (36) we have

$$C = p^2 / ma^2 (1 - \epsilon^2) = eE/a \tag{38}$$

to determine the constant of integration in (35). If now the reader will take the expression for the energy of the system

$$W = \frac{1}{2}mv^2 - \frac{e^2}{r} = \frac{1}{2}m((\frac{dr}{dt})^2 + \frac{r^2}{d\phi}(\frac{dt}{dt}))^2 - \frac{e^2}{r}$$
(39)

and substitute for  $(d\phi/dt)$  according to (33) and for (dr/dt) according to (35) and (38), he should arrive at

$$W = -e^2/2a. \tag{40}$$

This is the equation giving the energy of the system in terms of the constants of the ellipse; we see that the energy depends only on the major axis, not on the eccentricity, of the ellipse.

The period of revolution T is a little more difficult to calculate. The most logical procedure would be to take the reciprocal of the expression (35) for dr/dt, and integrate

$$t = \int \left( -\frac{p^2}{m^2 r^2} + \frac{2eE}{mr} - \frac{eE}{a} \right)^{-\frac{1}{2}} dr$$
(41)

around a complete revolution. The derivative dr/dt passes twice through zero in the course of the revolution, once at the point of the orbit nearest to the nucleus (perihelion) and once at the point farthest away. At these points  $r=a(1 \mp \epsilon)$ , as can be seen from the geometry of the ellipse or by inserting these values into the expression for dr/dt. By integrating (41) from one of these values to the other and doubling the result, we get the period of the revolution

$$T = 2\pi \sqrt{ma^3/eE}.$$
(42)

## J2. Motion of an Electron in a Central Field Differing Slightly from an Inverse-square Field

Suppose we modify the atom-model composed of a nucleus and an electron by imagining that the force exerted by the one upon the other varies not exactly, but very nearly, as the inverse square of their distance apart. For instance, one might imagine that the force varies as  $r^{2.001}$ ; or that the nucleus acts upon the electron with an attraction equal as heretofore to  $eE/r^2$ , plus an additional attraction (or repulsion) varying inversely as the cube of the distance. In any such case the potential energy of the atom-model would not be quite equal to -eE/r; there would be an additional term f(r). In the case of an inverse-cube field superposed upon an inverse-square field, the expression for the potential energy would be

$$V = -eE/r - C/r^2 \tag{43}$$

The second term on the right hand side will be much smaller than the first, at and only at distances much greater than 2C/eE; but by imagining C sufficiently small, we can arrange to have the inversecube field very much smaller than the inverse-square field, over all the region in which the orbit of the electron is likely to lie; and this is all that matters.

The orbit of the electron may be described, in all these cases in which the force deviates very slightly from an inverse-square force, as an *ellipse precessing in its own plane*. That is to say: an ellipse of which the major axis swings at a uniform rate around the nucleus as if around an axle perpendicular to its own plane—as though the electron were a car, running around and around an elliptical track, quite unaware that the track itself is endowed with a revolving motion of its own. (Or, in other and more sophisticated words, the orbit of the electron is an ellipse stationary in a coordinate-system revolving around the nucleus at a uniform rate). Such an orbit is known as a "rosette," and a part of a rosette is shown in Fig. 3.

Another way of describing the important feature of this orbit is to say that the two coordinates r and  $\phi$  of the electron in its orbit (referred to O as origin and OP as the direction  $\phi=O$ , in Fig. 3), while they are both periodic, do not have the same period. While ris running through its entire cycle from  $r_{max}$  to  $r_{min}$ , and back again,

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the electron is moving from one point of tangency with the dashed circle, inward around the nucleus, back to the next point of tangency; meanwhile,  $\phi$  is running through an entire circuit amounting to  $2\pi$ , and in addition through the angle  $\Delta\phi$ . Thus the period  $T_r$  of r stands to the period  $T_{\phi}$  of  $\phi$  as

$$T_r: T_\phi = \frac{2\pi + \Delta\phi}{2\pi} = \frac{2\pi + 2\pi\omega T_r}{2\pi}$$
(44)

in which expression the symbol  $\omega$  stands for the frequency of the precession (i.e., the reciprocal of the time the major axis requires to



Fig. 3-Rosette orbit, resulting from a precession superposed upon an elliptical orbit

trace out the entire dashed circle). One might say that the two frequencies  $\omega_r = 1/T_r$  and  $\omega_{\phi} = 1/T_{\phi}$  are slightly out of tune with one another. So long as the force acting upon the electron is exactly an inverse-square force, these two frequencies are perfectly in tune, the ellipse is stationary; when the inverse-square force is slightly altered, the two frequencies fall out of tune and the ellipse revolves. In general, the two frequencies will be incommensurable with one another; the rosette will never return into itself, the electron will go on winding its path over and over and over the interior of the dashed circle, passing eventually within any assignable distance, no matter how small, of any point selected at random, and "covering the interior of the circle everywhere dense" as the mathematicians say. Therefore, although the variables r and  $\phi$  are individually periodic, the motion of the electron never quite repeats itself. Such a system is called *conditionally periodic*.

When we come to consider the atom-models proposed for atoms with more than one electron, we shall make use of these ideas; but that will not occur before the Third Part of this article. However, one application can be made to the theory of hydrogen and ionized helium.

## J3. Motion, in an Inverse-square Central Field, of an Electron of Which the Mass Varies as Prescribed by the Theory of Relativity

According to "relativistic mechanics," as distinguished from "Newtonian mechanics," the mass m of an electron (or anything else) varies with its speed v in the manner

$$m = m_o / \sqrt{1 - v^2 / c^2} \tag{45}$$

and the force F acting upon it produces an acceleration dv/dt given not by the familiar equation  $force=mass \times acceleration$ , but by the equation

$$F = d(mv)/dt \tag{46}$$

If we suppose the electron revolving in a perfect inverse-square field about the nucleus, and apply these equations of relativistic mechanics, we arrive at the same result as though we had used the equations of Newtonian mechanics, but had assumed that the field acting upon the electron is the sum of an inverse-square attraction and an inverse-cube attraction. Specifically, the result is formally equivalent to the result attained by continuing to use Newtonian mechanics, and assuming that the potential energy of the atommodel is given by (43) with the following value inserted for the constant C:

$$C = -e^2 E^2 / 2m_0 c^2 \tag{47}$$

The orbit is a rosette; and all the general remarks made in section  $J^2$  about rosette orbits may be repeated for this case.

## J4. Motion of an Electron in a Field Compounded of an Inverse-square Central Electric Field and an Uniform Magnetic Field

Here we have a famous theorem of Larmor's to help us. According to this theorem, a magnetic field H acting upon a revolving electron, or a system of revolving electrons, produces no other effect than a

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precession of the entire system about the direction of the magnetic field at the frequency

$$\omega_L = eH/4\pi mc \tag{48}$$

In other words, the motion of the electron or electrons is, when referred to a coordinate system revolving about the direction of the field with frequency  $eH/4\pi$  mc, the same as without the field it would be, when referred to a stationary coordinate system.

If the field happens to be normal to the plane of an elliptical orbit being described by an electron about a nucleus, the ellipse will be transformed into a rosette. If the field is neither exactly normal nor exactly parallel to the plane of the ellipse, this plane may be imagined to swing around the direction of the field (around the line through the nucleus parallel to the field) like a precessing top, carrying the orbit with it.

These statements are inexact if the rate of precession so calculated is not quite small in comparison with the rate of revolution of the electron.

### J5. Motion of an Electron in a Field Compounded of an Inverse-square Central Electric Field and an Uniform Electric Field

This problem may be regarded as the limiting case of a more general problem phrased as follows: to determine the motion of a particle attracted by two fixed points according to the inverse-square law. Imagine one of the fixed points to recede to infinity, its attractingpower meanwhile rising at the proper rate to keep the field in the region of the other at a finite value; and you have the case described in the sub-title above. Jacobi solved the general problem a century or so ago.

The motion is difficult to realize and impossible to describe in words, and seems also to be impossible to represent by any adequate twodimensional sketch. The electron makes circuits around the line through the nucleus parallel to the uniform field, and in each circuit it describes a curve which is very nearly an ellipse; but the consecutve loops, as in the case of Fig. 3, do not coincide; furthermore, they are not alike in shape, and they are not plane. The electron winds around and around through the volume of what I am tempted to call a doughnut, surrounding the aforesaid line as its axis; and in the course of time its path fills up the doughnut "everywhere dense," as the path of the electron in Fig. 3 would fill up the interior of the dashed circle. I hope it will be appreciated that the foregoing statements about the orbits are fatally incomplete, except in the first case. Nothing could be done unless it were possible to know, not merely the general shape of each type of orbit, but the exact mathematical expression for it, and for the energy-value of each orbit of each type. In some cases this knowledge is available; in others, it is not. For the cases designated here by J3, J4 and J5, it is available; wherefore it is possible to go about the process of seeking the distinctive features of orbits possessing the preassigned energy-values, or inversely the energy-values of orbits distinguished by certain features.

## K. Further Interpretation of the Spectra of Hydrogen and Ionized Helium

Continuing for the moment to accept the energy-values of the stationary states of the hydrogen atom as given by

$$W_1 = -Rh, W_2 = -Rh/4, W_3 = -Rh/9, \ldots$$

and continuing to accept the atom-model consisting of a nucleus and a revolving electron; let us consider what are the properties of the *elliptical* orbits, in which if the electron revolved, the atom-model would possess one or another of the required energy-values.

According to equation (40), the energy of the atom-model, when the electron is revolving in an ellipse of which the major axis is 2a, is given by

$$W = -eE/2a$$

irrespective of the eccentricity of the ellipse. In this, as in all following equations, E is equal to e for hydrogen and to 2e for ionized helium. If we set this expression equal to one of the required energyvalues, for instance to  $W_1$ , we have

$$2a_1 = -eE/W_1 = eE/Rh.$$
 (50)

The atom-model therefore has the proper energy-value  $W_1$  for the normal state of the hydrogen atom, if the electron is revolving in *any* ellipse for which the major axis is eE/Rh. The circle of diameter eE/Rh of which we have heretofore been thinking is only one of these ellipses, it is the one for which the major and the minor axes are identical and  $\epsilon = 0$ ; there is an infinity of others.

Should we then divest the circular orbits of the prominence which has been accorded to them, and assume for instance that when the atom is in its normal state the electron is moving in any one of the infinity of ellipses of which the major axis is eE/Rh? This might be

dangerous, for we have identified certain distinctive features of the permissible circular orbits which may be essential; and these features may not be transferable to the ellipses. Let us test them.

The second and the third of the three distinctive features which I cited are transferable—that is they can be extended to the totality of all ellipses having one or another of the energy-values  $-Rh/n^2$ , and they differentiate these from all other ellipses. For it can be shown, by integrating the kinetic energy K (the first term on the right hand side of (39)) around an elliptical orbit, that

$$I = \int 2Kdt = 2\pi \sqrt{ameE}$$
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depending only on the major axis *a* of the orbit. Now we have shown that I = nh for the *n*th of the permissible circles; hence for each ellipse having the same major axis as the *n*th permissible circle, in other words for each ellipse of energy-value  $-Rh/n^2$ , we have

#### I = nh

and the second of the distinctive features is transferable to the ellipses. It is the same for the third; for T is by (42) dependent on a only, and so

$$Lim \ \omega = Lim \ \nu.$$

But it is otherwise with the first.

In the first place it was shown that the angular momentum of the electron in the circle of diameter eE/Rh is equal to  $h/2\pi$ . Obviously this cannot be true of all the ellipses of major axis eE/Rh. For according to (37), the angular momentum of the electron in such an ellipse is

$$p = \sqrt{eEma(1 - \epsilon^2)} \tag{52}$$

depending on the eccentricity. This is equal to  $e\sqrt{ma}$ , which by (12) is equal to  $h/2\pi$ , only if  $\epsilon=0$ . The circle therefore is the only orbit for which the energy-value and the angular momentum of the atom are simultaneously equal to -Rh and to  $h/2\pi$  respectively. If we admit the ellipses to equal value with the circle, we concede that the equality of the angular momentum with  $h/2\pi$  is of no significance.

There is a partial escape from this conclusion for the remaining stationary states. Take for instance the second, of energy-value -Rh/4. The circular orbit of diameter 4eE/Rh, for which the atom possesses this energy-value, is distinguished by the angular momentum  $2h/2\pi$ . For each of the infinity of ellipses possessing the same major axis 4eE/Rh there is a different value of the angular momentum:

but there is one among them for which the angular momentum is equal to  $h/2\pi$ . And in general for the *n*th stationary state of energy-value  $-Rh/n^2$ , there are *n* elliptical (including one circular) orbits which would give the same energy-value and *n* values of angular



Fig. 4a—Diagram to show the proportional dimensions of ellipses with identical total quantum-number n = I/h and different azimuthal quantum-numbers k = 1, 2..., n 1 rom left to right we have the cases n = 1, 2, 3, 4, on scales varying as indicated by the subjoined arrows.

momentum equal respectively to  $nh/2\pi$ ,  $(n-1)h/2\pi$ , ...,  $h/2\pi$ . These, as the reader can show from (52), are distinguished by the following values of  $\epsilon$ :

$$\sqrt{1-\epsilon^2} = k/n \qquad k = 1, 2 \dots n.$$
(53)

Thus if we desire to regard the equality of angular momentum with an integer multiple of  $h/2\pi$  as being essential to the permissible orbits, we can keep, along with the circles, some of the other elliptical orbits compatible with the prescribed energy-values; but except for these



Fig. 4b—The same ellipses as appear in Fig. 4a, drawn confocally as they should appear, instead of concentrically

few, the infinity of elliptical orbits will remain unavailable. There is additional reason for liking to do this; for it amounts to a quite natural generalization of the condition imposed on the angular momentum, which as we saw it is highly desirable to generalize if possible. The angular momentum  $mr^2(d\phi/dt)$ , which I shall hereafter call  $p\phi$ instead of simply p, stands on an equal footing with the radial momentum pr = m(dr/dt) of the electorn; in the Hamiltonian equations for the motion of the particle, these two quantities stand side by side. Now the condition imposed upon the angular momentum  $p\phi$  of the electron in its various circular orbits is  $p\phi = nh/2\pi$ , which may be written

$$\int_{0}^{2\pi} p_{\phi} \ d\phi = nh \tag{54}$$

the integral being taken around a complete revolution, a formulation in which the somewhat distressing factor  $1/2\pi$  conveniently vanishes. Corresponding to this integral we have another

$$\int p_{\phi} dr = m \int \frac{dr}{d\phi} d\phi \tag{55}$$

also to be taken around a complete revolution, therefore from  $r_{min.} = a(1-\epsilon)$  to  $r_{max.} = a(1+\epsilon)$  and back again. The materials for performing this integration are furnished in equation (35); if the reader can perform it he will arrive at the value.

$$\int p_r \, dr = 2\pi p_\phi \left[ \frac{1}{\sqrt{1 - \epsilon^2}} - 1 \right] \tag{56}$$

and if the eccentricity of the ellipse conforms to equation (53), so that the integral of the angular momentum of the electron is kh, then the integral of the radial momentum is

$$\int M_{t}dr = (n-k)h. \tag{57}$$

Our position may now be described in the following words. We have accepted the values  $-Rh/n^2$  (n=1,2,3...) for the successive stationary states of the hydrogen atom; we have accepted an atom-model consisting of a nucleus and a revolving electron; we have traced the orbits which would entail these various energy-values, and we have found that for each of these energy-values there are infinitely many elliptical orbits which would entail it,—to wit, for the *n*th stationary state, all the infinitely many ellipses of which the major axis is given by

$$2a_n = n^2 h^2 / 2\pi^2 m e E.$$
 (58)

Furthermore we have sought for distinctive features which might discriminate these ellipses from all the others which entail "wrong" energy-values, i.e., energy-values which are not included in the list -Rh, -Rh/4, -Rh/9.... One such we found in the integral  $\int 2Kdt$  of the kinetic energy of the electron around the ellipse; this integral assumes the value nh for each ellipse which entails the energy-value  $-Rh/n^2$ , so that we could define the permitted orbits as those

for which  $\int 2Kdt = any$  integer multiple of *h*. Another such distinctive feature we found in what was expressed by the equation (23)  $Lim \ \omega = Lim \ \nu$ . First of all, however, we tried to apply a principle of the effect that the angular momentum of the atom when the electron is revolving in one of the permitted orbits must be an integer multiple of  $h/2\pi$ . We found, in essence, that this attempt amounted to picking out for each of the prescribed energy-values, one or several out of the infinity of elliptical orbits which would entail it, and eliminating all the rest. But is there sufficient reason for doing a thing like this?

Apparently there is; and the reason for so believing lies precisely in the details of the hydrogen spectrum which I have hitherto passed over—in the doubleness of the lines of the Balmer series, which shows that instead of a stationary state of energy-value -Rh/4 there are two stationary states of which the energy-values lie extremely close to one another and to this value, and which suggests that the other stationary states may likewise be resolvable into groups of stationary states (a suggestion confirmed by the spectrum of ionized helium). At the beginning, let us consider only the state of which the energyvalue is -Rh/4. We have seen that this is the energy-value corresponding to any and every one of the elliptical orbits of which the major axis is

$$2a_2 = 4h^2/2\pi^2 \ meE \tag{59}$$

among which infinity of elliptical orbits, there is just one (a circle) for which the angular momentum of the atom is  $2h/2\pi$ , and just one other for which it is  $h/2\pi$ , and no others for which it is any integer multiple of  $h/2\pi$  at all. But these two, like all the rest characterized by (58), entail the same energy-value and so are indistinguishable among the crowd-if every one of our assumptions is absolutely true. But if one of them should deviate slightly from the truthif for instance the law of force between the nucleus and the electron should deviate slightly from the inverse-square law, or if a small extraneous force should be impressed upon the atom, or if the mass of the electron should slightly vary as it revolves in its orbit-then we have seen that all the orbits would be altered, and these two orbits may be so altered as to be distinguishable from the rest. And this in fact is what appears to be responsible for the fine structure of the hydrogen and ionized-helium. Owing to the variation of the mass of the electron, with its speed, each ellipse is transformed into a rosette; and though the energy-values of all the ellipses would be equal, the energy-values of the rosettes are not.

Let us now reverse the procedure of the foregoing paragraphs. Instead of asking what is the angular momentum of the atom when the electron is revolving in such an orbit that the energy of the atom is -Rh/4, let us ask what is the energy of the atom when the electron is revolving in a rosette such that the angular momentum of the atom is  $2h/2\pi$ . It is best to put the question thus: what is the energy of the atom when the electron is revolving in a rosette<sup>10</sup> such that the integral of the angular momentum around a revolution is 2h?

$$\int p_{\phi} \, d\phi = 2h. \tag{61}$$

The energy-value in question, which I designate by  $W_{22}$  for a reason which will presently appear, is found by calculation to be

$$W_{22} = -Rh/4 - Rh\alpha^2/64 \tag{62}$$

in which  $\alpha$  is a symbol meaning

$$\alpha = 2\pi e^2 / hc = 7.29 \ 10^{-3}. \tag{63}$$

(This expression incidentally is not the exact consequence of the equations of the motion, but an approximation to it, quite sufficiently accurate under these circumstances). Next let us ask what is the energy of the atom when the electron is revolving in a rosette<sup>10</sup> such that

$$\int p_{\phi} \, d\phi = h. \tag{64}$$

Calling this energy-value  $W_{21}$ , it is calculated that

$$W_{21} = -Rh/4 - Rh5\alpha^2/64.$$
(65)

Incidentally it is found, as in the previous simpler case, that when  $\int \phi_{a} d\phi = h$ , then also  $\int \rho_{r} dr = h$ .

The energy-values corresponding to the two orbits defined by (68) and (71) therefore differ by the very small amount

$$W_{22} - W_{21} = -Rh\alpha^2/16 = -Rh(3.32^{\circ}10^{-6}).$$
(66)

I said at first that the various "lines" of the Balmer series in the spectrum of hydrogen correspond to transitions into the stationary state of energy-value -Rh/4 from other stationary states; and that unusually good spectroscopes show each of these lines to be a pair of lines very close together. May this be explained by the theory culminating in equation (66)? If so, the frequency-difference between the two lines of each doublet must be the same, and equal to

<sup>&</sup>lt;sup>10</sup> This rosette is degenerated into a circle; the precession amounts effectively to an additional term in the expression for the angular velocity of the electron.

 $(W_{22}-W_{21})h=R \alpha^2/16=1.09$  10. The wave-length difference, which is the quantity directly measured by spectroscopists, varies from one doublet to another; for the first doublet of the Balmer series, known as  $H\alpha$ , the mean wavelength of which is  $6.563 \cdot 10^{-5}$  cm., it should be equal to  $1.58 \cdot 10^{-9}$  cm.

Many independent measurements of these wavelength differences have been made, most of them upon the first doublet of the series, a few upon other doublets as far along as the fifth. Some were made long before, others after Sommerfeld published the foregoing theory. The various values found for the various wavelength-differences have all been within 20% of the value required by equation (66); within this range they have fluctuated, one or two spectroscopists of repute have maintained that the actual values are unmistakably different from the computed value; but the balancing of evidence **now** seems to point more and more closely to the desired value as the right one <sup>11</sup>.

This prediction of the wavelength-differences between the components of the doublets which make up the Balmer series may be taken tentatively as the third of the numerical agreements which fortify Bohr's atom-model. So taking it, let us generalize the theory to the full extent already suggested. Returning for a moment (merely for ease of explanation) to the over-simplified case of an atom consisting of a nucleus and a revolving electron of which the mass does not vary with its speed: we saw that the energy-value  $-Rh/n^2$  is entailed by each and every one of the *n* elliptical orbits for which the integral of the angular momentum and the integral of the radial momentum are given by assigning the *n* values k = 1, 2, 3 ... n to the symbol *k* in the following equations:

$$\int p_{\phi} d\phi = kh, \int p_r dr = (n-k)h.$$
(67)

This I will express in another way by saying that the energy-value  $-Rh/n^2$  is entailed by each of the *n* orbits having the *azimuthal* 

<sup>11</sup> This is one of those embarrassing questions as to which the experimental doctors still disagree, making it folly indeed for anyone else to pretend to decide. The three latest measurements, which are those of Shrum, Oldenberg, and Geddes, agree passably with the value resulting from the theory I have presented. Yet Gehrcke and Lau defend their measurements, made in 1920 and 1922, which give values about 20% too low; and Gehrcke at least is an authority to whom lack of experience in this field certainly cannot be imputed. I evade this issue by referring the reader to the articles by Shrum (*Proc. Roy. Soc. Altos, pp. 259-270; 1923*) for the bibliography of earlier work and the account of the latest; of Ruark (*l. c. supra*) for the contention that the data sustain the theory; of Lau (*Phys. ZS.* 25, pp. 60-68; 1924) for the contrary contention.

The issue is further complicated by the predictions quoted in the next paragraph above, although not seriously enough to disqualify the foregoing remarks.

quantum-numbers  $k=1, 2, \ldots, n$ ; meaning by azimuthal quantumnumber the quotient of  $\int p_{\phi} d\phi$  by h. If now we take account of the variation of the mass of the electron with its speed, and calculate the energy-values for the n rosettes obtained by assigning the values 1, 2, 3 . . . n successively to the symbol k in (67), we shall find that these *n* energy-values are all distinct, deviating slightly from  $-Rh/n^2$ and from each other. Therefore, there should be three stationary. states of energy-values  $W_{33}$ ,  $W_{32}$ ,  $W_{31}$ , all differing by a little from -Rh/9 and from each other; there should be four stationary states of energy-values  $W_{44}$ ,  $W_{43}$ ,  $W_{42}$ ,  $W_{41}$ , all nearly but not quite equal to -Rh/16 and each other; and so forth. (The reason for such symbols as  $W_{21}$  will now appear; the first subscript represents the total, the second the azimuthal quantum-number of the orbit in question.) In general there are n stationary states in the group corresponding nearly to the mean energy-value  $-Rh/n^2$ ; and the expressions for their several values are obtained by putting k equal to the various values 1, 2,  $3 \dots n$  in the formula.

$$E = -Rh/n^2 \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{k} - \frac{3}{4} \right) \right].$$
(68)

Owing to these complexities the lines of the Balmer series should be not doublets, but groups of many more lines; e.g., the transitions from what I had called the stationary state of energy-value -Rh/9to the stationary state of energy-value -Rh/4 are transitions of six sorts, from each of three initial states to each of two final; and the first "line" of the Balmer series might be expected to be sextuple.

The trial of these ideas is best made upon the spectrum of ionized helium. The separation between the energy-values of stationary states sharing the same total quantum-number and differing in azimuthal quantum-number is increased, when we pass from an atom-model in which the charge on the nucleus is e to one in which it is Ze, in the ratio  $Z^4$ :1; in this instance 16:1. The system of component lines, or the so-called "fine structure" to be expected for any "line" of the hydrogen spectrum should be spread out on a scale sixteenfold as great for the corresponding "line" of the ionizedhelium spectrum. The trial was made by Paschen; the comparison between the fine structure of several of the "lines" of ionized helium and the components to be expected from the foregoing theory, yielded what appear to be very satisfactory results. This matter I discussed over several pages of the First Part of this article; and for economy of space I refer the reader back to them, and at this place say only that the "other numerical agreements between the production and the data" to which I there allude, are agreements of the same character as the agreement between the spacing of the component lines of the Balmer series doublets, and the numerical value of the expression in equation (73). That is to say: the pattern of the fine structure, into which by a good spectroscope the lines of ionized helium are resolved, agrees more or less with the pattern to be expected from the theory, not only in appearance but in scale. Combining these agreements with the other one, we are probably justified in counting the latter as the third of the conspicuous numerical agreements which make Bohr's atom-model plausible <sup>12</sup>.

Now let us examine the situation again. (Considering the abstruseness of these matters. I hope that few readers will resent these frequent repetitions of past remarks.) Accepting for the atom of hvdrogen (and of ionized helium) an atom-model consisting of a nucleus and an electron, we have traced orbits for the electron such as entail energy-values for the atom equal to those of the known stationary states. At first we ignored both the experimental fact that the lines of hydrogen and those of ionized helium have a fine structure, and the theoretical likelihood that the mass of the electron varies with its speed; and we found that the orbits are ellipses. Later on, we took cognizance of both these things; and we found that the orbits are rosettes. Yet merely to trace the orbits which yield the required energy-values, the so-called "permissible" orbits, amounts to little. It is essential to find distinctive features which set the permissible orbits apart from all the others-on success in achieving this, the whole value of the theory depends.

Now at the very beginning it was shown that, if we ignore the variation of the mass of the electron with its speed, and if we consider circular orbits only—then the permissible circular orbits which yield the required energy-values  $-Rh/n^2$  of the stationary states (fine-structure being ignored!) are those for which

$$\int p_{\phi} d\phi = nh \tag{69}$$

in which equation  $p_{\phi}$  stands for the angular momentum of the motion, and *n* for any positive integer; and the integral is taken around a complete cycle of  $\phi$ .

<sup>&</sup>lt;sup>12</sup> For the experimental results and the comparison of data with predictions see Paschen's great paper (Ann. d. Phys. 50, pp. 901-940; 1915) which however is anything but easy to read, so that Sommerfeld's presentation will probably be preferred; likewise Birge's article (Phys. Rev. 17, pp. 589 ff, 1921) to which the same words apply. The agreements are impressive. On the other hand I note that Lau (l. c. subra) concludes from the same data that there is a disagreement between data and predictions, in the same sense and of about the same magnitude as the disagreement which he claims to occur in the hydrogen spectrum.

It was next shown that when we make allowance for the variaton of the mass of the electron with its speed, then the permissible rosette orbits which yield the required energy-values of the stationary states (fine structure being taken into account!) are those for which

$$\int p_r dr = n_1 h \qquad \int p_\phi d\phi = n_2 h \tag{70}$$

in which equations  $p_r$  and  $p_{\phi}$  stand for the radial and angular momenta—the momenta belonging to the variables r and  $\phi$  respectively —and  $n_1$  and  $n_2$  for any positive integers; and the integrals are taken around complete cycles of r and  $\phi$  respectively.

The equations (70) look like a very natural and pleasing generalization of the equation (69). It is possible to go somewhat further. Consider that, when the electron was supposed to move in a circle, its position was defined by one variable  $\phi$ ; and the permissible circles were determined by one integral. Further, when the electron was supposed to move in a rosette, its position was defined by two variables r and  $\phi$ ; and the permissible rosettes were determined by two integrals. Now when the electron is subjected, for instance, to an uniform magnetic field superposed upon the field of the nucleus, its motion is three-dimensional. Three variables are required to define its position; for instance, the variables r,  $\theta$  and  $\psi$  of a polar coordinate system with its polar axis parallel to the direction of the magnetic field. Three corresponding momenta  $p_r$ ,  $p_{\theta}$  and  $p_{\psi}$  can be defined. It seems natural to generalize from (69) through (70) to a triad of equations, and say that the permissible orbits are those for which

$$\int p_r dr = n_1 h \qquad \int p_\theta d_\theta = n_2 h, \qquad \int p_\psi d_\psi = n_3 h \tag{71}$$

in which equations  $n_1$ ,  $n_2$ ,  $n_3$  all stand for positive integers, and the integrals are taken around complete cycles of r,  $\theta$  and  $\psi$  respectively.

When this is done for the specific case of an electron moving under the combined influence of a uniform magnetic field and the field of a nucleus, the result is entirely satisfactory. That is to say: when the permissible orbits are determined by using the equations (71) upon the general type of orbit described in section J4, and when their energyvalues are calculated, it is found that they agree very well with the observed energy-values of the stationary states of hydrogen in a magnetic field. This may be regarded as the fourth of the numerical agreements which fortify Bohr's atom-model. As I shall end this part of the present article by a presentation of the effect of the magnetic field made in a somewhat different manner, I reserve the details for the following section.

Yet it cannot be said that equation (71) is the utterance of the much-desired General Principle, of the distinctive feature *par excellence* which sets all permissible orbits apart from all non-permissible orbits in every case. The most that can be said is this, that equation (71), if properly interpreted, is the widest partial principle that has yet been discovered. But it suffers limitations. I do not mean, as might be thought, that cases have been discovered in which the permissible orbits determined by such equations as (71) have energy-values not agreeing with those of the observed stationary states. The difficulty is, that equations such as (71) cannot even be formulated in many cases, because the necessary mechanical conditions do not exist.

This matter is a hard one to make clear; but the limitation can be at least partially expressed in the following way. Revert to the equations (70) which were applied to the rosette orbits. The first of the integrals in (70) is to be taken over an entire cycle of the variable r. Now it was said in section J2 that the periods of the two variables r and  $\phi$  are not equal, and in general they are incommensur-When the variable r describes a complete cycle, r and dr/dtable. both return to their initial values; but  $\phi$  and  $d\phi/dt$  do not have, at the end of the cycle of r, the same values as they had at its begin-It follows that if  $p_r$  depends on  $\phi$  or on  $d\phi/dt$ , the first of the ning. two integrals in equation (70) will have different values for different cycles of r. If so, the conditions imposed upon the permissible orbits by (70) would have no meaning. The conditions have a meaning, only if each of the integrals in (70) has the same value for every cycle of its variable-therefore, only if  $p_r$  depends on ronly, and  $p_{\phi}$  depends on  $\phi$  only. And in general, such a set of equations as (71) has a meaning, only if it is possible to find a set of variables such that the momentum corresponding to each of them depends on and only on the variable to which it corresponds; or, in technical language, only if it is possible to effect separation of variables.

Separation of variables is possible in some cases, and in others it is not. When the periods of all the variables are equal, as they are when we imagine an electron of changeless mass revolving in an inverse-square field, it is clearly always possible; the difficulty described in the foregoing paragraph does not occur. In the other cases which I have outlined—when the electron is imagined to move in an inverse-square field according to the laws of relativistic mechanics, and when it is imagined to move in a field compounded of an inverse-square field and an uniform magnetic field—separation of variables is possible. For these cases, therefore, the conditions (70) and (71) are applicable, and have meaning.

There is one other important case in which it is possible so to select the variables that separation can be effected. This is the case of an electron moving according to the laws of Newtonian mechanics in a field compounded of an inverse-square field and an uniform electric field. Although the motion is three-dimensional, and three coordinates are required and suffice to determine it, these three coordinates may not be chosen at random; and the three obvious ones would be worthless for our purpose. If we should choose the polar coordinates r,  $\theta$ , and  $\psi$  employed in formulating the equations (71), we should find that the momenta  $p_r$ ,  $p_{\theta}$  and  $p_{\psi}$  do not depend each exclusively upon the variable to which it corresponds. The procedure to be followed is anything but obvious; but Jacobi found that if paraboloidal coordinates are used instead of polar, separation of variables can be effected. One must visualize two families of coaxial and confocal paraboloids, their common focus at the nucleus, their noses pointing in opposite directions along their common axis which is the line drawn through the nucleus parallel to the electric field. The position of any point through which the electron may pass is given by the parameters  $\xi$  and  $\eta$  of the two paraboloids which intersect at that point, and by an angle  $\phi$  defining its azimuth in the plane normal to the axis, quite like the angle  $\psi$  of a system of polar coordinates. When the motion of the electron is expressed in terms of these coordinates, the corresponding momenta  $p_{\xi}$  and  $p_{\eta}$  depend only upon  $\xi$  and  $\eta$  respectively and  $p_{\phi}$  is constant; hence the integrals taken over cycles of  $\xi$ ,  $\eta$ , and  $\phi$  respectively, on the right-hand sides of the equations.

$$\int p_{\xi} d\xi = n_1 h, \qquad \int p_{\eta} d\eta = n_2 h \qquad \int p_{\phi} d\phi = n_3 h \tag{72}$$

have definite meanings, and the equations themselves define particular orbits. Epstein determined the orbits defined by these equations, and calculated their energy-values. These agreed well with the energy-values of the stationary states of hydrogen in an electric field, inferred from its spectrum. This is the fifth of the striking numerical agreements upon which the credit of Bohr's atom-model chiefly depends <sup>13</sup>.

<sup>13</sup> See Epstein's article (Ann. d. Phys. 50, pp. 489-520; 1916), or the more perspicuous account by Sommerfeld, in which it is stated that the pattern of the components into which the first four lines of the Balmer series are resolved by the electric field agrees with the predictions so far as the number and relative spacings of the components are concerned; while to attain agreement in regard to the absolute spacings, it is necessary only to assume that Stark's estimate of the field was 3%in error, which is quite easy to accept.

It is important to note that if we had made allowance for the variation of the mass of the electron with its speed-if in other words we had used the equations of relativistic mechanics, which are probably the right ones to use-separation of variables could not have been effected either in this paraboloidal coordinate-system, or in any other. Yet the stationary states are found by experiment to be sharply defined, and to have approximately the energy-values determined by (72). This can mean only that the desired General Principle for determining the permissible orbits is not completely expressed by such sets of equations as (71) or (72). Those equations are valid only for systems of a certain kind (those for which separation of variables is possible). The General Principle must be valid for systems of this kind and the other kind as well. For systems of this kind, it must become equivalent with the conditions formulated in (71) and (72)-the General Quantum Conditions for Separable Systems. Or at least, the results to which it leads must be indistinguishable from the results to which these lead. The General Principle for systems of every kind has not been discovered; perhaps it does not exist. Bohr is striving to infer it by generalizing from the third of the properties of the permissible circular orbits, which I mentioned in Section H and expressed by equation (23). He has attained some notable successes, which I hope that it will be possible to expound in the Third Part of the article.

#### L. MAGNETIC PROPERTIES OF THE ATOM MODEL

After this rather arduous pilgrimage through a succession of abstract reasonings, the reader may welcome an account in simpler fashion of the manner in which Bohr's atom-model is adapted to explain the behavior of the atom in a magnetic field. This is an alternative method of arriving at the same results as are attained by means of equations (71).

It was stated in section E9 of the First Part of the article, that the spectrum of a radiating substance in a magnetic field indicates that the field acts by replacing each of the stationary states, which the substance possesses when there is no magnetic field prevailing, by two or more new stationary states. The energy of each of the new stationary states differs from that of the stationary state which it replaces, by the amount

$$\Delta U = seHh/4\pi mc \tag{73}$$

in which H stands for the magnetic field strength and s for an integer,

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which must possess two or more values spaced at intervals of one unit <sup>15</sup>.

The atom-model which we have been discussing at such length consists of an electron circulating in an elliptical orbit about a stationary nucleus: the minor variations due to the variation of the mass *m* of the electron with its speed, and to the motion of the nucleus. are now of comparatively little importance. An electron circulating in a closed orbit with frequency  $\nu$  passes  $\nu$  times per second through any point of its orbit, so that the charge passing per second through any such point is equal to that which would pass, if a continuous current  $I = e\nu/c$  (measured in electromagnetic units) were flowing around the orbit. Now a current I flowing continuously around the curve bounding an area A is equivalent—so far as its field at a distance goes—to a magnet, of which the magnetic moment M is directed normally to the plane of the curve and is equal in magnitude to IA. The area of an ellipse of which the major axis is denoted by *a* and the minor axis  $b = a\sqrt{1-\epsilon^2}$  is equal to  $\pi ab = \pi a^2 \sqrt{1-\epsilon^2}$ . Hence the magnetic moment of the atom-model is equal to

$$M = e\nu\pi a^2 \sqrt{1 - \epsilon^2}/c \tag{74}$$

Further we have seen, by equations (37) and (42), that the angular momentum of the electron in its orbit is equal to

$$p = 2\pi m \nu a^2 \sqrt{1 - \epsilon^2} \tag{75}$$

Consequently

$$M/p = e/2mc \tag{76}$$

a rather surprisingly simple relation!

Now when a magnet of moment M is placed in a magnetic field of field-strength H, it acquires a certain potential energy  $\Delta U$ —in addition to the intrinsic energy which it possesses when oriented normally to the field—which depends on the angle  $\theta$  between the

<sup>&</sup>lt;sup>14</sup> Unlike some of the preceding derivations, this theory is not essentially limited to the case of an atom-model consisting of a nucleus and one electron. If there are several electrons describing closed orbits, the Larmor precession affects them identically; or, otherwse put, the magnetic field treats the atom as a unit having an angular momentum and a magnetic moment equal respectively to the vectorial sums of the angular momenta and the magnetic moments of the individual electrons. In fact the best verification of (73) is obtained from the lines belonging to the singlet systems of certain metals, which display "normal" Zeeman effect, against which this theory is powerless, we are not now concerned. In the case of hydrogen, the effect is complicated by the fine structure of the lines. With small magnetic fields it is normal, at least so far as the observations go, Each of the two stationary states of which the energy-values are given by (62) and (65) is replaced by two or more, conforming to (73).

direction of its magnetic moment and the direction of the field, and is given by

$$\Delta U = MH \cos \theta \tag{77}$$

According to equation (73), the observed stationary states of hydrogen atoms in a magnetic field have specific discrete energy-values. These must correspond to specific discrete values of the angle  $\theta$ ; the orientation of the atom in the magnetic field must be constrained to certain particular directions, an extraordinary idea! We ascertain these "permissible directions" by equating the two values of  $\Delta U$ figuring in (73) and (77), obtaining

$$seh/4\pi mc = M \cos\theta \tag{78}$$

into which we then insert the expression for M in terms of p:

$$sh/2\pi c = \phi \,\cos\,\theta \tag{79}$$

We have experimented at length with the notion that the angular momentum p of the electron in its orbit is constrained to assume only such values as are integer multiples of  $h/2\pi$ ; let it be introduced here also. If  $p = kh/2\pi$ , then

$$s = k \cos \theta \tag{80}$$

The angle  $\theta$  may assume only such values, as will give to the quantity  $s=k \cos \theta$  two or more values, differing by one unit. For instance, if k=1, the values  $\theta=60^{\circ}$  and  $120^{\circ}$  will suffice.

This, the most spectacular of all the remarkable consequences of Bohr's interpretation of the stationary states, is also the only one which has ever been directly verified.

The verification has not been made upon hydrogen nor upon ionized helium, but upon the atoms of certain metals <sup>15</sup>. I shall therefore reserve the account of it for the following sections of the article, where also there are certain other reasons for desiring to put it. Nevertheless, the reader should be aware of it at this point.

<sup>15</sup> I gave an account of the earliest of these experiments in the first article of this series (This Journal, 2, October, 1923; pp. 112-114). The subsequent experiments have added nothing fundamentally new.

#### (To be continued)

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