THE PICKERING SERIES AND BOHR'S ATOM[*]

By H. H. Plaskett

MANY of the important developments of modern physics have taken their origin in or have been verified by astronomical observations. Such, is for example, the fact in the case of the Pickering series. The lines composing this series were originally found in 1896 by E. C. Pickering in the star ζ Puppis. Rydberg, on the basis of his work on spectral series, assigned the lines to the element hydrogen. Fowler later found the series in the laboratory, and finally Bohr was able succesfully to account for its appearance as a result of his theory of atomic structure. It is the purpose of this article to give some account of these various investigations which had their inception in Pickering's discovery.

1. The 4686 Series

It is possible from the multiplicity of lines which forms the spectrum of an element to select groups of homologous lines. The lines of such groups are characterized by a like appearance (sharp, nebulous or easily self-reversed), and by the same behaviour under varying conditions of excitation, or under the Zeeman effect. In 1890 Rydberg[1] was able to show that the lines in such a group formed a series, the members of which conformed to a relation

$$\nu(=10^8/\lambda)=\nu_\infty - N/(m+\mu)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where ν is the wave-number of a line (reciprocal of wave length in cms.), N a universal constant (=109,677.7), μ an empirical parameter, and where m takes on integral values 2, 3, 4..., thus giving rise to succeeding members of the series.

Further, in general, Rydberg found that each element showed three types of series. These were: a series of strong lines, the Principal (P) Series; one of sharp lines, the Sharp (S) Series; and one of nebulous lines, the Diffuse (D) Series. Between these three

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[*] Summarized from an address read before the "Victoria Branch of the Engineering Institute of Canada".

series of an element there were certain important relations. (1) The D and S series had a common limit. (2) The difference between the limit of the P series and the common limit of the D and S series gave the first member of the P series. And (3) when m was put equal to unity in the formula for the S series, the first member of the P series was obtained with a negative sign. These relations are shown in figure 1 for the lithium spectrum. The first row shows the brighter lines of lithium. In the second, third and fourth rows the lines are sorted out respectively into the P, S and D series. The abscissae are wave numbers. Relations (1) and (2) given above are immediately evident on reference to the diagram; the third relation is not shown. These inter-series relations may also be put analytically since clearly the limit of the series ν_∞ can be expressed in a form $N/(m+\mu)^2$. This results directly in the following expressions.

$$(2)\quad \begin{cases} \text{P series } \nu = N\{1/(1+s)^2 - 1/(m+p)^2\} & m=1, 2, 3\ldots\ldots \\ \text{S series } \nu = N\{1/(1+p)^2 - 1/(m+s)^2\} & m=2, 3, 4\ldots\ldots \\ \text{D series } \nu = N\{1/(1+p)^2 - 1/(m+d)^2\} & m=2, 3, 4\ldots\ldots \end{cases}$$

It is evident that if the S series of an element is known, the P series may be calculated, and vice versa.

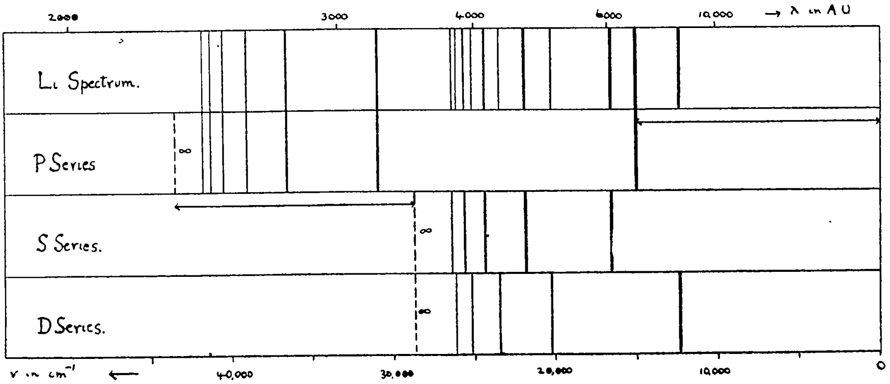


Fig. 1.—Relation between Series in Lithium Spectrum.

Rydberg was able to find series, and series relations such as these, in elements in the first three columns of the periodic system. Further, elements in the same column showed spectroscopically, as well as chemically, progressive similar tendencies. For example the series limits of elements in a column shifted to the red with increase in atomic weight. To the very complete scheme that

Rydberg was thus able to formulate there was one noteworthy exception. This was due to the element hydrogen. From analogy with the spectra of other elements, and from its position in the periodic table it should have shown three series with somewhat similar values of the empirical constant μ to lithium, sodium and potassium. In other words it should have shown a system of series like figure 1. Actually it showed only one very simple series, called the Balmer series, after J. J. Balmer who discovered the formula which represented it,—$\nu = N(1/2^2 - 1/m^2)$.

The discovery in 1896 by E. C. Pickering[2] of the unknown lines λλ5411,4541,4200, etc., in the star ζ Puppis seemed to indicate a way out of this difficulty. In a later note Pickering[3] showed that the new lines could be grouped with the Balmer hydrogen lines in a formula of the type $\nu = N(1/2^2 - 1/m^2)$ where the Balmer lines are given by integral values of m, and the Pickering lines by 5/2, 7/2, 9/2, etc. Kayser[4] deprecated this procedure, and Rydberg[5] followed with a brief but highly important note. He computed series formulae for the Pickering lines and the Balmer series, and showed that both series had a common limit. His formulae may be put in the form

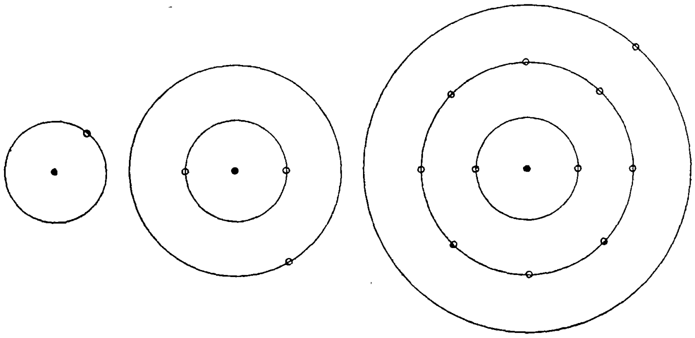
Pickering Series $\nu = N\{1/2^2 - 1/(m+0.500737)^2\}$ $m = 2, 3, 4 \ldots.$
Balmer Series $\nu = N\{1/2^2 - 1/(m+1.00)^2\}$ $m = 2, 3, 4 \ldots.$

By comparison with (2) it is seen that these series are similar to the S and D series of an element. Their proper assignment, Rydberg pointed out, may be made by a comparison of the values of μ. In the second column of the periodic table for the S series $\mu = 0.597337$ (Li), $= 0.649840$ (Na), and for the D series $\mu = 0.998063$ (Li), $= 0.988436$ (Na). From these values and their progression Rydberg was justified in assuming that the Pickering lines formed the S series and the Balmer lines the D series of hydrogen. He could then proceed, as has been previously indicated, to the calculation of the wave-lengths of the members of the P series. As a result he found that the first line should occur at λ4687.88, and succeeding lines at λλ2734.55, 2386.50, 2253.74, 2187.60 which are all below the limit of atmospheric transparency. However, in ζ Puppis itself and in numerous nebulae, there was an excessively bright line with wave length λ4686. There was, therefore, since inter-series relations only hold approximately, ample justification for assuming that the line 4686 was the first number of the P series of hydrogen.

In this identification there was only one flaw. The so called P and S series of hydrogen were never observed in the laboratory. However, in 1912, in a tube containing helium with hydrogen impurity, Prof. A. Fowler[6], who had long been interested in this problem, observed a line flickering near λ4686. With this as a clue Fowler experimented until he found that the line 4686, and the remaining members of the series as predicted by Rydberg, could be produced at will with a sufficiently condensed discharge. At the same time under these conditions there appeared very faintly the Pickering series. In addition, however, there appeared lines at λλ3203.30, 2511.31, 2306.20 which by their behaviour were clearly related to the 4686 and the Pickering series. These new lines Fowler grouped into a "second principal series". In the lack of positive experimental proof, since hydrogen was always present, it was concluded that the 4686 series, the 2nd P series (3203, 2511, etc.), and the Pickering series were due to hydrogen.

2. BOHR'S THEORY

Shortly after Fowler's discovery of the 4686 series in the laboratory, Dr. N. Bohr[7] announced the preliminary results of his theory of atomic structure. His problem was to determine from the characteristic line spectrum of an element the structure and dynamics of the atoms of that element. Certain fundamentals of atomic structure had already been made clear. A long series of experiments, initiated by J. J. Thomson's work on the discharge of electricity through gases, had shown that there was, common to all elements, certain minute carriers of unit charges of negative electricity. These were called *electrons*. The charge carried by an electron is 4.77×10^{-10} electrostatic units, the electron diameter is of the order of 1.8×10^{-13} cms. and its mass is approximately 1/2000 of the mass of the hydrogen atom. From their universal occurrence such electrons must be a standard part of all atoms. Two questions then arise: (1) how many electrons are there in the atoms of the various elements, and (2) since the atom as a whole is electrically neutral, what is the nature of its positive part? The experiments of Barkla, Crowther and Sir E. Rutherford were decisive in showing that the number of electrons in an atom is approximately one-half the atomic weight of the element; and also in showing that the positive part of the atom and almost its entire mass are centred in a minute positive *nucleus*, of diameter less than 1/100,000 of the diameter of the atom. Our resulting knowledge of atomic structure is shown schematically in figure 2.



H—At. No. 1. Li—At. No. 3. Na—At. No. 11.

Fig. 2—Illustrations of Atomic Structure.

The number of electrons, and equally the positive charge on the nucleus in terms of the unit charge carried by the electron, is given by the *atomic number* (which is approximately ½ the atomic weight) of the element (*i.e.*, by the ordinal number of the element in a list of the elements in order of increasing atomic weight). Thus hydrogen has 1 electron since its atomic number is 1, lithium 3 electrons since its atomic number is 3, sodium has 11 electrons since its atomic number is 11, and so on. The electron arrangement in the diagram is that of the Lewis-Langmuir theory, save that in sodium the eight electrons in the second ring are actually at the corners of a cube.

Bohr selected the hydrogen atom consisting of a nucleus with a single revolving electron as the simplest to attack. The problem for solution was how such an atom emitted the characteristic hydrogen spectrum consisting of the Balmer series, and, presumably from Rydberg's theory and Fowler's investigation, the Pickering, the 4686 and the second principal series. According to classical dynamics the electron could revolve about the nucleus in any one of an infinite number of orbits. On the basis of Planck's quantum theory, which requires an electron to radiate energy in discrete quanta of the size $\epsilon = h\nu$ ergs where ϵ is the size of the quantum, $h(=6.55\times10^{-27}$ erg-seconds) is Planck's constant and ν is the frequency of the emitted radiation, Bohr fixed certain of these infinity of possible orbits. His first assumption was that an electron could revolve only in those orbits in which the angular momentum of the electron $m_0\omega a^2$ was equal to $nh/2\pi$, where m_0 is the electron mass, ω its angular velocity, a the radius of its orbit, h is Planck's constant and n takes on integral values 1, 2, 3. . . . From this it immediately follows, using the ordinary condition for circular motion, $eE/a^2=m_0\omega a^2$ that the diameters of these possible orbits are given by

$$2a=n^2h^2/2\pi^2m_0eE\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where E is the nucleus charge and e the charge on the electron. For the normal hydrogen atom $n=1$ (potential energy a minimum), and $E=e$, we find inserting the necessary numerical values that $2a=1.1\times10^{-8}$ cms., a quantity of the right order of magnitude. Other possible orbits have diameters 4, 9, 16 . . . times this as n takes on the successive integral values 2, 3, 4. . . . The radii of the possible orbits are shown on a correct relative scale in figure 3.

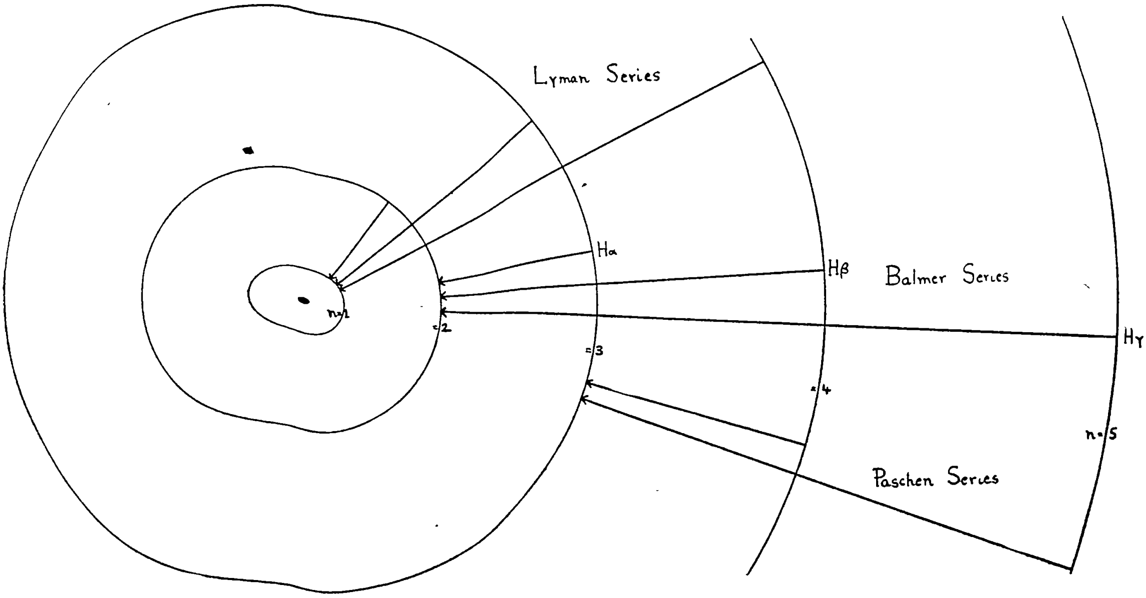


Fig. 3.—Relative Radii of Orbits of Hydrogen Electron.

The system considered has certain definite amounts of negative energy in each one of these stationary possible orbits. This energy is given by the potential energy of the electron less its kinetic energy of revolution. In fact it may be readily shown that W, the negative energy for a given orbit defined by the quantum number n, is

$$W = -2\pi^2 m_0 e^2 E^2/n^2 h^2 \qquad (4)$$

Bohr then considers what will happen, when, for some unspecified reason, the electron skrinks from a stationary orbit m to n, where $m > n$. There will be a certain loss of energy $\Delta W = W_m - W_n$, and this loss of energy (here Bohr makes his second assumption) will appear as monochromatic radiation of frequency given by the quantum relation $\Delta W = h\nu$, from which it follows that

$$\nu = (W_m - W_n)/h = (2\pi^2 m_0 e^2 E^2/h^3)[1/n^2 - 1/m^2] \qquad (5)$$

Equation (5) embodies the fundamental result of Bohr's theory. Contrary to the classical theory the electron does not radiate while revolving about the nucleus, but radiation only takes place, when the atomic system suffers a loss of energy due to an electron shrinkage from an outer to an inner orbit. This loss of energy then appears as radiation of frequency ν given by equation (5).

Since for hydrogen $E = e$ (5) reduces to the form

$$\nu = (2\pi^2 m_0 e^4/h^3)\,[1/n^2 - 1/m^2] = N_H\,[1/n^2 - 1/m^2] \qquad (6)$$

Inserting the necessary numerical values, $2\pi^2 m_0 e^4/h^3 = 1.09 \times 10^5$ cms.$^{-1}$ whereas from spectroscopic measurements N, the universal constant, $= 1.09678 \times 10^5$. Different series of hydrogen according to Bohr will be given by different values of n, while integral variations of m will produce the various members of any one series. Thus with reference to figure 3, which gives a diagrammatic representation of the Bohr hydrogen atom, a series of lines will be given by atoms in which electrons are falling from outer orbits to the first orbit ($n = 1$). Such a series was found in the ultra-violet spectrum of hydrogen by Lyman. The Balmer series is given by atoms in which electrons are falling from outer orbits to the second ($n = 2$). Finally atoms in which the electrons are falling to the third orbit ($n = 3$) will give a series in the infra-red found by Paschen. But, and this is important, Bohr's hydrogen atom does not emit radiations that will account for the Pickering series or the two principal series found by Fowler.

Bohr next discussed a helium atom which had permanently lost one electron,—ionized helium. In its outward appearance this helium atom would be similar to the hydrogen atom, as it would consist of a nucleus and a single electron. The difference would lie in the helium nucleus which would have a double positive charge and four times the mass of the hydrogen nucleus. Since the constant is of the form $2\pi^2 m_0 e^2 E^2/h^3$ and for helium $E=2e$, then $N_{He}=4N_H$ for a helium atom with a single electron. With this new constant Bohr showed that all the lines discovered by Fowler, viz. 4686, 3203, 2734, 2511, etc., would fall into a single series of the type $\nu=4N_H(1/3^2-1/m^2)$ where $m=4, 5, 6. \dots$ The physical interpretation of this formula is that the complete 4686 series is emitted by ionized helium, not hydrogen, atoms in which the single electrons are falling from outer orbits to the third.

The Pickering series, Bohr found, would be given by a formula of the type $\nu=4N_H(1/4^2-1/m^2)$ where $m=5, 6, 7\dots$ This on his theory means that ionized helium atoms in which electrons are falling from outer orbits to the fourth would give rise to the Pickering lines. But as Bohr pointed out $m=7, 9, 11\dots$ gave in this formula the Pickering lines 5411, 4541, 4200, etc., while even values of m gave lines coinciding with the Balmer series. This coincidence is not exact since a refinement of the theory, which takes account of the finite masses of the nuclei and their consequent motion, gives for the ratio N_{He}/N_H not exactly 4 but $4(M_H+m_0)/(M_H+m_0 M_H/M_{He})=4.001635$, where M_H is the mass of hydrogen nucleus and $M_{He}=$approx. $4M_H$ is the mass of the helium nucleus. The consequence of this refinement of the Bohr theory is that even values of m in the formula $4.001635N_H(1/4^2-1/m^2)$ will give lines displaced 1 or 2A to the violet of the Balmer lines. In fact Bohr predicts that, in a star or in a vacuum tube containing hydrogen and helium and under proper conditions of excitation, the resulting spectrum will appear as in figure 4. The heavy unbroken lines are the first five members of the Balmer series. The dotted lines are the first ten members of the complete Pickering series, even values of m giving, it will be noted, close companions to the Balmer hydrogen lines. Evidently the discovery of such companions to the Balmer series would furnish the strongest evidence that the Pickering series is due to ionized helium, not hydrogen.

3. VERIFICATIONS OF BOHR'S THEORY

Since its first enunciation, considerable evidence has accumulated as to the correctness of Bohr's theory. Some of this evidence, taken by itself, is not entirely satisfactory as a verification of the theory. Thus for example, Evans, Stark and Fowler have all observed the line 4686 in vacuum tubes which showed no trace of the hydrogen spectrum. But, as Fowler pointed out, it is not always possible to be sure that hydrogen, occluded in the electrodes or in the walls of the vacuum tube, has not come out when least expected. Subject to no such uncertainty as this, however, are three independent lines of evidence which afford the strongest confirmation of Bohr's theory.

1. The first of these is due to Fowler.[3] By the condensed discharge required for its production, the 4686 series found by him in the laboratory is evidently composed of enhanced lines. As having a possible bearing on the origin of this series, Fowler therefore investigated other enhanced spectra in an endeavor to find series relations. Particularly in the enhanced spectrum of magnesium he was able to get four main series, a Fundamental (containing the doublet 4481), two Subordinate and a Principal Series. These new enhanced series had a Rydberg constant $4N$ like the 4686 series. Further, and this is important, there were no relations between these enhanced series and the ordinary arc series of the element. Accordingly the numerical relations found by Rydberg between the 4686 series which is enhanced, and the Balmer series of hydrogen which is of the arc type, can have no significance. Further, by analogy with the enhanced spectra of magnesium, calcium, barium and strontium, the 4686 series must be a part of the enhanced spectrum of helium. Thus by a method independent of theory, Fowler arrived at a like conclusion with Bohr, namely that the 4686 series was due to helium. This then furnishes a confirmation of Bohr's theory.

2. By virtue of its directness and simplicity, probably the most important verification would be that afforded by the discovery of the Pickering components of the Balmer series (see figure 4). Such a discovery would clearly show, in view of the correction for the motion of the nucleus previously discussed, that the electron and the nucleus, exactly as pictured by Bohr, *revolved* about their

common centre of gravity. The difficulty with this investigation has been in the diffuseness of the Pickering lines, whether observed in the laboratory or in a star.

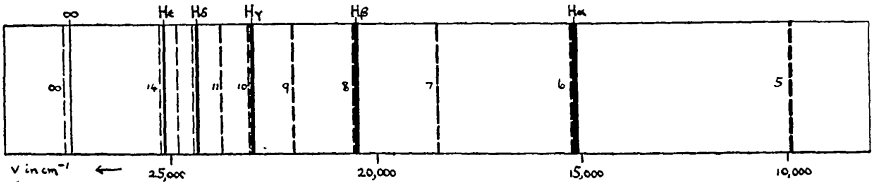


Fig. 4.—Pickering Components of the Balmer Series.

The first attempt was made by E. J. Evans.[9] With low dispersion and long exposures in a highly purified helium tube, he was able to measure lines near the position of the Balmer series. His measured wave lengths indicated blends of the hydrogen lines and the Pickering components, and thus furnished fair evidence of the existence of the predicted components.

The next attempt was a completely successful one by F. Paschen.[10] He used a special form of helium tube with a "hollow box-shaped cathode". Within this cathode, when the tube was operated with a continuous current, there appeared a yellow glow. Examined spectroscopically this glow showed the ordinary helium spectrum, the 4686 series and the Pickering lines. Under these conditions the Pickering lines were comparatively sharp. A trace of hydrogen impurity enabled him, with various orders of a small grating spectrograph, to photograph the Balmer lines and their ionized helium components. His measured wave lengths are given in the table. The first column gives the wave lengths of the Balmer series, the second the wave lengths of the complete Pickering series as computed according to Bohr, and the third column contains Paschen's measured wave lengths. There thus can be no doubt that in the laboratory, Bohr's prediction and consequently his theory, is beautifully verified.

In view of the importance of this verification and for the sake of completeness, it was of interest to examine stellar spectra to determine whether such components existed there. This investigation was undertaken by the writer.[11] A preliminary investigation of O-type stars with low dispersion indicated that 10 Lacertae had lines of sufficient sharpness. In addition J. S. Plaskett pointed out that the Pickering lines in 9 Sogittae were well defined. Using

Balmer Hydrogen Lines	Bohr's Helium Lines		
	Computed	Laboratory	Star
6562.79	6560.15	6560.13	6560.04
	5411.53	5411.55	5411.62
4861.33	4859.35	4859.34	4859.09
	4541.62	4541.61	4541.67
4340.47	4338.70	4338.70	4338.79
	4199.86	4199.86	4200.06
4101.74	4100.00	4100.05	4100.26

two and three prism dispersion, spectra were made of these stars which clearly showed the existence of Bohr's predicted components. In 10 Lacertae components were found to $H\alpha$, $H\beta$, $H\gamma$, $H\delta$, and in 9 Sagittae to $H\gamma$ and suspected for $H\beta$ and $H\delta$. The stellar wave lengths, resulting from measures of many plates, are given in the fourth column of the table. The cases where the observed wave lengths differ from the computed by 0.2A or more, are due chiefly to blends with enhanced nitrogen lines. The evidence from the laboratory and the stars clearly substantiates Bohr's prediction.

3. The final important verification of Bohr's atom is that which takes its origin in a refinement of the theory due to Sommerfeld.[12] So far only circular orbits characterized by the quantum numbers $n=1, 2, 3 \ldots$ have been treated. Elliptical orbits are also of course possible and these orbits Sommerfeld "quantizes" not only with respect to angular momentum, n', but also radial momentum, n'', $n=n'+n''$. He finds that the one quantum orbit may be a circle, the two quantum orbit a circle or an ellipse of eccentricity $\sqrt{3}/2$, the three quantum orbit a circle or ellipses with eccentricities $\sqrt{5}/3$, $\sqrt{8}/3$ and so on. The Balmer-like series are generated as before with frequencies given by

$$\nu = N[1/(n'+n'')^2 - 1/(m'+m'')^2]$$

where the lines are sharp but now depend upon four integers instead of two as formerly. Sommerfeld then considers the relativity correction due to the variation in mass with velocity of the electron. This introduces a correcting term containing the out that the Pickering lines in 9 Sagittae were well defined. Using factor n'/n''. Thus this term may have different values for the same value of the sum $n'+n''$. The relativity correction therefore requires that the lines be no longer single but have a complex structure. The multiplicity of the ring into which the electron falls determines the main structure of the lines. Thus the Balmer hydrogen lines, generated by an electron falling from outer rings into either the circle or ellipse of the two quantum orbit, are doublets of constant separation. Similarly the 4686 series lines are triplets.

With the "hollow box-shaped cathode" discharge tube already described, Paschen,[10] working in communication with Sommerfeld, examined the structure of the ionized helium lines. He found that the line 4686 and also higher members of the series showed the predicted structure and correct component separations. The structure for hydrogen is much more difficult to determine and is complicated by a Stark effect due to the electrical field of neighbouring atoms. As far as the observations go for hydrogen, they are qualitatively in agreement with Sommerfield's theory.

Taken collectively, the three chief lines of evidence summarized above furnish the strongest confirmation of Bohr's theory. Each line of evidence taken individually seems to pick out one particular feature of the atomic structure. The Rydberg numbers N and $4N$ confirm the existence of stationary orbits, the existence of enhanced helium components shows that the electron and nucleus revolve about their common centre of gravity, and Sommerfeld's predicted fine structure shows the variation in mass of the electron in its orbit.

CONCLUSION

The various investigations described in this paper had their origin in the discovery of the Pickering series in ζ Puppis. They have served to establish a far-reaching theory of atomic structure. Incidentally they have shown that the Pickering series in the laboratory and in the stars is due to ionized helium. This typical example of scientific work illustrates the importance of hypothesis which, though not necessarily correct, yet serves to collate groups of unrelated facts and to direct investigation into new and important channels.

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