

Rydberg and the development of atomic spectroscopy (Centennial of J. R. Rydberg's paper on the laws governing atomic spectra)

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A historical and methodological analysis is given for an important stage in the development of atomic spectroscopy, which was completed by the introduction of the spectral-term concept and the formulation of the Rydberg-Ritz combination principle. J. R. Rydberg's life and scientific activity are briefly reviewed. His fundamental paper of 1890 on the laws governing atomic spectra is considered in detail. Rydberg's decisive contribution to the discovery of the basic spectroscopic laws, whose determination created the necessary prerequisites for interpreting line spectra in the context of the Bohr model, is shown. It is shown that the final step in constructing Bohr's theory, the introduction of the frequency condition, was achieved in the process of reconciling his preliminary model with the spectroscopic scheme of Balmer, Rydberg, and Ritz.

1. INTRODUCTION

One of the most important spectroscopic constants bears Rydberg's name, and such terms as the Rydberg-Ritz combination principle and the Rydberg states of atoms and molecules have permanently entered the modern scientific household. The source of the corresponding concepts is the classical paper "Research on the structure of the emission spectra of the chemical elements"¹ by the outstanding Swedish scientist Johannes Robert Rydberg, which was published exactly 100 years ago in 1890. This paper occupies a special place both in the history of spectroscopy and also in the scientific heritage of the scientist himself.

Rydberg's creative route was very unusual. After starting from attempts to mathematically describe the periodicity of the physical properties of the elements, he then completely switched over to investigating atomic spectra; the discovery about 1890 of the basic laws governing spectroscopy was the result of this. After obtaining fundamental results on atomic spectroscopy, which he summarized in 1900 in a report at the International Physical Congress in Paris,² Rydberg forever abandoned the problem of optical spectra and again turned to the investigation of the questions of periodicity.³

Rydberg's outstanding contribution to the development of atomic spectroscopy and to the investigation of the periodic law were noted repeatedly, including the 1954 citation by N. Bohr and W. Pauli in connection with his centennial jubilee.⁴ Thus, in his presentation, Bohr said of Rydberg: "I would like to especially emphasize the direct continuity between his remarkable discoveries and the development of our ideas about the structure of the atom... As is well known, Rydberg's discovery of the laws governing spectroscopy was the result of his great interest in the problem of the interrelations between the chemical elements, and which the papers by Mendeleev mainly pushed to the forefront in the second half of the last century. The remarkable periodicity of the physical and chemical properties of the elements arranged in order of increase of their atomic weights impressed Rydberg's inquisitive imagination. Inclined towards numerical calculations, he was especially interested in optical spectra" (see Ref. 5, p. 470).

Pauli also noted the non-trivial character of the connection between both main directions of Rydberg's scientific activity: "Not everyone knows that, to his spectral line studies, Rydberg added interest in the periodic system of the elements, an interest which he did not abandon over his whole life" (see Ref. 6, p. 233).

The evaluation which Mendeleev gave even in 1886 and 1887 for the first stage of Rydberg's activity was extremely interesting. "Rydberg studied many aspects of the periodic law, which is the current question of the world view of chemistry, and therefore merits attention. Rydberg tackled a new aspect by considering the periodic dependence of properties on atomic weight, and he especially dwelled on the atomic weights themselves... There were repeated attempts to enter into these particulars, but Rydberg's was the first that was very rational and worthy of attention" (see Ref. 7, p. 486).

A fairly extensive literature is devoted to Rydberg's biographical and creative record and his scientific activity.⁸⁻¹³

Johannes Robert Rydberg was born November 8, 1854 in Halmstad (Sweden). After completing high school in 1873, he entered Lund University, which he completed in 1875, receiving a bachelor's degree in philosophy. His first scientific papers were of a purely mathematical nature: "The algebraic integrals of algebraic functions" (1878), and "The construction of conic sections at three- and four-point contacts" (1879, his doctoral dissertation). In 1879 he obtained the degree Doctor of Mathematics, from 1880 he held the office of Docent of Mathematics, and soon finished a physics paper, "A study of frictional electricity" (1882). The period from 1882 to 1887, when Rydberg was an assistant at the Institute of Physics of the Lund University turned out to be fruitful in his scientific activity. His papers in this period were devoted to the functional dependence of the physical and chemical properties of the elements on atomic weight: "The periodic system of the chemical elements" (1885), "Valence and atomic weight" (1885), and "The laws of the values of atomic weights" (1886). Next followed a series of papers on the study of the spectra of the elements, including the classical paper "Research on the structure of the emission spectra of the chemical elements" (1890),¹ and "Dis-

tribution of spectral lines" (1900).² From 1897 Rydberg was Adjunct Professor, and from 1901, Ordinary Professor of Physics at Lund University, holding this post right up to his retirement in 1919. He was elected a member of the Swedish Academy of Sciences and also a foreign member of the Royal Society of London. Rydberg died on December 28, 1919.

Rydberg's ideas on the problem of the periodic system evolved from considering atomic weight, as the main parameter on which the properties of the elements depend, to "ordinal numbers," i.e., the number of the element in Mendeleev's table. The papers "The electron, the first element" (1906),³ "Research on the system of the elements" (1913), and "The ordinal numbers of the elements and high-frequency spectra" (1914) were the culmination of this.

Rydberg wrote a total of about forty thematically fairly diverse papers. His scientific interests were mainly concentrated in two fields closely associated with the periodic system; the first is the study of the properties of the elements as a function of the atomic weight (later on, on the "ordinal numbers"), and the second one is an investigation of the optical spectra of the elements. At the same time, among his papers there are also such that are devoted to the asymmetry of the Rowland concave grating (1893), to determining the dispersion of air (1893), the Crookes tube (1896), determining periodic errors (1896), the theory of comets (1896), the motions of the satellites of Uranus (1898), the theory of gravity (1904), and even to the questions of the age of long-lived persons (1891).

The multifaceted personality of J. Rydberg both in science and as a person was repeatedly noticed by his contemporaries. Thus, M. Siegbahn, Rydberg's successor in the post of Director of the Physics Institute at Lund University, wrote: "His changing interests and live intellect were often expressed in stimulating combinations of thought. He interpreted everyday psychological experience in the light of physical laws and phenomena in popular lectures that evoked lively discussions. This intellectual game occupied him as a variety of mental gymnastics and satisfied the need to discharge his fantasies. He was very critical in his research and did not stop until definite results were obtained. Rydberg's superb mastery of an unusually enormous and difficult to understand mass of observations may be considered as a measure of his powers and turns out to be the best possible demonstration of his capacity to synthesize and analyze details" (see Ref. 8, p. 217).

A curious detail is contained in the memoirs of G. Borelius, who noted that Rydberg "was possibly unique in his time as one who took books in Chinese in the library at Lund" (see Ref. 10, p. 69).

In characterizing Rydberg's scientific activity, one must emphasize that the actual degree of influence of his papers on the development of quantum physics, the true theoretical status of the laws governing spectroscopy that he established, as well as the true scale of his standing as a scientist have still not been completely evaluated.

First of all, the importance of the circumstance that the decisive step towards the creation of the Bohr theory, the formulation of the frequency condition, turned out to be possible primarily thanks to that fact that an enormous set of spectroscopic experimental data was systematized about this time on the basis of the combination principle, remains

insufficiently realized. Thanks to the use of this principle, Bohr could establish the connection between the quantum energy states of atoms and spectroscopic terms. At the same time, the introduction of spectroscopic terms is specifically and rightly considered as one of Rydberg's main scientific merits.

The significance of Rydberg's contribution to the establishment of the general laws governing spectroscopy undoubtedly became obvious for Bohr from the very start of his acquaintance with atomic spectroscopy. In order to be convinced of this, it is sufficient to quote Bohr's opinions made directly "hot off the press." Thus, even in the first part of his "trilogy," Bohr refers to the 1908 paper by Ritz in the following manner: "According to Rydberg's theory generalized by Ritz, the frequency corresponding to a line of some element may be represented by the expression $\nu = F_r(\tau_1) - F_s(\tau_2)$, where τ_1 and τ_2 are integers, and F_1, F_2, F_3, \dots are functions of τ of the form $K/(\tau + \alpha_1)^2, K/(\tau + \alpha_2)^2, \dots$, and K is a universal constant" (see Ref. 14, p. 93). A more developed evaluation of the situation is contained in Bohr's paper "The hydrogen spectrum": "As is well known, Balmer's discovery led to the discovery of the line spectra of other elements. The most important papers in this field were done by Rydberg (1890) and Ritz (1908)... Rydberg proved even in his first paper that there are simple relationships between the constants of the different spectroscopic series of the same element. These laws were generalized by Ritz in the so-called combination principle" (see Ref. 15, pp. 152-153). Bohr thereby emphasizes the pioneering nature and high theoretical status of Rydberg's research. Also the heuristic role played by the basic laws governing spectroscopy established by Rydberg and Ritz in the formulation of the initial assumptions of Bohr's concept appears to be undoubted. It is sufficient to refer to Bohr's widely known and often quoted in the literature (see Ref. 16 by L. Rosenfeld, p. 163) phrase: "As soon as I saw Balmer's equation, everything immediately became clear to me." At the same time, it is reliably known that Bohr did not touch upon the question of atomic spectra at all in his research right up to the first days of February 1913. This is entirely clear from the contents of Bohr's notes that refer to this period. Thus, in a letter to Rutherford on January 31, 1913, Bohr notes that he is not studying the calculation of frequencies in the visible spectrum. There is no direct mention of the theory of line spectra in Bohr's letter to Hevesy on February 7, 1913. Nevertheless, the very voluminous first part of the "trilogy," containing an explanation of Bohr's original theory in essentially final form, was already sent to Rutherford on March 6, 1913.

Of course, this turned out to be practically feasible only thanks to the fact that about this time Bohr had already at his disposal, even if unfinished, a nevertheless fairly well developed and ready for assimilation outline of the theory of the spectroscopy laws that were established about that time. In connection with this, it seems to us that, for the modern historical and methodological literature devoted to the genesis of the quantum theory, a certain underestimate of the significance of that preliminary, "non-optical" stage of its development, in the course of which a basis was given for the mechanical stability of the Rutherford atom in its ground state and the idea of steady states was essentially formed, is typical.

Our further exposition is constructed in the following manner. First an analysis is given of Rydberg's research on atomic spectroscopy, which led to the discovery of the combination principle. Next, the preliminary stage, with no allowance for radiative processes, of the formation of Bohr's quantum concept is considered; This resulted in the creation of the theoretical foundations for the formulation of the stationary-states postulate, and the transition to the radiating atom model, for which the frequency condition holds, turned out to be possible.

2. RYDBERG'S PAPERS AND THE COMPLETION OF THE ORIGINAL STAGE OF THE DEVELOPMENT OF ATOMIC SPECTROSCOPY

The idea of the presence of a connection between the optical spectra of matter and its internal structure was expressed repeatedly in one form or another in the nineteenth century by a number of researchers.

Even in 1834 the English physicist W. Talbot, after detecting a yellow line in the spectrum of the flame from a wick wetted with table salt and a red line with strontium salt present, made the following statement in a very careful form: "One may expect that optical research at once throws new light onto chemistry," after remarking here that "an optical analysis makes it possible to distinguish very small amounts of matter with the same accuracy as any of the well-known methods" (see Ref. 17, p. 114).

G. Kirchhoff's pioneering paper, "The Fraunhofer lines" appeared 25 years later; it indicated for the first time the spectroscopic analysis possibilities connected with the presence of a correlation between the spectrum and composition. Kirchhoff began this paper, which afterwards became famous, with the words: "In connection with the investigation of the spectra of colored flames, which I carried out jointly with R. Bunsen, it turned out to be possible to judge the qualitative composition of complicated mixtures from the form of their spectra" (see Paper 4 in Ref. 18, p. 52). The discovery (in 1860 and 1861) of new elements, rubidium and caesium, by Bunsen and Kirchhoff (see Paper 6 in Ref. 18) was practical evidence for how great were the possibilities of spectroscopic analysis for determining the chemical composition of matter. Let us notice that significant successes in chemical research were achieved after this as a result of using spectroscopic analysis; in 1864, on the basis of the qualitative comparison of different spectra, A. Mitscherlich¹⁹ expressed the idea that spectroscopy must be considered not only as a method of chemical analysis, but also as the key to the secrets of the internal structures of atoms and molecules (see Ref. 20, p. 71). In 1869, E. Mascart²¹ noted that the observed multiplet structure of the lines of sodium (a doublet) and of magnesium (a triplet) is hardly a chance effect and expressed the hypothesis that "these groups of similar lines are harmonics connected with the molecular structure of the radiating gas" (see Ref. 1, p. 4).

Thereby, attention was first turned to the existence of definite quantitative relationships between the wavelengths of a series of spectral lines from one and the same element.

This was expressed in this sense even more definitely by G. Stoney. Thus, in Ref. 22 that is based on wavelength measurements in the spectrum of hydrogen made by A. Ångström,²³ he emphasized that "the lines in gas spectra must be connected with periodic motions within an individ-

ual molecule and not with the random motions of the molecules with respect to each other" (see Ref. 20, p. 72). In attempting to find a mathematical basis for his ideas, Stoney discovered the following regularity for the H_α ($\lambda_\alpha = 6562.8 \text{ Å}$), H_β ($\lambda_\beta = 4861.3 \text{ Å}$), and H_δ ($\lambda_\delta = 4101.7 \text{ Å}$) spectral lines of hydrogen (for the first, second, and fourth lines of the spectral series for hydrogen):

$$\frac{1}{\lambda_\alpha} : \frac{1}{\lambda_\beta} : \frac{1}{\lambda_\delta} = 20 : 27 : 32, \quad (1)$$

introducing in advance (for the first time in the history of spectroscopy) the wave-number scale.²⁴ Stoney himself interpreted the results as evidence for these lines being the overtones of some fundamental frequency. As is well known, in 1885 Balmer discovered his famous general equation for the lines of this series (which afterwards received his name)

$$\lambda = \frac{A m^2}{m^2 - 2^2} \quad (m = 3, 4, 5, 6, \dots), \quad (2)$$

where A is a constant. Relation (1) is obtained from Eq. (2) as a particular case for $m = 3, 4, 6$. Rydberg wrote afterwards: "... the merit of this discovery partly belongs to Stoney..., who left it for Balmer to find the connection between these lines and the H_γ ($\lambda_\gamma = 4340.5 \text{ Å}$) line, after which one could state that the series extends accurately in the ultraviolet spectral region" (see Ref. 1, p. 7).

The papers by P. Lecoq de Boisbaudran²⁵⁻²⁸ occupy a significant place in the history of spectroscopy; he actually suggested the first modeling theory for the origin of spectral lines, on the experimental study of which he worked for a long time. Indicating the significance of these papers, Rydberg wrote that Lecoq de Boisbaudran "is undoubtedly the first one who saw some connection between different spectra since, by studying the photographs of Bunsen and Kirchhoff for spectra, he discovered this connection with exceptional accuracy: 'The spectral lines of the alkali (and of the alkaline-earth) metals that are classified according to their refractivity are arranged, as are also their chemical properties, following the order of their atomic weights.' " Later on he says: "Thus, the spectrum of rubidium appears to be analogous to the spectrum of potassium, being only, as a whole, shifted into the red region." Later on Rydberg noticed: "It appears that Lecoq de Boisbaudran since then has even extended his comparative research on spectra; one may judge this by his use of real or hypothetical connections for calculations by means of interpolating the atomic weights of gallium and germanium" (see Ref. 1, p. 4).

Rydberg also noticed the papers by J. Lockyer,³⁰ emphasizing that this scientist "did not study in detail the structure of spectra or the correspondence between spectral lines... Lockyer's entire theory is based on the fundamental idea that each substance possesses a definite spectrum which does not change as long as the substance remains the same from a chemical point of view" (see Ref. 1, p. 6).

Also it appears to be relevant here to quote the following opinion of Mendeleev: "The question of the connection between the spectra of complicated bodies and their compositions is among those on whose development many are now working and the solution of which can have a great effect on many branches of physics and chemistry" (see Ref. 33, p. 44).

Thus, a general idea about the connection of spectra with atomic structure was being formed and secured in the

"general scientific consciousness."

We find the clearest realization of the presence of an organic correlation between the internal structure of matter and its optical spectra in the work of Rydberg himself, who made the idea of the existence of this connection the basis for the general program of his theoretical search.

This is entirely, distinctly evident from the text of his fundamental paper "Research on the structure of the emission spectra of the chemical elements" (published in 1890 as a separate issue in "Proceedings of The Swedish Academy of Sciences"), which we already cited above.¹ In this paper, Rydberg defines the general objective of his research thus: "To obtain by means of systematic study and comparison of the physical and chemical properties of the elements a more accurate knowledge of the nature and structure of atoms" (see Ref. 1, p. 8). Later on he writes: "Today one can consider as generally accepted by science the hypothesis that all physical phenomena are caused exclusively by the motion of matter; this enables one to hope that physics might some day become, the same as chemistry too, the mechanics of atoms. But there is still an obstacle, and moreover, a very serious one, to the realization of this idea. Very little is known about the structure of atoms, which is doubtless caused by the fact that science has still inadequately pointed out the suitable questions, ... I do not exaggerate by saying that a systematic and comprehensive study of the properties of matter with the objective of establishing the structure of the elements and to create a mechanics of atoms on this basis has not yet been started. But one must complete this work if science must some day cross the boundaries within which it is now located. Gravity, adhesion and the chemical bond, heat and light, electricity and magnetism all still represent the names of large, isolated fields of physical science about the connection between which we have confused and foggy ideas. If all these phenomena have their sources in different motions of matter, then it is absurd to think that we shall be able to ever understand them not knowing the structures of this matter itself, of atoms, and of the ether. ... Going still further, we arrive at a very plausible hypothesis that adhesion, the chemical bond, and chemical affinity basically depend on the periodic motions of atoms. Therefore, a general study of periodic motions as a whole would be the most natural course, and since the spectra of the chemical elements are caused by motions of a similar kind, we return to the field of spectroscopic analysis" (see Ref. 1, pp. 8,9).

Justifying the choice of spectra as the main subject for investigation, Rydberg first notes that such a course enables one to directly study the natural motions of atoms, emphasizing that "a study of these fluctuations gives us in every case very valuable information about the structure of atoms and will lead us closer to our objective than any other investigation..." (see Ref. 1, p. 10).

The high information content and accuracy of spectroscopic data, which Rydberg clearly realized, is the next important argument in favor of such a choice: "...The quality of the data on which one must base the research was an important reason which brought me to the decision to take spectra as the starting point for the serious study of the general properties of the elements. First of all, these data are incomparably the richest of all and are the most homogeneous as far as all the known elements are concerned. However, this is not their most important property. A significant one is that ev-

ery phenomenon is related to the motions of the smallest parts of matter, the atoms themselves, so that we can not only find the simplest functions expressing the relations between the forms of the moving bodies, their dimensions, and the forces which act, but also we can always obtain the same values for the wavelengths of an element's lines without random deviations." (see Ref. 1, p. 10).

The exceptionally comprehensive and complete information content on the state of the problem in his time and also the depth and completeness of the thematic analysis of the literature published by that time are the distinguishing features of Rydberg's 1890 paper and also of a number of his subsequent papers.

Rydberg realized the need to search for general regularities in the line spectra of the elements. Therefore, along with the papers by Mitscherlich, Stoney, Lecoq de Boisbaudran, and Lockyer that are indicated above, a paper by N. Nordenskiöld,³⁴ who "studied this curious problem while wintering in Arctic regions. He assumed that he could determine a simple law such that the wavelengths of different spectral lines could be expressed by the equations $\lambda = a^n k$ or $\log \lambda = k_1 + n\Delta$, where n is an integer, and a and k or k_1 and Δ are characteristic constants for each element" (see Ref. 1, p. 7), attracted his attention. Rydberg made a reference to Mascart's paper²¹ with an indication of a fundamental property for the constancy of frequency differences for double lines in spectra with a series structure for the sodium doublet and magnesium triplet examples, and to Hartley's paper,³⁵ in which repeating frequency differences were found between the components of double and triple lines in the line spectra of magnesium, zinc, and cadmium with series structures. Rydberg supposed that "he discovered this first (in 1885)," and had not yet become aware of the indicated paper; here he noted: "Since Hartley had not made greater use of the superb materials which he obtained by means of his measurements in the ultraviolet spectral region, one could have concluded that he did not attach great significance to the relationships found (see Ref. 1, p. 12).

Rydberg emphasizes that "before the research of Living and Dewar,³⁶ no one was in a position to find for a series of lines the real connection between them" (see Ref. 1, p. 13). He notes that these scientists found the principal, the sharp or "second secondary," and the diffuse or "first secondary" line series in the spectra of the alkali metals.

Rydberg summarizes the general situation in the following manner: "...if one excludes the Balmer equation for the hydrogen spectrum, one must recognize that the problem of constructing optical spectra still remains unsolved" (see Ref. 1, p. 3).

Let us notice that, along with the papers by Rydberg himself^{1,2,38,39} the research of Kayser and Runge^{40,41} occupied a special place among the papers oriented towards searches for series regularities in spectra. Their comparative analysis was exceptionally important for an adequate evaluation of that decisive contribution which Rydberg made to the development of the science of atomic spectra. We shall return to this question below.

Rydberg's relation to the theoretical models of optical spectra is an important feature of his general scientific concept, which is clearly traced in the 1890 paper. As a rule, he especially singled out those papers which contained, in one form or another, attempts at a theoretical explanation of the

laws governing spectroscopy (see Ch. VIII in Ref. 42, pp. 205–206).

In this respect, the fairly detailed analysis of that part of Lecoq de Boisbaudran's paper which contains the historically first attempt to give a theoretical basis at the modeling level for the connection between the spectral characteristics of radiation and the motions of the particles of matter that are considered as the emitters, which exists in Rydberg's pioneering 1890 paper,¹ merits special attention. According to Lecoq de Boisbaudran's hypothesis, "the molecules which oscillate, giving light, have isochronous oscillation periods; therefore they give lines with wavelengths that are definite and constant for each substance... The force which tends to return the molecule towards the center and its motion are reactions of the ether, reactions that are constant for one and the same velocity and mass of the molecule, but which vary with variation of the relationships of the masses of the ether and molecule... In this case, a heavier molecule will return to its center of equilibrium with less energy than another molecule, and consequently, it will take a longer time for an oscillation around this point and its wavelength will be longer" (see Ref. 25, p. 446).

There appears to be no doubt that the very idea of using similar models is close to Rydberg's idea. Thus, an attempt at a theoretical explanation of the cause of the periodic properties that is based on the hypothesis of the existence "of periodicity for the forces acting between atoms,...which arise through their periodic motions, and thanks to which the surrounding ether is set into vibrations; the amplitudes of these vibrations are determined by the energy of atomic motion" (see Ref. 37, p. 26) is already contained in his 1885 paper "On the periodic system of the chemical elements." Right there Rydberg expressed the hope that he would succeed in his subsequent publications in introducing something more for the solution of this, as he remarked, "very involved problem." However, there is no doubt that, towards 1890, Rydberg realized the premature and physically unpromising nature of this type of theoretical structures. Although he also spoke more about his reluctance "to subject theory (Lecoq's, as an example of authors) to a detailed critique," he nevertheless definitely emphasized that "Lecoq, with all his indisputable merits in spectroscopic analysis, had little success in this theory," and that "the fantastic world of the atoms which he constructed in order to explain the origin of different oscillations did not have any support besides the name of its author" (see Ref. 1, p. 4).

Of course, Rydberg's use of such terms as "atom" and "the periodic motion of atoms" was needed in commentaries. It is a fact that, in the 1880s, when Rydberg was doing his research work, i.e., before the discovery of the electron and the recognition by the scientific community of Maxwell's electromagnetic theory, a theoretical basis for creating a plausible concept of the atom that models its structure and processes of interaction with radiation was not yet necessary. The level of physical science at that time, primarily the successes of the kinetic theory of gases and the experimental results in the fields of chemistry and molecular physics gave only some evidence in favor of the atomic hypothesis's validity and enabled one to estimate the effective dimensions of atoms and molecules (see Ch. 5 in Ref. 43 and Chs. 4 and 8 in Ref. 42). In 1900, Rydberg wrote the following "...the majority of the properties of the elements are as

yet still determined only by a crude approximation, and the numerical values of constants are averages which refer to an enormous number of molecules or atoms that are in different conditions and are mixed, in poorly known relationships, with atoms of other kinds. This is molecular statistics" (see Ref. 2, p. 200).

At the same time he singled out the spectroscopy of gases as just the field where the connection of the optical spectra of atoms with their structure can, in principle, be established in its purest form. This position of Rydberg has been entirely clearly indicated: "Everything is entirely different for gas spectra. The atoms and molecules act individually; each atom emits its lines independently of the line emission by other atoms. We can say that spectra are the language of atoms; each element always speaks in its own typical and unchanged language that is the same on the Earth and on the most remote stars. Just this constancy also enables us to determine the wavelengths of lines with exceptional accuracy and promises great reliability and success in synthesizing numerical data" (see Ref. 2, p. 200).

Thus, Rydberg defined completely unambiguously the strategy of his scientific search as the establishment of the general connection between the spectral characteristics of matter and its internal structure. At the same time, he also saw clearly the main obstacles in the way of the successful realization of such a program: on the one hand, the ever increasing abundance of purely empirical material in the field of spectroscopy, and, on the other hand, the acute shortage of experimental information with respect to the "internal motion of atoms" in combination with the clear inadequacy of the general theoretical means which were at the disposal of physics at that time.

In a similar way, Rydberg made the correct choice of his original research problem. He formulated this problem as "a search by means of a purely empirical method for the relationship between the lines in one and the same spectrum in order, if possible, to approximately calculate all the lines of a spectrum for which a limited number of them are known. Along with this research, one must also study the similarities between the spectra of different elements, in order to be in a position to distinguish seeming laws governing a specific spectrum from the real laws inherent to all spectra" (see Ref. 1, p. 10).

Actually, Rydberg posed the problem of systematizing the existing experimental spectroscopic material according to certain semi-empirical schemes which would nevertheless have a fairly universal nature.

The history of science shows that, in the course of its formation, any field of physics passes through a phase when its accumulated empirical material is subjected to a "preliminary processing" by means of singling out certain fairly general laws governing this field but that do not yet have a profound theoretical basis. Such, for example, were Kepler's Laws in celestial mechanics, the Boyle-Mariott Law in the physics of gases, and Coulomb's and Biot-Savart's laws in the field of electrostatics and magnetism.

Similar "primary" theoretical models fulfill a dual function: first, they create a certain general basis for systematizing experimental data, performing the role of empirical laws, as if accumulating experimental data. Second, they play an important constructive role in creating generalizing, more fundamental theories, performing here as distinctive

mediators between theoretical knowledge and empiricism.^{44,45,46}

Thus, for example, in the process of constructing the theory of electromagnetism, Maxwell never turned directly to the experimental data, but used the theoretical knowledge of the preceding level (such as the models of Coulomb, Faraday, Biot-Savart, etc.) as distinctive "empirical" material (see Ref. 47).

If one views the state of spectroscopy in the 1880s from this position, then one must recognize that the problem of finding general laws governing line spectra was specifically the most important problem at that time.

In similar cases, as a rule, a situation arises that is typical for the development of science, where different researchers attempt to find a solution of the problem which has developed practically simultaneously and independently of each other. In this sense, the stage of the history of spectroscopy under consideration was also no exception. Actually, the well known spectroscopists Kayser and Runge suggested and attempted to carry out a similar program to establish general mathematical equations describing the laws governing spectroscopy at the same time as Rydberg.

These two programs competed with each other for a fairly long time. This process was accompanied by fairly sharp polemics, and moreover, the choice which Rydberg subsequently defended and which, as we now know, turned out to be right, received final recognition only towards the end of the 1890s.

This interesting part of the development of spectroscopic science merits special historical and methodological analysis.

Here we shall limit ourselves to only a general comparison of the concepts of Rydberg on the one hand and of Kayser and Runge on the other for the purpose of finding those differences in their approaches, whose existence, in the final analysis, decided the rivalry in favor of Rydberg.

A general understanding that the required analytical expression for spectral equations must appear as some function of an integer which, in the case of the hydrogen atom, goes over into the Balmer equation, unites the approaches of Rydberg and of Kayser and Runge.

However, the explicit form of the relation differs significantly in both approaches. Rydberg investigated the dependence of wave number k on the ordering number m of a series term by a graphical construction method for three types of spectral lines from different elements. The dependence found is characterized by a monotonic decrease of the difference $\Delta k = k_{m+1} - k_m$ with increasing m . Rydberg posed the problem of finding the simplest function which satisfies this condition. He chose the equation

$$k = k_0 - \frac{C}{m + \mu} \quad (3)$$

as the first possibility. But it turned out that this relation gave only a "very superficial idea of the structure of a spectrum."¹ Therefore Rydberg, without completely rejecting the general structure of the expression, tested the next more complicated power function, one with a quadratic dependence in the denominator.

There is every reason to think that the final choice of such a function as basic was dictated not only by its good agreement with the experimental data, but also by the ac-

quaintance with the Balmer equation which had taken place at that time.⁴⁸ Rydberg determined that an equation of the general form

$$k = k_0 - \frac{N_0}{(m + \mu)^2}, \quad (4)$$

is valid with high accuracy for line series, where k_0 and μ are constants which characterize a given series (k_0 corresponds to the series limit as $m \rightarrow \infty$), and N_0 is a constant that is the same for all series. According to his own statement, Rydberg "was busy studying this equation when he saw Balmer's published calculation for the hydrogen spectrum" (see Ref. 1, p. 41). By comparing his own expression with Balmer's (see Eq. (2)) written in the form

$$k = \frac{1}{\lambda} = \frac{1}{A} - \frac{4/A}{m^2}, \quad (5)$$

he determined that $N_0 = 4/A$ for $\mu = 0$. As is well known, at present the quantity N_0 is denoted by R , and one calls it the Rydberg constant in his honor.

Thus, the wave numbers for the lines of each series are determined by the differences of two spectral terms; a constant one which determines the series limit (these limits coincide for the sharp and diffuse series of each element), and a variable term, which depends on m and contains the constant μ that is characteristic for the series, which gives

$$k = k_1 - \frac{N_0}{(m + p)^2}, \quad k = k_2 - \frac{N_0}{(m + s)^2}, \quad k = k_2 - \frac{N_0}{(m + d)^2}, \quad (6)$$

where $\mu = p, s$, and d are for the principal, sharp, and diffuse series, respectively, and k_1 and k_2 are values of the constant k .

The method used by Kayser and Runge was made up so as, by means of a purely mechanical trial and error, to search for an equation which would, with the best possible accuracy, give agreement with the observed wavelengths for lines of the alkali metals (starting with lithium and going on in increasing order of atomic weight), and would be in agreement with Balmer's equation for hydrogen. In Ref. 40 Runge showed an equation of the form

$$\frac{1}{\lambda} = A + Bm^{-1} + Cm^{-2}, \quad (7)$$

as giving excellent agreement for one of the lithium series.

However, two years afterwards Kayser and Runge⁴¹ already gave preference to an equation of the following form

$$\frac{1}{\lambda} = A + Bm^{-2} + Cm^{-4}, \quad (8)$$

which, starting from $m = 3$, "in the best manner reproduces the lines in different series of the alkali metals" (see Ref. 31, p. 141).

While recognizing the validity of Rydberg's comments regarding the fact that the expression that they used is simply an interpolation formula and that, in principle, one may select a great many other equations which lead to just as satisfactory results, nevertheless Kayser and Runge insisted that just their equation turned out to be significantly more accurate than any other one with the same or a larger number of constants.

It is very important that Rydberg continually strove to retain a universal form for the relation sought, whereas similar arguments were not significant for Kayser and Runge.

They were always skeptically disposed regarding the expediency of searching for a single equation which would unify all the lines in a given spectrum. Furthermore, the main subject of the criticism from their position turned out to be just that point of Rydberg's entire concept which was its heart; that the wave numbers of all the lines of a spectral series could be represented as values of one function (Eq. (4)) of $(m + \mu)$ with a single value of the constant N_0 for all the series. The position of Kayser and Runge was purely pragmatic; the main thing for them was for the most accurate possible reproduction of the experimental data to be obtained without using any additional considerations. In connection with this, Rydberg was entirely justified in making the following comment: "It would be easy to compile equations which represent line series with considerably greater accuracy than that which Kayser and Runge have attained, if one does not fear increasing the number of constants" (see Ref. 1, p. 134).

Thus, we see that Rydberg's research activity was guided by definite normative considerations which were not part of the realm of specific scientific regulatives, but were closer to the field of methodological ones. The criteria of simplicity and universality which he used undoubtedly belong here primarily, which enabled him to make a choice between alternative forms of theoretical knowledge which describe one and the same empirical data set that is uniquely satisfactory in the sense of a numerical relationship. In this respect, Rydberg's position is close to that which J. H. Poincaré held and subsequently developed.

Rydberg obtained an especially important result for the connection between the principal and the sharp series of lithium (Li), sodium (Na), and potassium (K), which are determined according to the following equations:

$$k = k_1 - \frac{N_0}{(m + p)^2} \text{ for the principal series, } m = 1, 2, 3, \dots, \quad (9)$$

$$k = k_2 - \frac{N_0}{(m + s)^2} \text{ for the sharp series, } m = 2, 3, 4, \dots,$$

and moreover, $k_1 > k_2$.

It turned out that the equations

$$k_1 = \frac{N_0}{(1 + s)^2}, \quad k_2 = \frac{N_0}{(1 + p)^2}, \quad (10)$$

are valid with high accuracy for the limits, and therefore, the expressions for the series take the forms

$$k = \frac{N_0}{(1 + s)^2} - \frac{N_0}{(m + p)^2} \quad (m = 1, 2, 3, \dots), \quad (11)$$

$$k = \frac{N_0}{(1 + p)^2} - \frac{N_0}{(m + s)^2} \quad (m = 2, 3, 4, \dots).$$

Both equations give the same value of k for $m = 1$, only with opposite signs, and this enabled Rydberg to draw the conclusion (for the example of lithium) that "the first term of the sharp series would be nothing other than the least refracted line of the principal series, i.e., the well known red line of lithium ($\lambda = 6705.2 \text{ \AA}$)" (see Ref. 1, p. 61).

By combining the two Eqs. (11) for the principal and sharp series into one equation (and adding the \pm sign "to

indicate that it is always necessary to take positive differences"), Rydberg wrote it in the form

$$\frac{\pm k}{N_0} = \frac{1}{(m_1 + s)^2} - \frac{1}{(m_2 + p)^2}, \quad (12)$$

where m_1 and m_2 can assume all integer values from 1 to ∞ . Later on, Rydberg gave the general equation for spectral series in the form (see Ref. 1, p. 64)

$$\frac{k}{N_0} = \frac{1}{(m_1 + \mu_1)^2} - \frac{1}{(m_2 + \mu_2)^2}, \quad (13)$$

"where m_1 and m_2 are variable integers, and μ_1 and μ_2 are constants typical for the series." Let us notice that he wrote: "In each series m_1 has a definite value not exceeding 2 for calculated series, and which is possibly always equal to 1 under the assumption that μ can have values > 1 . However, it appears to be more probable that series with $m_1 > 1$ are weaker than other ones and are situated in still unstudied spectral regions." This hypothesis was verified later on.

Thus, Rydberg's 1890 paper already contained a representation of the wave numbers of spectral lines for atomic spectra with a series structure in the form of the differences of two spectral terms (as one came to call them later on) of the form $T = N_0/(m + \mu)^2$, i.e., in other words, it contained the combination principle for such spectra. One must consider this as the most important result of this paper.

In 1896, Rydberg formulated the conclusion of a connection between the principal and sharp series, which follows from Eqs. (11), in the following manner: "The difference between the common limit of the diffuse and sharp series and the limit belonging to the corresponding principal series gives the wave number...of the first term that is common to the sharp and principal series."³⁸ A. Schuster,⁵⁰ who started, however, not from Rydberg's general representation of the wave numbers of spectral lines in the form of the differences of two terms, but from equations of the type (see Eq. (8)) $k = 1/\lambda = A + Bm^{-2} + Cm^{-4}$ obtained by Kayser and Runge and which, at $m = \infty$, give values for the limits of the series under consideration, independently arrived at a similar conclusion.

Let us notice that, in his well known monograph (see Ref. 20, p. 75), M. Gemmer explains Rydberg's paper¹ inaccurately, without showing the general Eqs. (12) and (13), and he talks about the connection between series by referring only to Rydberg's 1896 paper³⁸ (and also to Schuster's paper⁵⁰), whereas this connection was established by Rydberg back in 1890.

The fruitfulness of Rydberg's general approach appeared clearly in his 1897 paper on new line series in the hydrogen spectrum,³⁹ and which contained important predictions of new lines in the series spectra based on the use of the combination principle. The new spectral series which E. C. Pickering⁵¹ discovered in the spectrum of the star ζ Pup-pis and attributed to hydrogen for the reason that the wavelengths of this series, for odd $m = 5, 7, 9, \dots$ satisfy the simple general equation

$$\lambda = 3646,1 \frac{n^2}{n^2 - 16} \text{ \AA}, \quad (14)$$

which gives the lines of the Balmer series for even $n = 6, 8, 10, \dots$ (the Balmer Eq. (2) is obtained from Eq. (14) for the integers $m = n/2$),⁵² was considered in Rydberg's

paper. Actually, the Pickering series belongs to ionized helium He II, as Bohr first showed theoretically in 1913 in the first part of the trilogy (see Ref. 14, p. 93) and later was confirmed experimentally, and is determined by the equation

$$k = 4R \left(\frac{1}{4^2} - \frac{1}{n^2} \right) \quad (n = 5, 7, 9, \dots), \quad (15)$$

which contains the quadrupled Rydberg constant $N_0 = R$. The coefficient 4 for R represents the square of the nuclear charge $Z = 2$ for the He^+ ion, which has one electron, just like the hydrogen atom. For $n = 6, 8, 10, \dots$, Eq. (15) gives lines which approximately agree with the lines of the Balmer series. However, in 1897 and in all subsequent years up to 1913, it was thought that the Pickering series belonged to hydrogen, and Rydberg started from this. He, however, made the clever assumption that, by analogy with the series spectra of the alkali metals and other elements, that the Balmer series represents the diffuse series of hydrogen that is determined by the equation

$$\frac{k}{N_0} = \frac{1}{(m_1 + p)^2} - \frac{1}{(m_2 + d)^2} = \frac{1}{(m_1 + 1)^2} - \frac{1}{(m_2 + 1)^2}, \quad (16)$$

where $m_1 = 1$ and $m_2 = 2, 3, 4, \dots$, and that the Pickering series represents the sharp series of hydrogen that is described by the expression

$$\frac{k}{N_0} = \frac{1}{(m_1 + p)^2} - \frac{1}{(m + s)^2} = \frac{1}{(m_1 + 1)^2} - \frac{1}{(m_2 + 0.5)^2}, \quad (17)$$

where $m_1 = 1$ and $m_2 = 2, 3, 4, \dots$. Here $m = n/2$, and the values $s = 0.5$ and $p = d = 1$ are adopted for the constants s , p , and d . Starting from the general Eq. (11), Rydberg obtained the equation

$$\frac{k}{N_0} = \frac{1}{(m_1 + s)^2} - \frac{1}{(m_2 + p)^2} = \frac{1}{(m_1 + 0.5)^2} - \frac{1}{(m_2 + 1)^2}, \quad (18)$$

for the corresponding principal series, where $m_1 = 1$ and $m_2 = 1, 2, 3, \dots$, which gives the lines $\lambda = 4687.88 \text{ \AA}$, 2734.55 \AA , 2386.50 \AA , \dots . It turned out that, in accordance with this prediction, an extremely intense line with the wavelength $\lambda = 4688 \text{ \AA}$ was observed in stellar spectra, and Rydberg wrote: "The $\lambda = 4688 \text{ \AA}$ line is more intense than all the known hydrogen lines, it agrees almost exactly with the calculated value of 4687.88 \AA , and we can with complete confidence consider it as the first line of the hydrogen spectrum which is simultaneously the first line of the principal series and of the sharp series" (it is found from Eq. (17) for $m_2 = 1$). Although it turned out later that the series of Eq. (18) belongs to He II and not to hydrogen, the method itself of predicting new lines on the basis of the general Eq. (13) and Eq. (17) also turned out to be entirely correct for the Pickering series belonging to He II. Of course, the separation of the Pickering series from the Balmer series also was correct, as opposed to joining these series in Eq. (14), although Rydberg also could not know that these series belong to different atoms (hydrogen and helium).

One must notice that, in giving the general Eq. (13) in Ref. 39, Rydberg referred in a note to Ref. 1 and indicated

that he gave this law in explicit form also in a summary of Ref. 1 in a number of journals ("Zs. Phys. Chem.," "C.R.," and "Phil. Mag."), and that "therefore, it appears to be impossible that Professor Schuster proved his claim to the second discovery of the law, since he has not published it to a sufficient degree." The credit for the discovery of the general Eq. (13) belongs entirely to Rydberg, and it is incorrect to speak of the connection between spectral series resulting from this law as the Rydberg-Schuster law, as Jammer does (see Ref. 20, p. 91).

In Ref. 2 in 1900, Rydberg called spectra with a series structure for which he established the fundamental Eq. (13) Type I spectra, unlike the Type II spectra not possessing such structure (see Ref. 53, p. 365). He showed for the example of argon that, for Type II spectra, one can arrange the values of the wave numbers for the spectral lines in the form of orthogonal tables with constant differences between the rows and columns. Similar tables were also found by other scientists (see Ref. 54); the elements of the table correspond to the differences of terms from combining systems of terms, which became clear considerably later, after W. Ritz formulated the combination principle in generalized form (the papers by W. Ritz from 1903 through 1909 are contained in a one-volume collection of his works.⁵⁵ The references in the literature are usually to Ritz's 1908 papers (Refs. 56 and 57). The following formulation of the combination principle taken from an abstract attached to Ref. 56 is quoted in Ref. 55 (p. 162): "By combining by means of addition or subtraction either the series equations themselves or the constants entering them, one can construct new equations which enable one to completely calculate new lines of the alkali metals that have been discovered in recent years by Lenard and others, and also make possible far-ranging applications to other elements, in particular, to He." Just this quotation in abbreviated form is given in Ref. 20 (in a reference on page 77). Actually, however, in our opinion, Ritz gave the most meaningful formulation of the combination principle in his general 1909 review "Line spectra and the structure of atoms."⁵⁸ After considering two-term series equations, Ritz wrote: "It is evident that: 1° Simple laws refer always to $1/\lambda$, i.e., to frequency. 2° As one of the integers goes to infinity, the frequencies obtained converge toward a limit. 3° To some degree, each of the two terms of the equation is independent, and one obtains the lines of a spectrum by intercombining such terms by different methods."

One must emphasize here that Ritz's interest in the problems of atomic spectroscopy was by no means occasional; his papers on the theory of spectra comprise over half of his total scientific legacy, which is startlingly large for a theorist whose active research work was limited to at most six years.²¹

Ritz attempted to rigorously solve the problem of the theoretical derivation of series equations based on the equations of classical mechanics and electrodynamics while drawing on certain special modeling hypotheses about internal atomic structure. This important part of Ritz's activity has been practically ignored in the literature on the history of science. However, there is no doubt that it was well known to Bohr, who considered it especially necessary to make a well-developed evaluation of it in his report presented to Rydberg's centennial jubilee, which we have already quoted:

"As is well known, Ritz, inspired by the explanation of

the Zeeman effect given by Lorentz, attempted to explain spectroscopic laws by means of the idea introduced by him of atomic magnetic fields, whose effects on the electrically charged components of the atom, in contrast to the effects of ordinary mechanical forces, depend significantly on their velocities. However, notwithstanding all such clever attempts in this direction, he did not succeed in explaining spectroscopic laws without contradicting the interpretations of other atomic properties.

Nevertheless, the profound investigation of spectroscopic problems by Ritz, especially strengthened by his close collaboration with Paschen, led him to various improvements of the numerical equations for spectral series and to the prediction of new series, which essentially completed the analysis of many line spectra. In connection with this work, for which the discoveries and original concepts of Rydberg undoubtedly had great importance, Ritz in 1908 established the general law that is now known as the Rydberg-Ritz combination principle, according to which the wave number of any spectral line can be rigorously represented in the form

$$k = T_1 - T_2,$$

where T_1 and T_2 are two terms of a set of terms that are characteristic for a given element" (see Ref. 5, p. 473).

Thus, Rydberg's research specifically played a decisive role in the correct systematizing of spectroscopic data by using the combination principle which, as we saw, was already contained in his fundamental 1890 paper.

Actually, Rydberg had created the necessary prerequisites for the subsequent theoretical description of the laws governing spectroscopy according to the Bohr model, which originally arose and was developed as the basis for solving a number of problems of atomic physics that are unrelated to the problem of line spectra.

3. RYDBERG AND BOHR'S QUANTUM THEORY

It is well known that Bohr's theory entered science primarily as a quantum theory for line spectra. In particular, Rutherford evaluated it as just that in his 1936 lecture: "I consider the original quantum theory of spectra which Bohr put forward to be one of the most revolutionary of all those ever created in science; and I don't know of another theory which would have had greater success... The basis of its success lies in the introduction of completely new ideas into the theory" (see Ref. 52, p. 490).

In speaking of these ideas, Rutherford undoubtedly had in mind Bohr's two famous postulates; the one about steady states and the frequency condition, which later on received both direct experimental confirmation and also a comprehensive theoretical basis in quantum mechanics and quantum electrodynamics.

The organic connection of Bohr's theory with the spectroscopy of atoms and molecules appears today to be so natural and usual that certain points which are extremely important for understanding the features of the genesis and development of Bohr's quantum theory continue to be in darkness until now.

Those difficulties of a conceptual and psychological nature, with which the perception by the scientific community of one of the most characteristic properties of Bohr's theoretical model, the independence of the radiation frequency

from the frequency of the radiating charge's periodic motion, was associated, are generally known (see Ref. 60 and the literature cited there).

On the other hand, as far as one can tell from the existing historical material, Bohr himself did not have to overcome any significant psychological barrier at the deciding point of this stage of his creative activity in forming the frequency condition.

Of course, one can understand and share in the delight of Einstein, who called this step by Bohr "a wonder" and a manifestation of "the highest form of music in the realm of the mind," and can completely associate with Einstein's evaluation of Bohr as "a man with an intuition of genius and fine taste" (see Ref. 61, p. 275), etc. However, it is clear that similar opinions refer entirely to the realm of the psychology of scientific creativity.

Of course, without denying the very important role of the psychological factor in the process of scientific discovery, one must, nevertheless, attempt each time to recognize the twofold logical foundations of the similar process that are determined primarily by the structure and features of the physical model being used which, in turn, is dictated by the nature of the problem being solved.

One must keep in mind that even an investigation that is most fundamental by its final results is, as a rule, started from the solution of some specific problem. The history of science gives many examples illustrating the correctness of such a statement. It is sufficient to only recall the discovery by Planck of the quantum of action, which was the result of solving a problem that was fairly narrow in its original formulation, that of calculating the spectral density of the equilibrium radiation of an absolute black body based on the use of simple model representations.

If one approaches the genesis of the Bohr model of the atom from these positions, then one must notice immediately that Bohr's investigation here started from the determination of the energy losses for α -particles in matter based on the use of Rutherford's nuclear model.³⁾ It is typical here that the theory he developed turned out, according to his own statement, to be "in many ways similar to the usual dispersion theory in electrodynamics" (see Ref. 62, p. 66).

It is natural that, in such problems, the properties of the electrons that are part of an atom must be allowed for only with respect to the effect on their charges from an external electric field that is created by a moving α -particle or light wave, when dispersion is being discussed.

This means that Bohr considered the electrons only as reacting to the field, but not as the sources of it. Consequently, the characteristics of the problem which Bohr solved led to the situation that, from the very start, an electron appeared in it only as a mechanical object (a test charge), which enters into the expression for the Lorentz force, but not as a radiating electron (a charge which determines the current in the right hand part of Maxwell's field equations). This predetermined the whole further line of development of the Bohr model right up to that final stage, when the question first arose about the possibility of using this model to explain atomic spectra.

About this time, Bohr was able to solve the problem of the mechanical stability of the Rutherford atom in the ground state. Furthermore, he had already formed a preliminary idea for the possibility of the existence of a discrete

series of excited states for an atom.

Here it is very important to settle in just what specific context the corresponding problems arose and were solved. According to Bohr, the basis of the mechanism for stopping α -particles in matter is the transfer of their kinetic energy to the electrons bound in an atom. Here, as Bohr noted in his report before the Physical Society in Copenhagen (in September 1912), "The absorption, which depends on the motion of the electrons, supplies us with information about their frequencies" (see Ref. 63, p. 67). On the other hand, Bohr used values for these frequencies that have been obtained from dispersion data.

As a result, Bohr came to the following conclusion: "One can satisfactorily explain the absorption of α -rays in hydrogen based on an assumption of the same number of electrons in a molecule and of the same frequencies which were adopted to explain the refraction and dispersion in this gas" (see Ref. 62, p. 77).

However, the lateral effect of both the field of a charged particle and also of the periodic field of an electromagnetic wave on an electron bound inside an atom inevitably leads to the occurrence of oscillations of the electron about some position of equilibrium.

No sort of difficulties arises at this point in considering electrostatic systems of the Thomson model type as a consequence of the quasielastic nature of the bond between the diffuse positive and point negative charges.

The situation changes radically in the case of the Rutherford model; the problem of the mechanical instability of the system arises in the problem of the motion of a point charge in the field of a Coulomb center.

From a purely formal approach, it is impossible to discuss constructing the system from the atomic constants that characterize the nucleus and electron, i.e., from their masses and charges, one cannot find a length parameter that would have the needed order of magnitude and specify the needed "equilibrium" distance.

From the point of view of dynamics, the mechanical instability of the simplest planetary two-particle system (of the hydrogen atom type) lies in the fact that Coulomb attraction, functioning as centripetal force ($mv^2/r = e^2/r^2$), specifies the functional relation between velocity and orbit dimensions; the actual value of the velocity is not fixed and is determined by the initial conditions. Since the initial velocity may be arbitrary (also including values arbitrarily close to zero), then the formation here of a dynamically stable planetary system of fixed size turns out to be impossible.

On the other hand, the length parameter a , which agrees numerically (in order of magnitude) with the dimensions of an atom, is formed naturally from the atomic constants by using Planck's constant ($a = h^2/me^2$). Thereby, purely formally, the mechanical-stability problem is eliminated, since specifying the characteristic length leads to a fixed value of velocity and, consequently, also of energy, which is now according to classical dynamics.⁴⁾

The problem consists of trying to find some theoretical grounds for introducing such a parameter.

Actually, only the Planck relation, which specifies a relation between the oscillator's energy and its frequency, could serve as such a basis at the start of the 1910s.

Bohr went along just such a route. The "definite relation between kinetic energy in an annulus and period of revolution"

($E_{\text{kin}} = K\nu_{\text{rev}}$, where K is the constant of the dimensionality of action), which he postulated in the "Rutherford Memorandum" (see Ref. 63, p. 136), is essentially a transfer of the Planck relation, which expresses a relation between an oscillator's energy and frequency, to the more general case of a system executing periodic motion.

One must emphasize that the idea of needing to generalize Planck's quantization idea to mechanical systems more complicated than the linear harmonic oscillator was inserted fairly intensively into the general scientific consciousness just at the start of the 1910s.

Let us mention only a few such examples (see Ref. 65 and the literature quoted there).

In 1911, W. Nernst indicated the need to allow for the quantization of rotational energy in heat capacity theory.

In 1912, N. Bjerum used the quantization of rotational energy ($J(2\pi\nu_{\text{rot}})^2/2 = nh\nu_{\text{rot}}$) to explain band structure in infrared absorption spectra.

H. Lorentz spoke of quantizing a rotator's energy in general form in discussions on Einstein's report at the Solvay Congress in 1911. At about this same time, the idea of quantizing rotational motion was used to explain the discrete nature of the value of the magnetic moment (the Weiss magneton).

In 1911, A. Haas, in accordance with the Thomson model, equated the kinetic energy of motion of an electron along a circular orbit to a multiple integer of the value of $h\nu$, obtaining here the relation which essentially determines the radius of the first Bohr orbit.

The formation of Bohr's ideas about the "permanent" (ground) state in the model of the Rutherford atom occurred in this "super saturated" atmosphere.

One must emphasize that a similar situation often produces an effort by historians of science to constantly search for a direct or indirect predecessor of Bohr for each key point realized by his research program. Thus, for example, A. Hermann (see Ref. 66, p. 165) attempted to connect Bohr's idea about the lack of a length parameter in the classical planetary system genetically with the similar sounding opinions of Larmor in 1900. Just there he posed the question about "did not the ideas of Haas turn out to be fruitful as the basis of the Bohr theory."

One can hardly consider a similar posing of the question to be justified. As we already noticed, at those periods in the development of science, when fundamental changes mature in it, ideas, conversely speaking, start to "be carried in the air." In similar situations, statements that are similar in meaning can, as a rule, be expressed by several researchers completely independently of each other.

It is very likely that everything happened in just the same way in the situation under discussion, when the formation of the ideas about steady states took place.

For example, the absence of any mutual influence whatsoever between Bohr on the one hand and Haas on the other in postulating the relation between the energy of an atomic electron and its frequency of revolution appears to be entirely without doubt.

It is not even a fact that Bohr in his time unequivocally stated that he did not know about Haas's work. It is more important that both scientists introduced this fundamental relation in completely different research contexts.

Haas considered the motion of the electron along a cir-

cle of fixed radius corresponding to the boundary of the diffuse positive charge in Thomson's model.

Bohr started from Rutherford's planetary model in connection with the problems connected with the action of external fields on atomic electrons, and here, as we already saw, the question of the atom's mechanical stability was the principal problem. The solution of this problem required introducing a suitable length parameter. Bohr's relation $E_{\text{kin}} = K v_{\text{rot}}$ was postulated for just this objective. It is obvious that a similar problem did not generally arise when using Thomson's model, since the parameter required in this model was specified from the start. The difference in the proportionality coefficients between energy and frequency that were used also tells us about the independent approaches by Bohr and Haas: Haas used Planck's constant, and Bohr used a different value.

Thus, Bohr solved the problem of the mechanical stability of the Rutherford atom in the ground state by using the Planck relation between the kinetic energy of the electron and the frequency of its revolution. It is important to emphasize that the stable state concept in the model of the Rutherford atom functioned as a necessary element of that single theoretical concept, according to which one succeeded in constructing a description of a fairly wide range of atomic phenomena which is internally consistent and agrees with experiment. Relevant here were: 1) the results of Rutherford's experiments on the angular scattering of α -particles by atomic nuclei, 2) the experimental data on the energy losses of α -particles in different materials, and 3) the experimental data concerning optical dispersion phenomena in these same materials.

In other words, even at that intermediate stage of the formation of the Bohr model of the atom, when only the first basic element of it, the concept of the stable ("permanent" in Bohr's terminology) state, had crystallized out in it, this model was already entirely meaningful in the sense that it adequately described a fairly extensive and specific range of atomic phenomena. The fact that, in all the problems which were solved here, a moving charge appeared as only reacting to a field but not as its source, was extremely significant. In this respect, Bohr's model differed radically from the one which J. Nicholson⁶⁷ suggested in 1912. At the same time the latter had a number of similar features to it, and it undoubtedly aided the formation of Bohr's idea of a discrete series of states.⁵⁾

As is well known, Nicholson started from Nagaoka's model (see Ref. 69, p. 24), which was based on the idea of an electron annulus rotating with respect to the massive positive nucleus. Nicholson developed this model by introducing a connection between the energy of the annulus and its frequency of revolution in agreement with Planck's idea ($E = nh\nu_{\text{rev}}$). This purely mechanical part of Nicholson's model specifically and directly fitted in with Bohr's ideas. Thus, in a letter to Rutherford, Bohr emphasized: "In his calculations, Nicholson, as I do too, deals with systems with the same structure as your model of the atom; and, in determining the system's dimensions and energy, he, as I do too, seeks the basis of the relation between energy and frequency assumed in Planck's theory of radiation. The state of the system that is considered in my calculations is, however, distinguished from the number of states that agree with this relation as that state in which the systems possess the mini-

mum possible amount of energy" (see Ref. 63, p. 576). In other words, the lowest energy state of the possible set of states in Nicholson's model could be treated as a stable state in Bohr's model.

However, in accordance with the research problem posed by Nicholson, his model represented the atom primarily from the aspect of its relation to radiation since, from the very start, it functioned as a basis for the theory of spectra. Thereby, the charges of the electrons entering the annulus determined the current density in Maxwell's equations, by virtue of which the relation between the radiation frequency and the characteristic frequency for the periodic motion of the radiator actually turned out to be established in the model from the start. Therefore, according to Nicholson's own model, there was no other way out for him than to identify the discrete frequencies of the observed spectral lines with the frequencies of the specially postulated mechanical oscillations of the electrons perpendicular to the plane of the annulus. It is natural that here Nicholson immediately encountered the problem of the stability of the atom, but moreover, not the mechanical but the radiative problem turned out to be difficult and, for a system of the hydrogen atom type, fundamentally insoluble. Actually, attempts to explain the radiationless motion of an electric charge that is considered as the source of a field inevitably required introducing additional, fairly artificial assumptions. In particular, there is the Larmor condition that Nicholson used, according to which an absence of radiation is caused by the vector sum of the accelerations of two electrons equaling zero (see Ref. 66, p. 167). Besides the fact that it serves as a typical *ad hoc* hypothesis, the unsatisfactory nature of such an assumption also lies in the fact that the simplest system with one valence electron is thereby automatically excluded from consideration, i.e., the hydrogen atom, with the explanation of the spectrum of which the first decisive success of Bohr's theory turned out to be associated.

At the same time, Bohr especially emphasized in letters to his brother Harald on December 23, 1912⁶⁾ and to Rutherford on January 31, 1913⁷⁾ that, unlike Nicholson's theoretical scheme, the question of the radiation of an atom was not generally raised in his model; the very features that are common to both models are limited only by agreement with their structural basis (Rutherford's model), and also by postulating the Planck relation between the system's energy and the frequency of its mechanical motion. It is typical that, in the process of getting acquainted with Nicholson's model, Bohr, although he noticed the presence of a series of excited states in it, in no way associated this fact with a possibility of optical transitions between them.

There is every reason to suppose that, at the moment he became acquainted with the Balmer equation, Bohr had already obtained in explicit form the general expression for the energy levels of the hydrogen atom, $E_n = (-2\pi^2 me^4/h^2)(1/n^2)$, since the very presence of the quadratic dependence on the integer in the denominator created the basis for identifying this quantity with the corresponding terms in the expression for the spectral lines

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

The required dependence on n arose in an elementary way if one used Nicholson's condition $E = nh\nu_{\text{rev}}$ in connection

with a single electron which, as we already noticed, did not have meaning in Nicholson's model but looked completely natural in Bohr's approach, which fundamentally was occupied with considering only the simplest systems. Along with the condition for quantizing rotational energy, for this it was sufficient to use the well known expression from classical dynamics which connects the electron energy E with the frequency of its revolution ν_{rev} along an ellipse: $\nu_{\text{rev}} = \sqrt{2E}^{3/2} / 2\pi^2 e^2 \sqrt{m}$. At the same time, a relation of the form $E_n \sim n^{-2}$ found by this means, alone by itself before Bohr became acquainted with the laws governing spectroscopy, still did not give any basis for a physical interpretation. However, his acquaintance with the Balmer equation and the Rydberg-Ritz combination principle enabled Bohr to identify the expression which he had found with spectroscopic terms and to formulate the frequency condition.⁸⁾

Thus, in our opinion, Bohr achieved the formulation of the frequency condition as the result of projecting his preliminary model, which encompassed the purely mechanical aspects of the interaction of charges, including the mechanical stability problem, onto the theoretical scheme of Balmer, Rydberg, and Ritz describing the main spectroscopic regularities of line spectra.

If one adheres to such a point of view, then one must recognize the question of searching for a direct predecessor from whom Bohr could borrow the very idea of the independence of radiation frequency from the mechanical frequency of the motion of the radiating charge as meaningless. In particular, both the hypothesis of Hermann (Ref. 66, p. 172) that Bohr borrowed the frequency condition from Stark's model and also the attempts to look for sources of this condition in Einstein's photoelectric effect theory⁷¹ appear to us to be groundless.

The research procedure, which consists of transferring physical models and the mathematical schemes associated with them that give an adequate description of some limited range of phenomena onto a different, still unexplored subject field, is the usual standard for constructing theoretical knowledge.

It appears to be very probable that just an approach of this kind formed the basis of the final stage of Bohr's investigation, in the process of which the frequency condition also was formulated.

4. CONCLUSION

The history of the development of atomic spectroscopy is subdivided in a natural way into several stages. The stage which preceded the creation of the quantum theory of atomic spectra was the original one; the establishment of the basic laws governing spectroscopy unconditionally concluded it.

Here Rydberg was undoubtedly predominant; he singled out the spectroscopic terms in series equations, established their characteristic analytical structure in the form of a function of a definite form of integer, introduced a universal spectroscopic constant, and gave the original formulation of the combination principle.

It is typical that, in the process of his activity of systematizing spectroscopic data, Rydberg started from a general idea of the presence of a profound connection between the structure of the atom and its spectra, and was continually guided by considerations of universality and the condition of

a minimum number of parameters used in searching for the required analytical relation. Both these criteria were not determined by the requirements of the best numerical agreement with experiment, but functioned as certain normative conditions not of a specific scientific, but of a methodological guide. In this respect, the realization of Rydberg's research program differed fundamentally from the purely empirical approach of his principal opponents. As a whole, the relationships established by Rydberg had that degree of universality which indicated their significantly higher theoretical status in comparison with the scheme of Kayser and Runge. The fundamental nature of the general expressions for the spectroscopic terms found by Rydberg was, as is well known, verified later on by a rigorous quantum mechanical basis, in particular, by the quantum defect method (see for example, Ref. 72, p. 141).

At the same time, there exists in the historical and methodological literature a definite underestimation of the constructive role which the Rydberg's results played in the very process of creating the quantum theory of the atom. However, there appears to be no doubt that the systematizing of the extensive experimental spectroscopic material on the basis of the original theoretical schemes constructed by Rydberg was a necessary preliminary condition for the subsequent successful description of line spectra according to Bohr's original theory. In particular, the spectroscopic term model and the Rydberg-Ritz combination principle played a key role in formulating Bohr's frequency condition.

It is extremely important to pay attention to the fact that Bohr developed a preliminary model according to which he solved the problem of the mechanical stability of the ground state of the atom and obtained an explicit expression for the energy levels of the hydrogen atom right up to his acquaintance with the basic laws governing spectroscopy. Here the internal logic of the process of forming the Bohr theory did not require borrowing the frequency condition from theoretical schemes created earlier (of the type of the Stark and Nicholson models or Einstein's theory of the photoelectric effect).

The entire set of existing historical material very definitely indicates that the final step in the formation of Bohr's original theory, postulating the frequency condition, was taken directly in the process of the mutual matching of his preliminary, purely mechanical model with the spectroscopic scheme of Balmer, Rydberg, and Ritz. Bohr's physical interpretation of the spectroscopic terms and the Rydberg-Ritz combination principle based on his idea of atomic electron energy levels and of radiation transitions between them had decisive significance for the development of atomic spectroscopy.

Special attention is allotted in the modern stage of development of spectroscopy to highly excited electron energy levels in atoms and molecules that are close to the ionization limit. The corresponding quantum states have rightly been named Rydberg states, and one speaks of atoms in similar states as Rydberg atoms.⁷² The basic Rydberg equation $T = N_0 / (m + \mu)^2 = R / (m + \mu)^2$, which one writes in the form $T = R / (n - \Delta)^2$, where n is the principal electron quantum number (which differs from m by only a small integer), and Δ is a quantum defect connected with the Rydberg constant μ , which depends on the skeletal shielding of the nucleus and can be calculated quantum mechanically, is,

to a good approximation, valid for the spectroscopic terms of such atoms (in the particular case of the hydrogen atom, $\Delta = 0$ and $n = m$).

Modern methods of laser spectroscopy are successfully used to experimentally investigate the spontaneous and stimulated radiation of Rydberg atoms.⁷³

Research on transitions between close, very highly excited energy levels of Rydberg atoms (at values of n on the order of several tens or even hundreds) by the methods of radio astronomy by observing recombination radio lines (in the spectral region from millimeters to decameters) is of very great interest.⁷⁴

¹³ Here and below we use certain symbols which differ from those used in Rydberg's original papers. In particular, we denote the wave number by the now generally accepted symbol k instead of Rydberg's n .

²¹ Walter Ritz died in 1909 at the age of 31 years. A posthumous 1911 edition of a collection of his works⁵⁵ combines 28 of his original publications and is a volume containing 540 pages of text.

³³ Let us emphasize that the presence of an electron shell for an atom was generally not allowed for in any way in Rutherford's theoretical analysis. In this sense, Rutherford's model represents not the atom as a structural formation, but more its nucleus as a scattering center (see Ref. 60, p. 11).

⁴² See the general characteristics and an analysis of the methodological features of Bohr's theory in Ref. 64.

⁵³ An analysis of the influence of Nicholson's papers on the development of Bohr's theory is given in Ref. 60. Suitable references to the literature are given there. There is a superb scientific and historical analysis of Nicholson's atomic theory⁶⁸ to which we can refer for details.

⁶² "Even if this is not fitting for a Christmas card, but one of us (Bohr; the author's comment) would like to say that he does not consider Nicholson's theory to be incompatible with his own. Actually, his calculations will be valid for the final, classical state of atoms, whereas Nicholson deals with an atom emitting radiation..." (see Ref. 70, p. 563).

⁷² "Therefore the assumption that the state of the systems that are considered in my calculations must identify with a constant (natural) state of atoms..., appears to me as a reasonable hypothesis. According to this hypothesis, the states of the system that are considered by Nicholson, on the other hand, possess less stability; they are... states in which energy is radiated... However, I must note that the considerations mentioned here do not play a significant role in the investigation conducted in my paper. I absolutely am not studying the question of calculating the frequencies corresponding to lines in the visible spectrum (see Ref. 63, p. 576).

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