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ON THE ONE HUNDREDTH ANNIVERSARY OF THE MENDELEEV PERIODIC TABLE OF THE ELEMENTS

THE MENDELEEV PERIODIC LAW, A TOMIC SPECTRA, AND A TOMIC STRUCTURE

(On the history of the physical interpretation of the periodic table of the elements)

M. A. EL'YASHEVICH

V. I. Lenin Belorussian State University, Minsk

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A MONG the great scientific discoveries there are those whose value is revealed in its entirety only much later, during the subsequent development of science. Among such discoveries is the establishment by D. I. Mendeleev one hundred years ago of the periodic law of the chemical elements, which is inseparably connected with his name.

Mendeleev discovered the basic regularity determined by the structure of atoms and consisting of the periodicity of the properties both of the atoms themselves and of the particles made up of them-molecules. In the first article devoted to the periodic law which he had discovered, "The Relation of the Properties and Atomic Weight of the Elements," which was published in 1869, Mendeleev, in enumerating the results obtained, established the first point: "The elements, when arranged in order of atomic weight, present a distinct periodicity of their properties" ($^{[1]}$, p. 30). And in the concluding chapter of the first addition of his famous book The Principles of Chemistry (1871), Mendeleev formulated the basic postulate of periodicity as follows: "The physical and chemical properties of the elements, which appear in the properties of the simple and complex bodies formed by them, have a periodic dependence on (in mathematical terms, form a periodic function of) the atomic weight" (^[1], p. 384). Arranging all known elements in accordance with the periodicity of their properties as a function of atomic weight in the form of a periodic (or as he first called it, natural) system, Mendeleev assigned a definite place to each element. In the 1871 article "The Periodic Law of the Chemical Elements" he wrote that "On the basis of what is known at present, in one place of the system there is always only one element" (^[1], p. 133) and "for all presently known elements, regardless of how much is known about them, it was possible to find a proper place on the basis of our law" ([1], 136). As we known, the existence of vacant places in the periodic

system permitted Mendeleev to predict the existence of new elements which were not yet known at that time. The discovery of gallium (Mendeleev's eka-aluminum) by Lecoq de Boisbaudran in 1875, of scandium (ekaboron) by Nilson in 1879, and of germanium (eka-silicon) by Winkler in 1886 formed a striking confirmation of the periodic law. The inert gases, discovered at the end of the nineteenth century, also found their place in the periodic system, and Mendeleev with good reason called them "a new brilliant confirmation of the generality of the periodic law" (^[1], p. 492). It is important that in those cases where there were deviations in the behavior with increasing atomic weight, displacement of elements from their places in the periodic system based on their properties (perturbations, as Mendeleev called them), he nevertheless placed the elements in their natural place in the periodic system (argon before potassium, cobalt before nickel, tellurium before iodine).

The periodic law, after its establishment by Mendeleev and its wide acceptance, which was especially promoted by the discovery of the predicted new elements, became the firm foundation for the subsequent development of chemistry and physics. In the course of this development, the periodic law itself was broadened and perfected: all new elements filled vacant places in the periodic system, and the number of chemical and physical properties for which the periodicity was observed increased. The correctness and universality of the periodic law were confirmed more and more strongly; in Mendeleev's words, it was "consolidated." Of especially great value was the physical justification of the periodic law which became possible as the result of the development of physics at the end of the nineteenth century and the beginning of the twentieth century: the discovery of the electron, x-rays, radioactivity, and the quantum properties of light. In this connection it is necessary to emphasize that one

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of the bases on which atomic physics was developed was the periodic law itself. In the words of the pioneer atomic physicist Niels Bohr, it served as a "guiding thread" in the investigations (^[2], p. 84). In particular, the huge amount of material from spectroscopic studies, which played an extremely important role in the unraveling of the regularities of atomic structure, was systematized by means of the periodic law.

The explanation of the causes of the periodicity on the basis of the theory of atomic structure, which was given after Mendeleev's death, was the greatest triumph of his ideas. Mendeleev's conviction that, "As far as we can see, the future does not threaten destruction of the periodic law, but only further development"^[3] was justified.

Mendeleev's statements one hundred years ago on discovery of the periodic law reflect a strong scientific foresight. Mendeleev's words on the complexity of atoms in the first edition of The Principles of Chemistry are well known: "It is easy to assume, but so far not possible to prove and perhaps even completely untrue, and in any case still subject to considerable doubt ..., that atoms of simple materials are really complex structures formed by combination of some still smaller parts (ultimate particles), that what we call indivisible (the atom) is indivisible only by ordinary chemical forces, as molecules are indivisible under ordinary conditions by physical forces; however, in spite of the precariousness and arbitrariness of this assumption, one is automatically inclined toward it on acquaintance with chemistry" (^[1], p. 381). Much less well known but exceedingly remarkable is Mendeleev's estimate of the value of spectroscopic methods of investigation for solution of problems of the nature of atoms and for discovery of the causes of the periodicity.

Attaching great value to study of the physical properties of the elements and their compounds, Mendeleev devoted special attention to spectroscopic methods of investigation. Already in the first edition of The Principles of Chemistry in 1871 he describes in detail (in the second part, in the second chapter devoted to potassium and the other alkali metals) spectroscopic apparatus, presents data on the principal Fraunhofer lines and a table of the most intense spectral lines of hydrogen and a number of metals (citing the work of Angstrom in 1869 on study of the solar spectrum), discusses absorption spectra and their relation with emission spectra, discusses the results of spectroscopic investigations (the Sun, meteorites, flames, electrical discharges), and draws the conclusion: "Spectroscopic research has introduced to science not only ideas as to the composition of remote celestial bodies, but in addition has provided a new method for studying the materials which are at our disposal on the surface of the Earth" ($^{[4a]}$, p. 88). Later, Mendeleev gives examples of discoveries of new elements by the spectroscopic method (in particular, rubidium and cesium). Here it is quite appropriate to note that for the first element discovered in accordance with Mendeelev's prediction-gallium (eka-aluminum), Mendeleev correctly predicted also the means of discoverythe spectroscopic method. In his article "The Natural System of the Elements and its Application to Determination of the Properties of Undiscovered Elements,"

written at the end of 1870, is contained the following prediction: "The properties of this metal in all respects should represent a transition from the properties of aluminum to the properties of indium, and it is very likely that this metal will have a higher volatility than aluminum, and therefore we can hope that it will be discovered by spectroscopic studies, much as the elements following it, indium and thallium, were discovered, although it will naturally be less volatile than these two elements and therefore we cannot expect for it such strong spectroscopic manifestations as those which led to discovery of indium and thallium" (^[1], p. 92).

At the end of the section on spectroscopic studies in the first edition of The Principles of Chemistry Mendeleev wrote: "The circumstances entering into spectroscopic phenomena have not been very well studied as yet, but already the accumulation of data which exists at the present time indicates the importance of this type of research. It acquires still greater significance because the material is effectively divided into its smallest particles and so is not changed chemically. If the nature of matter is to be more fully understood than at present, this will undoubtedly be achieved by study not only of phenomena such as those of its chemistry, in which it undergoes changes, but also, and probably primarily, by means of phenomena such as those of spectroscopy, in which the nature of the material is not changed, and in which the molecules and atoms of the material occur in various relationships" $(^{[4a]}, p. 89)$. In the fourth edition of <u>The Principles of</u> Chemistry the latter sentence was supplemented:"... various relationships occurring as the result of the fundamental qualities of matter'' ($^{[5b]}$, p. 609): with this phrase, Mendeleev emphasized even more strikingly the fundamental value of spectroscopic research, which became completely evident to all several decades later in 1913 on the creation by Niels Bohr of the quantum theory of the atom, which related the spectra and the structure of the atom.

Mendeleev devoted special attention to the search for regularities in spectra. "Not one line of the spectra of well investigated simple materials coincides with the lines of other simple materials," he wrote after a general evaluation of the importance of the study of spectroscopic phenomena (^[42], p. 89) and he then indicated the directions for future research: "The most interesting question in spectroscopic research should be, in my opinion, to discover whether a valid relation exists between the atomic composition and weight of the luminescent material and the wavelength of the rays which characterize it." Then Mendeleev cited the work of Mitscherlich (1864) and Lecoq de Boisbaudran (1869), "who noted the known relation between the change of composition and the change in spectral lines," and drew the conclusion: "However, these and many other aspects of spectroscopic research still require numerous and accurate observations in order to lead to clear conclusions."

Mendeleev carefully followed the literature on spectroscopy and in subsequent editions of <u>The</u> <u>Principles of Chemistry</u> systematically supplemented and revised the section devoted to this field. In the third edition he considerably extended the table of the most intense spectral lines (^[5a], p. 756) and, two years before Lecoq de Boisbaudran discovered gallium by a spectroscopic method, gave a detailed discussion, based on the latter's work, of experimental methods of spectroscopy (he cites Lecoq de Boisbaudran's book published in 1874, Spectres Lumineux). Mendeleev emphasizes that the importance of application of spectra "for discovery of the elements in natural materials" is based, in the first place, on the difference of the spectra of the elements, and in the second place, on the sensitivity of the spectroscopic method (^[5a], p. 761). Summing up his discussion of the problems of the spectra of compounds, Mendeleev stresses that "...each physical compound has its own spectrum" and concludes that "spectral phenomena are determined by the molecules, and not by the atoms; that is, the molecules of the metal sodium, and not sodium atoms, produce those oscillations which are expressed in the spectrum of sodium. Where there is no free sodium metal, its spectrum is also absent" (^[52], p. 763*). Mendeleev repeats this conclusion in all subsequent editions of The Principles of Chemistry. In this edition (and also in the fourth edition^[5b]) he further writes: "The problem of the connection between the spectra of complex materials and their composition is one on which many persons are working at the present time and whose solution can have a great influence on many branches of physics and chemistry." Mendeleev's prediction, as we know, was justified. Later, citing the work of Lockyer, Mendeleev points out that the absorption spectra of metal vapors at low temperatures consist of broad, diffuse bands and are assigned to compounds, and at high temperatures consist of sharply defined lines, and writes: "In proportion to the dissociation resulting from increase in temperature, the spectra of compounds decrease in brightness, and the sharp line spectra of the elements or their atoms, and not of the complex molecules, begin to be more prominent." Thus, Mendeleev clearly represented the difference between the spectra of atoms and the spectra of molecules. Here we are discussing free atoms.

Mendeleev made major additions and some changes in the section on spectroscopy of the fifth edition of The Principles of Chemistry (see^[5C], pp. 406-417). He further extended the table of the most intense spectral lines and added to it a commentary, and included several illustrations of absorption and emission spectra; a portion of the material (as also in the rest of the book) was transferred to footnotes and in this process expanded, in particular, by discussion of the questions of the shift of spectral lines (due to the Doppler effect). The lines of helium are mentioned for the first time, and the possibility is discussed of discovering "a simple substance to which the helium spectrum belongs" ($[{}^{5C}]$, p. 413). In this section he inserts a portrait of Kirchhoff, whom Mendeleev esteemed highly. Kirchhoff had died shortly before (in 1887), and Mendeleev emphasized that "The remarkable advances in

the entire field of spectroscopic research have their origin in Kirchhoff's research in 1859 on the relation between absorption spectra and the spectra of luminescent, heated gases" ($^{[5C]}$, p. 411).

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In the sixth edition he mentions for the first time Balmer's formula for the hydrogen spectrum (^[5d], p. 398), and in the seventh edition he mentions also the work of Rydberg, Kayser and Runge, and others on the regularities in the spectra of complex elements (^[5e], p. 413). In this edition and in the last published in his lifetime, the eighth edition of <u>The Principles of</u> <u>Chemistry</u> (1906), Mendeleev repeats his opinion on the value of spectroscopic research:

"... Spectra make visible a great deal not only in huge, remote worlds such as stars, but also in limitlessly small words such as molecules, and development in this field promises to explain many things relating to atoms and molecules" (^[5e], p. 413, and ^[5f], p. 350). True, his statements became more cautious, which is generally characteristic of the last part of his life. In the last editions of The Principles of Chemistry (beginning with the fifth), he has already omitted the suggestions as to just how we will learn about the nature of matter (see the citation above from the first edition, which was amplified in the fourth edition^[5b]), and says more cautiously: "We can hope that with the passage of time, spectroscopic research will enable us to expand some aspects of the theoretical (philosophical) demands of chemistry, but up to the present time everything which has been done in this regard can be considered only attempts which have not yet led to any firm conclusions'' ([5C], p. 416*).

Mendeleev's statements on the relation between spectroscopy and the periodic law are very interesting. Speaking of the search for regularities in spectra, Mendeleev concludes in the seventh and eighth editions: "In all such comparisons we can see the seed of understanding of the connection between atomic weights, chemical similarities, and the location of the spectral lines of simple materials, but, in my opinion, we cannot yet see the exact laws which govern the relation of these subjects, but only the reflection of the periodic law" ($^{[5e]}$, p. 413). And even earlier, Mendeleev wrote: "I consider it useful to note that 1) the concept of simple materials and elements is in all respects more firmly established than any conclusions obtained by spectroscopes; 2) this comparatively young study of spectra of simple materials is none other than the fruit of the chemical study of simple materials; and 3) among spectral phenomena, except for Kirchhoff's law, there have not yet been any generalizations enabling us to make predictions, whereas the concept of simple materials has already grown to this state. And when, as it develops, the science of spectroscopy reaches the completeness of that of chemistry, then perhaps the current ideas will have to undergo major changes and improvements. At the present time, in the absence of laws and regularities, spectrometry is still in the stage of accumulating facts, and is not an organized body of information'' ([5C], p. 414). This pre-

^{*}Here we are discussing bound sodium atoms occurring in the composition of molecules (which Mendeleev called particles). In later editions Mendeleev clarifies the first sentence: "Each complex material which has not been decomposed into a vapor has its own spectrum" (see for example [^{5b},], p. 608).

^{*}In subsequent editions, at the end of the sentence he says: "... have not yet provided completely firm conclusions" (see, for example, [^{sf}], p. 351).

diction of Mendeleev has also come true. Now spectroscopy has turned into a science with its own firmly established regularities based on quantum theory, which permit deep understanding and prediction of the features of atomic and molecular structure.

Let us discuss briefly Mendeleev's views on the complexity and interconvertability of the elements (for more details see[6]). On this question, Mendeleev showed particular caution in the latter period of his life. This referred primarily to specific conclusions regarding the decomposition of elements or conversion of certain elements to others. Such conclusions were often drawn by investigators with little basis or with absolutely no basis. Thus, Mendeleev in his fifth edition of The Principles of Chemistry (1889) criticized the well known English astrophysicist Lockyer for his suggestion that in the Sun iron is decomposed into two elements, which was made on the basis of the different behavior of the two sets of spectral lines of iron (corresponding, as we now know, to neutral and ionized atoms of iron ([5C], p. 414; see also [4D], p. 545). We now know that the conversion of a neutral atom to an ion is not a decomposition of the element, and Mendeleev was correct in essence. Later, in 1898, in the article "Gold from Silver" Mendeleev criticized Emmons, who allegedly transformed silver into gold, and wrote: "... To me personally, as a participant in the discovery of the law of periodicity of the chemical elements, it would be extremely interesting to be present at the establishment of data proving the conversion of one element to another, because I could then hope that the cause of the periodic relation would be discovered and understood. Therefore, as a philosopher, I look with great interest at each attempt to demonstrate the complexity of the chemical elements. However, as a natural scientist, I see the futility of all attempts..." (^[1], p. 448). Mendeleev followed the study of radioactivity with great interest, although he did not accept the proofs of the transmutability of elements, which existed during his lifetime but which he considered unconvincing. In principle, Mendeleev hoped for the discovery of the causes of the periodicity in the future. In addition to his statements on this question in connection with spectroscopic research, which we have cited above, we can quote his words from the first edition of The Principles of Chemistry (in 1871): "... Questions automatically arise as to just what gives rise to the very weight of the atoms, what is the immediate cause of the dependence of the properties on weight, why does a small change in the weight of atoms produce the well known periodic change in their properties, and a whole series of similar questions, for which even hypothetical solutions, in our opinion, are still beyond the reach of contemporary science. In the future, when the time comes for solution of these problems, we can expect also a theoretical definition of the simplest materials, similar to our present theoretical definition of complex materials..." (^[1], p. 384). Considerably later, in 1898, in an article for the Encyclopedic Dictionary, The Periodic Law of the Chemical Elements, Mendeleev expressed hope that the periodic law "can serve to explain the nature of the chemical elements," and later, in a note to this sentence, wrote: "... The periodic law can and must be used,

even though its cause is not known. We can hope that with time it will be found and will still better promote the development of the subject, since from this indirectly arises our entire knowledge of the elements, to which the periodic law has already made major contributions..." (^[1], p. 258).

The causes of the periodicity were discovered sooner than Mendeleev suggested-in the second decade of the twentieth century, and the explanation itself was found by a specific route different from that contemplated by Mendeleev in one of his last works, written in 1902, An Attempt at a Chemical Understanding of the Universal Ether, ([1] pp. 470-517). However, the general foresight of this great scientist, expressed by him more than one hundred years ago, immediately after the discovery of the periodic law, and based on a thorough understanding of the properties of matter and on a correct estimate of the value of his discovery of the periodicity of these properties, was completely justified. It is very much to the point that Mendeleev proceeded from dynamic concepts of the structure of matter and of the behavior of chemical processes. This position was particularly clearly stated in his lecture given in London in 1889, "An attempt to apply to chemistry one of Newton's principles of natural philosophy." Emphasizing the similarity of atoms, as "individual entities of the invisible world" with the planets, their satellites, and the comets, and of particles (i.e., molecules) with such systems as the solar system or double star systems, Mendeleev wrote: "... Ever since the indestructibility of simple materials was recognized, it has been possible to understand chemical transformations only as displacements and motions, and the production by their means of electric current, light, heat, pressure, and the force of steam clearly convinces us that chemical action is inevitably attended with huge, invisible displacements originating from the motion of atoms in molecules" (^[1], p. 530). And although our current ideas of the motions in the microworld, governed by the laws of quantum mechanics, differ from the ideas of classical Newtonian mechanics by which Mendeleev was guided, the very idea that atoms and molecules are dynamic systems was undoubtedly correct and progressive.

Let us consider now the basic physical ideas which have permitted explanation of the periodic law, and whose development is due primarily to Ernest Rutherford and Niels Bohr. These outstanding scientists, together with Albert Einstein, can be called with complete justification the great physicists of the twentieth century. Although a number of other outstanding physicists and chemists have made major contributions to interpretation of the periodic law, the decisive role in uncovering the causes of the periodicity undoubtedly belongs to Rutherford and, particularly, to Bohr.

In 1911, four years after Mendeleev's death, Rutherford published his famous work^[7] in which, on the basis of experiments on α -particle scattering and the analysis of these results, he arrived at the atomic structure model which has received his name and which has been confirmed by the entire subsequent development of the physics of microscopic phenomena. According to Rutherford the atom consists of a central, positively charged nucleus of small size, in which is concentrated the principal mass of the atom, and negatively charged electrons surrounding it, whose mass is small in comparison with the mass of the nucleus. The charge of the nucleus is equal to +Ne, and the atom contains N electrons with a total charge -Ne (e is the absolute value of the electronic charge). The integer N (which we now designate by Z, in contrast to the initial designation used by Rutherford and Bohr by the letter N) for the hydrogen atom, according to Rutherford, as 1, for helium-2, and for heavy atoms-approximately half of the atomic weight A.

Rutherford's atomic model already contained an approach to explanation of the periodic law. The integer Z, which gives the magnitude of the nuclear charge in units of e, turned out to be the number which determines the location of the element in the periodic system. It quickly received the name atomic or order number. The periodicity of the elements turned out to be due to the properties of the electron system surrounding the nucleus.

The consequences of Rutherford's atomic model were first and most clearly recognized by the year 1912, in Rutherford's Manchester laboratory, and a particular part in this was played by Bohr, who arrived at Manchester in the spring of 1912 to work in this laboratory under the guidance of Rutherford. In his recollections about Rutherford^[8] Bohr writes about this period: "... I very rapidly became completely occupied with the general theoretical ideas which followed from the new atom model, and particularly the possibilities which were opened by this model for a clearcut separation of the physical and chemical properties of matter into those which are directly determined by the nucleus itself and those which essentially depend on the distribution of electrons bound to the nucleus but located at distances extremely large in comparison with nuclear dimensions. While explanation of radioactive decay had to be sought in the features of nuclear structure, it was evident also that ordinary physical and chemical characteristics of the elements reflect the properties of the electron system which surrounds the nucleus. From the very beginning it was clear that, as a result of the large mass of the nucleus and its small spatial extent in comparison with the size of the entire atom, the structure of the electron system should depend almost exclusively on the total electric charge of the nucleus. This reasoning immediately suggested that the entire set of physical and chemical properties of each element may be determined by a single integer; we all know now that this number is the atomic number, which expresses the nuclear charge in the form of an integral multiple of the elementary electric charge" (^[8], p. 217). Later, Bohr noted that he was supported by George Hevesy, "who was distinguished, among the entire Manchester group, by his unusually broad knowledge of chemistry"*, and wrote that when he learned from Hevesy that "the total number of already observed stable and unstable elements exceeds the number of places in Mendeleev's famous

table" (the italics are mine.-M. E.), it then "occurred to me that those indistinguishable chemical materials to whose existence Soddy had recently been devoting his attention and which were later designated by him as isotopes, possess the same nuclear charge and differ only in the mass and the features of the nuclear structure. Hence, it followed directly that in the radioactive decay of an element, quite independently of any changes in its atomic weight, it shifted in Mendeleev's table by two numbers to the left or one number to the right. according to whether the nuclear charge was decreased by α emission or increased by β emission". Thus, Bohr already represented clearly that the atomic number determines the place of the element in the periodic system, understood the nature of isotopes, and knew the essence of the law of radioactive displacement. This law was later formulated at the end of 1912 by Russell, who was working in Rutherford's laboratory, and independently in "completely perfected form" (^[8], p. 218), at the beginning of 1913 by Soddy at Glasgow and Fajans at Karlsruhe. The simultaneous discovery of the law by several scientists independently, as the result of the entire development of research on radioactivity, was quite natural. It is important, however, that the very fundamental relation of this law with the basic features of Rutherford's atom model was understood by Bohr. It was the same with the idea of the order number, which was introduced independently in 1913 by van den Broek in Amsterdam.^[9] "For those who were working at that time in Manchester," writes Darwin^[10] (he is speaking of the period 1911-1912), "the work on scattering by nuclei made the idea of an order number quite convincing; it was completely accepted, although in fact the principle of an atomic number was suggested in the literature only somewhat later" (here Darwin was referring specifically to van den Broek). Rutherford writes directly: "The notion that the nuclear charge may be the order number or atomic number was expressed and used for the first time by Bohr in his theory of spectra. By a strange negligence, Bohr himself assigned this thought to van den Broek, who later developed it, applying it broadly to all elements in general"^[11].

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However, while the ideas that the nuclear charge is the order number, that isotopes correspond to the same order number, and the idea of radioactive displacement law, were a natural and direct consequence of Rutherford's atomic model, and in essence were contained in it in concealed form, it was very much more difficult to explain the properties of the electron system and the periodicity of these properties as a function of the number of electrons Z (which is uniquely determined by the nuclear charge). Here the main difficulty lay in the fact that Rutherford's model contradicted all of the concepts of classical physics, according to which this model should be unstable. "It was evident from the very beginning", writes Bohr, "that if we adopt the Rutherford atom model, the characteristic stability of atomic systems can in no way be reconciled with the classical principles of mechanics and electrodynamics. In fact, according to Newtonian mechanics, no static system of point charges can exist in stable equilibrium, and any motion of the electrons around the nucleus, according to Maxwell's electrodynamics, involves dissi-

^{*}Hevesy later worked in Copenhagen (1920-1926 and 1934-1943) at the Bohr Institute of Theoretical Physics and discovered there in 1923, together with Coster, the element predicted by Bohr with Z = 72, which was named hafnium (after Hafnia, the old Latin name for Copenhagen).

pation of energy by radiation; the energy dissipation in turn leads to a constant decrease in the size of the system; finally this leads to a close approach of the nucleus and the electrons inside a region whose dimensions are considerably smaller than the size of the atom" (^[8], p. 218). It must be emphasized that Rutherford clearly understood the difficulties which arose, but, convinced of the soundness of his atomic model, was not afraid to publish his results.

The way out of the resulting situation was found by Bohr.^[12] This way consisted in use of the quantum concept, first introduced by Planck and developed by Einstein, - in application of the ideas of the discreteness of energy and the discreteness of the processes of emission and absorption of light. Bohr writes: "At the very beginning of my stay in Manchester in the spring of 1912, I became convinced that the electronic structure of Rutherford's atom was controlled by a quantum of action" ([8], p. 219). Bohr stayed in Manchester until the summer of 1912, when he returned to Copenhagen, where he continued his efforts to "clarify the role of the quantum of action in the electron structure of the Rutherford atom" (^[8], p. 220) and regularly corresponded with Rutherford. "After numerous attempts to use the quantum idea in a stricter form," Bohr wrote at that time, "in the early spring of 1913 it occurred to me that the key to solution of the problem of atomic stability, directly applicable to the Rutherford atom, is the amazingly simple laws which determine the optical spectrum of the elements". At that time the regularities observed in atomic spectra by Balmer, Rydberg, Kayser and Runge, and other investigators (the same regularities which Mendeleev wrote about in the last editions of The Principles of Chemistry and for which the "exact laws" responsible were not known; see above, page 8) had been generalized by Ritz in his "Combination Principle"^[13]. According to this principle, the wave numbers $\nu' = 1/\lambda$ (equal to the frequencies ν of the light, divided by the velocity of light c, $\nu' = \nu/c$) where λ is the wavelength for the various spectral lines of a given element, can be represented with exceptional accuracy in the form of the difference

$$\mathbf{v}' = T_h - T_t, \tag{1}$$

where T_k and T_i are any two members of the set of <u>spectral terms</u> T_1 , T_2 , T_3 , ..., characteristic of the given element and which in the simplest cases are functions of whole numbers. "This fundamental combination law," writes Bohr, "quite openly denied the ordinary mechanical interpretation of motion... In regard to the Rutherford atom, we could not even expect a line spectrum for it, since according to classical electrodynamics the frequency of the radiation arising on motion of an electron must change continuously as the electron loses energy. Therefore it was quite natural, as the basis for explanation of the spectrum, to attempt to adopt the combination law directly" (^[8], pp. 220-221).

In accordance with Einstein's idea of the existence of light quanta or photons with energy $h\nu$, where h is Planck's constant, Bohr suggested that emission and absorption of light of a definite frequency $\nu = c\nu'$ is an individual process in which such a quantum is emitted or absorbed, according to the relation

$$hc (T_k - T_i) = hcv' = hv, \qquad (2)$$

Here Bohr interpreted hcT_k and hcT_i as the energies E_k and E_i of the atom in stable states and concluded from the discreteness of the frequencies ν that the energies of these states are also discrete. In this way he arrived at his famous postulate of the existence of stable states of the atom-stationary states-with discrete energy values E_1, E_2, E_3, \ldots ($E_1 < E_2 < E_3 < \ldots$) and of quantum transitions between them involving emission and absorption (in individual processes) of light quanta according to the relation (the frequency condition)

$$E_i - E_k = hv. \tag{3}$$

Bohr's postulates marked the most important step in construction of a theory of atomic systems on a quantum basis—in construction of a systematic theory of microscopic phenomena. They were subsequently universally confirmed by massive experimental data in atomic and nuclear physics and turned out to be applicable not only for atoms but also for the molecules formed from them, on the one hand, and for nuclei, on the other hand. These postulates received their justification in quantum mechanics and quantum electrodynamics. At the same time, application of Bohr's postulates to the hydrogen atom and to more complex atoms has permitted, in combination with the use of models, an approach to the question of the distribution of electrons in atoms and on this basis an explanation of the periodicity of the properties of the elements and, thus, a physical interpretation of the periodic law.

Bohr first of all considered the hydrogen atom, as the simplest system, consisting of a nuclear with charge +e and one electron with charge -e, which gives hydrogen "an exclusive position among the elements" (^[2], p. 18). In this case the values of the terms are given with very high accuracy by the formula $T = R/n^2$, where n is an integer (n = 1, 2, 3, ...), and R is the Rydberg constant, and it is immediately found that the energies of the stationary states are

$$E_n = -hcT_n = -hcR/n^2. \tag{4}$$

The values of hcR/n^2 give the binding energy of the electron in the atom. As Bohr writes, "This interpretation leads to a sequence of decreasing values of electron binding energy in the hydrogen atom, indicating a stepwise process by which an electron located initially at a considerable distance from the nucleus approaches by a series of transitions, associated with radiation, to stationary states with ever increasing binding energy characterized by smaller and smaller values of n; finally it reaches the ground state, which is characterized by the value $n = 1^{"}$ (^[8], p. 221).

Later, Bohr used visual representations of Rutherford's hydrogen atom model and discussed the motion of the electron around the nucleus along Keppler-type elliptical orbits under the Coulomb attractive force, i.e., he discussed this motion according to the laws of classical (Newtonian) mechanics.

Bohr showed that the correct values (4) of the energies of the stationary states can be obtained if we assume that in the simplest case of motion in circular orbits the angular momentum of the electron around the nucleus M = mva (where m is the electron mass and v is its velocity in a circular orbit of radius a) is equal to an integral multiple of the quantity $h/2\pi^*$:

$$M = nh/2\pi$$
 (n = 1, 2, 3, ...). (5)

These quantization conditions lead to Eq. (4) for the energies of the stationary states, and the Rydberg constant turns out to be equal to

$$R = 2\pi^2 m e^4/ch^3 \text{ cm} \tag{6}$$

As Bohr then showed, Eq. (5) can be obtained from the requirement that, in the limiting case of large values of quantum numbers n, the frequency of the transitions between neighboring stationary states E_n and E_{n+1} coincide with the frequency of rotation of the electron in the n-th circular orbit. This requirement represented the initial form of the correspondence principle, according to which the results of the quantum theory must in the limiting case go over to the results of the classical theory, and which was developed by Bohr in his subsequent work (see, for example, ref. 2, p. 34 and following; the second article, 1920).

The value of the Rydberg constant calculated theoretically by Bohr from Eq. (6), on the basis of the known values of the constants m, e, and h, turned out to agree (within the accuracy of these constants) with the experimental value obtained from spectral data. This was a tremendous success of the Bohr theory, about which Darwin justifiably wrote: "In science there are few such cases, in which a theory is created with which we can obtain a definite number—the Rydberg constant in our case—only from known quantities, and not drawing on any additional constant" (^[10], p. 17).

It is extremely important that Bohr succeeded in explaining not only the hydrogen spectrum whose entire set of spectral series is determined by the generalized Balmer formula

$$v' = R \left(n_k^{-2} - n_i^{-2} \right), \tag{7}$$

where n_k and n_i are quantum numbers of stationary states between which transitions occur, but also the appearance of spectral series with half-integer quantum numbers. He showed convincingly that these series belong not to the hydrogen atom as then assumed, but to the ionized helium atom, which consists of a nucleus with charge +2e (i.e., an α particle) and one electron with charge -e, i.e., the ion He⁺. In the general case of a hydrogen-like ion consisting a nucleus with charge +Ze and one electron with charge -e, Eq. (4) is replaced by the formula

$$E_n = -hcRZ^2/n^2 = -hcR/(nZ^{-1})^2 = -hcR/n^{*2},$$
(8)

which for the He^{\dagger} ion leads to effective half-integer quantum numbers $n^* \approx n/2^{\dagger}$.

It must be particularly emphasized that, in applying

model representations of the electron motion in an atom based on the laws of classical mechanics and in applying to this motion the additional conditions of quantization in the form of Eq. (5), Bohr clearly understood the limitation of the classical representations and the necessity of searching for new, still unknown principles for construction of a systematic theory. "If we wish to establish in general a visual representation of stationary states," he said already in 1913, "we have no other means, at least at present, (italics mine-M. E.) other than ordinary mechanics" ($^{[2]}$, p. 22). And at the end of this same report, Bohr said: "Before concluding I wish only to express the hope that I have made it sufficiently clear for you to understand how strongly this reasoning is in conflict with the harmonic circular model which is appropriately called classical electrodynamics. On the other hand, I have tried to leave with you the impression that, specifically by emphasizing this contradiction, perhaps it will be possible with time to introduce some binding together into new concepts" (^[2], p. 29).

The successes of Bohr's quantum theory in application to the hydrogen atom and ionized helium opened the way for construction of a theory of the structure of more complex systems-atoms and ions with many electrons. In addition, they had considerable influence in initiation of important experimental research, among which a special place is occupied by the famous experiments of Rutherford's colleague Henry Moseley on the x-ray emission spectra of the elements-the socalled characteristic radiation, which he carried out in the second half of 1913 and the first half of 1914 (as nearly everyone knows, in the second half of 1914, after the start of the first World War, Moseley was mobilized, and in August of 1915 he was killed at the age of twenty-seven). Rutherford characterized in the following way the work on the atomic structure problem in his laboratory in the period 1912-1913, before the starting of these experiments: "There existed a firm conviction in the general validity of the nuclear theory of the atom, and it was generally accepted that the properties of an atom are determined by an integer which represents the number of units of positive charge of the nucleus. It seemed also likely that the nuclear charge may correspond to the order number of the element. It was noted that the number and motion of the external electrons depended on the nuclear charge. and Bohr made the first attempt to find an explanation of the spectra of the lighter atoms on the basis of quantum theory and thus to shed light on the distribution and motion of the external electrons. Bohr also indicated that there should be a sharp distinction between the properties which depend on the nucleus and the properties associated with the externally located electrons. Thus, for example it became quite clear that the principal radioactive properties should be assigned to the nucleus itself, and that the spectra of ordinary light and x rays are due to perturbations of the elec-tron motion" (^[11], p. 844). In June of 1913, Bohr visited Manchester, and he recalls this visit as follows "... I exchanged opinions with Darwin and Moseley on the question of whether the correct sequence of the elements should be based on their atomic number, and heard then for the first time from Moseley he intended

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^{*}Before Bohr, quantization of angular momentum was discussed by J. Nicholson [¹⁴], who, however, assumed that the frequency of the emitted light is equal to the frequency of the mechanical motion.

[†] If we take into account the motion of the nucleus, the Rydberg constant in Eq. (8) turns out to be somewhat different from that in Eq. (4), as is also found experimentally, which was particularly effective and convincing confirmation of the correctness of Bohr's theory.

to investigate this question by systematic measurements of the high-frequency spectra (i.e., x-ray spectra.-M. E.) of the elements by the method of Von Laue and Bragg" (^[8], p. 226). Eve also writes about this in his biography of Rutherford. Eve recalls that Moseley told him about his new, highly promising experiment and, in reply to a question about the subject of this experiment, said that he "proposed to bombard successive elements in the periodic system by cathode rays so as to excite their natural x rays, which will then be reflected from crystals in order to determine their frequencies" (^[15], p. 234).

As a result of his experiments, Moseley established the simple law^[16] (which received his name) that for successive elements the frequencies ν of corresponding x-ray spectral lines increase in proportion to $(Z - b)^2$, where Z is the order number of the element, and b is a constant for lines of a given type; in other words, $\sqrt{\nu}$ is proportional to Z - b and the dependence of $\sqrt{\nu}$ on Z - b is expressed graphically by straight lines (so-called Moseley diagrams). On the basis of Moseley's law, it was possible to assign an order number uniquely to any element. As Bohr emphasizes, "This law immediately gave not only convincing proof of Rutherford's atomic model, but also revealed the tremendous intuition of Mendeleev, who in certain places in his table departed from the correct sequence of increasing atomic weights" ([8], p. 226). Rutherford evaluated Moseley's law as follows: "... For all elements an extremely simple relation has been found, according to which their properties are determined by an integer which indicates the order of the element in the periodic system and at the same time the number of units of positive charge of the nucleus. This discovery of Moseley constitutes an epoch in the history of our knowledge of the elements; it fixes once and for all the correct order of the elements (actually, the order established by Mendeleev!-M. E.) and shows that only 92 elements can exist, beginning with hydrogen (1) and going up to the heaviest element-uranium (92)'' (^[11], p. 846).

In addition to revealing a unique and monotonic relation between the order, number of an element and its x-ray spectrum, Moseley's research had great value in study of the electronic structure of the atom. "In regard to the problem of the electronic configuration of an atom. Moseley's work served as the beginning of major progress in this field. Of course, the dominance in the interior parts of the atom of the attractive force, due to the nucleus and acting on the individual electrons, over their mutual repulsion, gives a basis for understanding the striking similarity between Moseley's spectrum and the expected spectrum of a system consisting of an individual electron bound with a "bare" nucleus. A more detailed comparison gives new information relating to the shell structure of the electronic configuration of atoms'' (^[8], p. 227). Note that Moseley's research was already based on Bohr's theory, of which he was an ardent advocate. At that time most scientists did not yet believe it to be correct, and Moseley in the very beginning of 1914 wrote to Rutherford at Manchester from Oxford (where he had recently arrived and where he was continuing his research): "Here, no one is interested in atomic structure. I would like to do something to strike down those who hold the very widespread view that Bohr's work is only the juggling of numbers until agreement is obtained. I myself am convinced that what I call the 'h'' hypothesis is correct, i.e., that it is possible to build atoms by means of e, m, and h, without anything else'' (^[15], p. 236) (the 'h'' hypothesis was Moseley's name for the quantum theory).

The explanation of the origin of x-ray emission spectra (and also of x-ray absorption spectra, which are continuous and have a short-wavelength limit—the absorption edge) was given in 1914 by Walter Kossel^[17], on the basis of the idea that the atom has electron shells which form successive layers around the nucleus, beginning with the innermost layer.

The idea that the electrons in an atom are separated into groups and that this produces the periodicity in the properties of the elements had already been introduced in 1904 by Joseph John Thompson on the basis of his atom model, which consisted of a positive charge distributed over a spherical volume, inside which were located negatively charged electrons. Thompson^[18] discussed various electron configurations consisting of concentric rings, each of which contained a definite number of electrons, and showed that there are stable configurations with an increasing number of electrons in the successive rings. This allowed him to explain the behavior of the positive and negative valences for successive elements by the release and attachment of the appropriate number of electrons by the outside ring. Bohr later wrote (in 1922): "From the time of J. J. Thompson's famous attempt to discuss the periodic system on the basis of a study of the stability of various supposed electron configurations, this idea of the separation of electrons in an atom into groups has been made the starting point of all succeeding, more detailed models. Thompson's assumption about the distribution of positive charge in the atom turned out to be incompatible with the experimental results obtained later in the study of radioactive materials. Nevertheless, because of the many ideas contained in it, his work had a great influence on the later development of atomic theory" (^[2], p. 86); even in his first work on the quantum theory of the atom. Bohr made definite assumptions regarding the distribution of electrons in the atom around the nucleus (he considered, like Thompson, the distribution of electrons in rings, suggesting that in their circular orbits they form regular plane polygons), but there were still not enough data for detailed explanation of the periodic properties of the elements. These data were obtained on the basis of study of the interpretation of atomic spectra, both x-ray and (in particular) optical spectra. This permitted Bohr in 1921-1922 to give a physical interpretation of the periodic law on the basis of the idea of sequential binding of the electrons with the nucleus, with formation of electron shells occupied by a definite number of electrons ([2], pp. 76-147).

Let us discuss in more detail the very important results relating to the structure and properties of atoms, which were obtained in the period from 1914 to 1921 and which formed the basis for Bohr's work on interpretation of the periodic system. This was a period of extremely rapid development of research on



FIG. 1. Diagram of quantum transitions according to Kossel.

In an article written in 1916, "On the Formation of Molecules as a Question of Atomic Structure," Kossel proceeded, on the one hand, from the general concepts of the separation of electrons in an atom into internal electrons, more firmly bound in filled shells and not taking part in chemical interactions, and external electrons less firmly bound and accounting for valence and optical spectra, and on the other hand, from the periodic law, the location of the element in the periodic

Higher oxides. Hydrogen compounds.	0	T R2O (RH)	II RO (RH ₂)	III R ₂ O ₃ (RH ₃)	IV RO2 RH4	V R2O5 RH3	VI RO3 RH2	VII R207 RH	VIII RO4
		H		1					
	He 2	Li 3	Be	B ₅	C 6	N 7	0,8	F ₉	
	Ne 10	Na 11	Mg 12	A] 13	Si 14	P 15	S 16	Cl 17	1
	Ar 18	К 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe, Co, Ni 26 27 28
		Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	
	Kr 36	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	43	Ru. Rh. Pd 44 45 46
		Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	
	X 54	Cs 55	Ba 56	Earths from 57 to 71	72	Та 73	W 74	75	Os, Ir, Pt 76 77 78
		Au 79	Hg 80		Pb 82	Bi 83	84	85	
	Eman- ation 86	87	Ra 88		Th 90	91	U 92		

FIG. 2. The periodic system according to Mendeleev, as given by Kossel [¹⁹].

atomic structure and further development of Bohr's quantum theory, based on the underlying studies of Rutherford, Bohr, and Moseley, which were a powerful stimulus for this development. First of all let us consider the work of Kossel, already mentioned above, on x-ray spectra and on the theory of the heteropolar chemical bond^[19].

According to Kossel, in order for x-ray emission spectra to occur, it is necessary that an electron be removed from one of the filled internal rings, beyond the limits of the atom (or to its periphery in a free orbit). An electron from a ring farther out can fall into the vacated place, and this leads to emission of a quantum of x-ray radiation according to Eq. (3). Removal of an electron to outside the atom, i.e., ionization of the atom, can be accomplished both by electron impact and by absorption of an x-ray quantum with energy $h\nu \ge W$, where W is the ionization energy of the atom, which explains the existence of absorption edges. If we designate the successive electron rings by K. L. M, ..., we obtain the scheme of quantum transitions illustrated in Fig. 1 (^[20], p. 157). An important consequence of this scheme is the combination relations for x-ray lines

$$v_{K_{B}} - v_{K_{a}} = v_{L_{a}}, v_{K_{y}} - v_{K_{B}} = v_{L_{y}} - v_{L_{a}} = v_{M_{a}}, \dots,$$
 (9)

which were predicted by Kossel and confirmed experimentally (the small but systematic deviations which were observed here were explained later as a finer structure of the energy levels; see below).

system being determined by the order number, which is equal to the number of units of positive charge and to the total number of electrons in the atom. In accordance with the behavior of the positive and negative maximum valences for successive elements of the short periods, Kossel discusses the filling of the outer electron shell by eight electrons, beginning with one electron in the atoms of the alkali metals. Limiting himself to inorganic compounds, he explains heteropolar chemical bonds as the transfer of electrons from electropositive atoms to electronegative atoms with formation of particularly stable electron configurations similar to the configurations of the inert gas atoms. It should be particularly noted that Kossel presents Mendeleev's periodic system (Fig. 2) in a short form with indication of the forms of compounds with oxygen and hydrogen "in order to obtain an initial verification of these assumptions and a unification with experimental results, $(^{[19]}, p. 246)$ and that in this table for the first time the order numbers of all elements known at that time from hydrogen to uranium are correctly indicated*. For the first twenty-five elements, Kossel also gives a scheme for the filling of shells (Fig. 3); in the parentheses are the numbers of electrons in the rings; for the outer ring these numbers are underlined and give the positive valence. This scheme corresponds to characterization of the electron groups by a single

^{*}Van den Broek [⁹] further suggested that Z = A/2 and in his table gave the value of Z correctly only for the first nine elements.



quantum number n which takes values 1, 2, 3, and 4 for the elements discussed. We will speak of these electron groups as "electron layers,"

Questions of chemical binding on the basis of atomic structure models were discussed independently by Gilbert Lewis in his article "The Atom and Molecule," also published in 1916^[21]. Lewis, in contrast to Kossel who proceeded from Rutherford's atomic model and the general postulates of Bohr's theory, utilized the static atom model consisting of a positively charged core (kernel) and an external shell consisting of from one to eight electrons and responsible for the chemical properties of the element. For the external shell be proposed a spatial distribution of the electrons at the vertices of a cube, and the greatest stability for the filled shell containing eight electrons and corresponding to the inert gas atoms. At the same time it was suggested that atoms in general have a tendency to contain an even number of electrons in the outer shell. This postulate of higher stability of configurations with an even number of electrons was applied by Lewis also to molecules. He distinguished even and odd atoms and molecules and emphasized that for an overwhelming number of chemical compounds there is an even number of electrons in the outer shells of the combining atoms, and the few compounds with an odd number of electrons are highly reactive and tend to form compounds with an even number of electrons. As we know, these regularities found explanation only later, on the basis of the Pauli principle. Lewis advanced the extremely important idea that the heteropolar bond and homopolar bond represent limiting cases, between which there is a continuous transition. Lewis discussed the purely homopolar bond as formed by pairs of electrons located between the corresponding atoms-one pair in the case of a simple bond, two pairs in the case of a double bond, and three pairs in the case of a triple bond. For these cases he introduced the designations of the bond by two, four, or six dots (for example, H : H for the hydrogen molecule, :O::O: for the oxygen molecule, and H:C:::C:H for the acetylene molecule; the dots not located between the atom symbols indicate electrons not taking part in the bond). It is interesting to note that Lewis, although he wrote about Bohr's theory as "the most interesting and stimulating" of the planetary theories of atomic structure, did not agree with the concept of stationary states and though that the radiation of the hydrogen atom can be explained by assuming that the electron can exist in the atom in different equilibrium positions with different characteristic frequencies of oscillation ($^{[21]}$, p. 773).

Lewis's ideas obtained further development in the work of Irving Langmuir in 1919, "The Location of Electrons in Atoms and Molecules"^[22]. Langmuir also FIG. 3. Kossel's scheme of filling of the electron rings for the first 25 elements.

proceeded from the static model of the atom. He suggested that the electrons form concentric spherical shells of identical thickness, consisting of cells, each of which is filled by two electrons (except for the first shell, which consists only of two cells, filled by one electron each). Following Rydberg^[23], Langmuir chose filling numbers of the shells determined by the series

$$Z = 2 (1 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2 + 4^2 + \dots),$$
 (10)

which gives 2, 8, 8, 18, 18, 32, ..., in agreement with the number of elements in the periods of the Mendeleev system (these shells he designated as I, IIa, IIb, IIIa, IVa,..., assuming that the radii of shells I, II, III, and IV are in the ratio 1:2:3:4). Like Lewis, Langmuir considered especially stable the spatial configurations consisting of eight electrons located at the vertices of a cube (or a deformed cube). Langmuir succeeded in explaining the chemical properties not only of the elements forming the short periods, to which Kossel and Lewis had for the most part limited themselves, but also of the remaining elements. However, even in Langmuir's work the separation of the electrons into groups corresponded to filling of layers with values of the quantum number n from 1 to 6 and there were no further subdivision of these layers. It is necessary to emphasize that Langmuir regarded Bohr's theory differently from Lewis, and wrote that "probably it will be possible to reconcile the two theories...; Bohr's stationary states are extremely similar to the cells postulated in the present theory. The series of numbers 1, 1/4, 1/9, 1/25 appear identically to substantial degree in the two theories' ($^{[22]}$, p. 931). Of course, it is necessary to take into account that this was written not in 1916, but 1919, and after three years the successes of Bohr's theory had led to its wide acceptance.

An important step in the later development of the science of atomic structure on the basis of Bohr's theory was the introduction of a more detailed characterization of the electrons by quantum numbers. Particularly important was the classification of electron states according to their orbital angular momentum. This characteristic later became the basic parameter in the quantum-mechanical theory of the chemical bond.

According to Bohr's theory, for circular orbits in the hydrogen atom and in hydrogen-like ions (He^{*}, Li^{2*}, Be^{3*}, and so forth) the quantum number n, which was later named by Bohr the principal quantum number, determines both the energy (according to formula (8)) and the angular momentum (according to formula (5)). In addition to circular orbits in motion of an electron around a nucleus under the action of the Coulomb force, the laws of classical mechanics permit also elliptical orbits, which Bohr had already taken into account in his first work in 1913 (see, for example ref. 2, p. 19). However, the quantum theory of elliptical orbits was given somewhat later, in 1915–1916, by Arnold Sommerfeld^[24], proceeding from a general formulation of the quantization conditions. For a mechanical system with N degrees of freedom, described by coordinates q_i and momenta p_i associated with them, these conditions have the form

$$\int p_i \, dq_i = n_i h \qquad (i = 1, \, 2, \, 3, \, \dots, \, N), \tag{11}$$

where n_i is the integral quantum number for the i-th degree of freedom (the integration is carried out over the entire region of variation of the variable q_i). Motion of the electron in an elliptical orbit (with the nucleus at the focus of the ellipse) corresponds to two degrees of freedom (plane motion), and can be characterized by two coordinates—the distance r of the electron from the nucleus and the angle of rotation φ of the radius-vector of the electron (azimuth). According to Sommerfeld, the corresponding quantum conditions have the form

$$\int p_r \, dr = n_r h \qquad (n_r = 0, \, 1, \, 2, \, 3, \, \ldots) \tag{12}$$

and

$$p_{\varphi} d\varphi = kh$$
 $(k = 1, 2, 3, ...),$ (13)

where n_r is the <u>radial</u> quantum number, and k is the <u>azimuthal</u> quantum number. The momentum p_{φ} associated with the angle φ is constant and represents the orbital angular momentum $(p_{\varphi} = M)$. Therefore condition (13) reduces to the condition

$$M = kh/2\pi$$
 (k = 1, 2, 3, ...), (14)

which is identical with Bohr's condition (5) for circular orbits (k = n) (Sommerfeld initially even designated the azimuthal quantum number by n and only later was the designation n reserved solely for the principal quantum number). As before, the energy of the atom is determined by Eq. (4) (or (8) in the case of hydrogenlike ions) where the principal quantum number

$$n = k + n_r \tag{15}$$

determines the value a_n of the major semiaxis of the ellipse (which increases in proportion to n^2), and the azimuthal quantum number k, which takes on (for a given value of n) n values $k = 1, 2, 3, \ldots, n$, determines the value bn of the minor semiaxes (and consequently the eccentricity of the ellipse); here b_n/a_n = k/n. It is very important that for a given value of n the angular momentum M takes on n values corresponding to n different states of the electron with the same energy E_n . In contemporary terminology a degeneracy of the energy levels occurs. The term "degeneracy" in application to quantized systems was introduced by Schwarzschild^[25] in 1916 and later used by Sommerfeld ($^{[20]}$, p. 500). As is well known, degeneracy of states of the hydrogen atom and hydrogenlike ions in orbital angular momentum, which is characteristic of an electron moving in the Coulomb field of a nucleus, is obtained also according to quantum mechanics if we do not take into account the dependence of mass on velocity according to the theory of relativity, i.e., if we do not take into account relativistic effects (among which are included the electron spin; the latter will be discussed below), the azimuthal quantum number k being replaced by an azimuthal quantum number

$$l=k-1$$
 $(l=0, 1, 2, ..., n-1),$ (15')

which determines the orbital angular momentum according to the formula

$$M^2 = l (l+1) h^2/4\pi^2$$
, i.e. $M = \sqrt{l(l+1)} h/2\pi$, (16)

which for the case $l \gg 1$ is identical with Eq. (14).

In addition to quantization of the two dimensional motion of the electron in a plane, Sommerfeld discussed also the three-dimensional case and introduced space quantization. Here the two quantization conditions (12) and (13) are supplemented by a third condition,

$$\int p_{\psi} d\psi = mh, \qquad (17)$$

for the angle ψ (Fig. 4) in the "equatorial" plane perpendicular to some selected direction z forming an angle α with a perpendicular to the plane of the electron orbit. The angle α determines the inclination of the orbit to the equatorial plane. The condition (17) reduces to the quantization condition

$$M_z = mh/2\pi \tag{18}$$

for the projection M_Z of the orbital angular momentum of the electron M on the selected direction z ($p\psi$ = M_Z), where m is the "equatorial" quantum number (which later received the name magnetic quantum number, since it characterizes the energy level in an external magnetic field directed along the z axis), which takes on 2k + 1 values from k to -k (m = k, k - 1 k - 1,..., -k) and which determines the orbit inclination according to the formula

$$\cos \alpha = M_z/M = p_{\psi}/p_{\varphi} = m/k.$$
(19)

Sommerfeld immediately pointed out the possible physical applications of space quantization for discussion of the splitting of spectral lines in an external field, and somewhat later wrote: "This space quantization is undoubtedly among the striking results of the quantum theory. In the simplicity of its derivation and results it looks almost like some kind of witchcraft" (^[20], p. 415). In the absence of an external field the energy of the atom does not depend on m and space quantization leads to appearance for given n and k of an additional degeneracy of multiplicity g = 2k + 1, which can be removed by an external magnetic field. However, in reality the multiplicity of the degeneracy turns

FIG. 4. Quantization condition for the angle ψ from Sommerfeld's article ([^{24a}], p. 29).



out to be 2(2k - 1) = 2(2l + 1), where the factor 2 appears on account of the spin, for which two orientations are possible, and 2l + 1 instead of 2k + 1 corresponds to replacement of k by l = k - 1. Before the introduction of l it was necessary to assume that not all orientations of the angular momentum M were possible $\binom{[20]}{2}$, p. 415).

A very important development was the discussion by Sommerfeld, on the basis of the theory of relativity, of the fine structure of the spectral lines of the hydrogen atom and hydrogen-like ions. Following Bohr, who proposed to explain the fine structure of the hydrogen lines by a relativistic effect^[26] (of order $(v/c)^2$, where v is the velocity of the electron in the orbit), Sommerfeld calculated the relativistic correction to the energies (8) of the stationary states of the hydrogen atom and hydrogen-like ions. This correction turned out to depend both on n and on k, i.e., to be different for a given value of n for ellipsoids of different eccentricity, which leads to a splitting of the energy levels into n components and to a corresponding splitting of the spectral lines-into their fine structure. The value of the correction is approximately equal to

$$\Delta E_{nk} = -\frac{hcR\alpha^2 Z^4}{n^3} \left(\frac{1}{k} - \frac{3}{4n}\right), \qquad (20)$$

where the fine structure constant α is determined by the formula

$$\alpha = 2\pi e^2 / hc = 1/137 \tag{21}$$

(this constant is equal to the ratio of the electron velocity in the first circular orbit in the hydrogen atom, n = 1, to the velocity of light, and its square is $\alpha^2 \approx 1/20\ 000$).

Sommerfeld successfully applied the formulas which he had obtained to explanation of the fine structure not only of the lines of the hydrogen atom and the He⁺ ion, but also to x-ray spectra, in which a doublet structure had been observed in the K and L lines with a splitting which increased rapidly with increasing order number. However, the structure of the x-ray terms, in particular the L term, turned out to be more complicated than followed from the assumption that for a given n a term is split into n components corresponding to the values k = 1, 2, ..., n. As was later established, the number of components of L, M, and N terms (n = 2, 3, 4) is 3, 5, 7, i.e., not n, but 2n - 1. This fact, like many features of the optical spectra of nonhydrogenlike atoms, received their explanation only later.

Sommerfeld's work was at once highly regarded by Bohr, who wrote Sommerfeld (who had sent him his articles): "Thank you for your excellent and extraordinarily interesting articles. I have read them carefully and wish to say that never before have I experienced such great satisfaction. It is hardly necessary to say that, not only I, but all the others here have a special interest in your brilliant and extremely important results"^[27]. A development very important for Bohr's subsequent physical interpretation of the periodic law was Sommerfeld's application of the classification of electron states by means of the quantum numbers n and k, which determine the values of energy and angular momentum, to the nonhydrogenlike atoms and their spectra. For these atoms in the simpler cases, first of all for atoms of the alkali and alkaline

earth metals, empirically found regularities in the spectra (described by Mendeleev in the later editions of The Principles of Chemistry; see above, p. 3) permitted construction of a term diagram (i.e., energy levels), combinations of which according to Eq. (1) give the wave numbers of the spectral lines of the various spectral series. Instead of one sequence (4) of terms for the hydrogen atom, a number of sequences are obtained, which were designated by the letters s, p, d, f (from the first letters of the English names of the spectral lines obtained on combination of a constant term with terms of a definite sequence: the sharp, principal, diffuse, and fundamental series). The values of terms of such sequences are expressed by empirical formulas which differ from the formula for the hydrogen terms R/n^2 by a different denominator. The simplest of these formulas-Rydberg's formula-has the form

$$T_n = R/(n+a)^2$$
, (22)

where a is a constant which is different for different sequences. For large values of n, formula (22) is identical with formula (4).

For nonhydrogenlike atoms, Sommerfeld in 1916, in developing his earlier work, discussed^[28] the motion of an electron in a spherically symmetric but non-Coulomb field. He proceeded from the fact that the energy of the outer electron in a many-electron atom must be a function of the two quantum numbers k and n_r , and for large values of k (corresponding to orbits of large area: for a given n_r the major semiaxis of the ellipse increases with increasing k, and the shape of the ellipse approaches that of a circle, for which $n_r = 0$) the value of the term $T_{k,n_r} = T_n$ must approach its value for the hydrogen atom:

$$\lim_{k \to \infty} T_{k, n_r} = \lim_{k \to \infty} \left[\frac{R}{(k+n_r+a)^2} \right] = \frac{R}{(k+n_r)^2} = \frac{R}{n^2}.$$
 (23)

Adding to the potential energy of the electron in a Coulomb field, $-e^2/r$, the term c_1e^2/r^3 , where c_1 is a constant, Sommerfeld obtained the Rydberg formula (22) with a constant $a = a_k$ which depends on k but which does not depend on n_r , and consequently which gives for a given k a sequence of terms with n = k $+ n_r = k, k + 1, k + 2, k + 3, ...,$ converging to the ionization limit. In the next approximation, Sommerfeld obtained also the more accurate empirical formula of Ritz.

Comparison of the theoretical results obtained with the empirical term diagrams permitted unique assignment to the s, p, d, and f terms the value l = 0, 1, 2, 3. Thus, it turned out that the term diagrams give sets of electron energy states characterized by different values of the quantum numbers n and k. Apparently these states correspond to different elliptical orbits. An orbit determined by a given pair of values of the principal quantum number n and azimuthal quantum number k was designated by Bohr by the symbol n_k (only later were this designation and the similar designation n_l displaced by the now generally accepted designations ns, np, nd, nf, ng,... of electron states characterized by the values n, l = 0, 1, 2, 3, 4, ...).

The quantum theory of atomic spectra was the subject of a major article by Bohr, "On the Quantum Theory of Line Spectra" and a review article (1920)

"On the Serial Spectra of the Elements" (^[2], pp. 30– 75). In these articles he developed the correspondence principle and applied it to the spectra of atoms with many electrons. Discussion of the spectra of these atoms and classification of electron states by means of the two quantum numbers n and k led him in real earnest to solution of the problem of a physical interpretation of the periodic law. He succeeded in solving this fundamental problem in 1921. On October 18 of that year he announced his theory of the periodic system in a remarkable paper "Atomic Structure in Relation to the Physical and Chemical Properties of the Elements"^[2] (p. 76), given before the Physical Society in Copenhagen. Let us discuss the content of this paper.

Bohr proceeds from Rutherford's nuclear model of the atom and at once emphasizes that the way out of the difficulties associated with the instability of this model according to the concepts of classical mechanics and electrodynamics is to be found in the quantum theory, which decisively breaks with the previous views and "introduces for the first time, in formulation of the general laws of nature, assumptions that there are discontinuities". Two basic postulates are then clearly formulated-the existence of stationary states and the frequency condition, "which exactly take into account the difficulties mentioned above." Bohr first discusses the "simplest imaginable atom, which consists of a nucleus and one electron." Bohr points out that "the hydrogen spectrum shows us the formation of the atom of hydrogen: the stationary states can be considered as different stages of the process in which an electron, emitting radiation, is bound in orbits of ever decreasing size, in accordance with the decrease in the value of n," and particularly emphasizes that the process of bonding leads to a completely defined final normal state of the atom with n = 1, corresponding to the lowest energy of the atom. Proceeding from the hydrogen atom to more complex atoms, Bohr first discusses the spectrum of ionized helium, which is very similar to the hydrogen spectrum, as corresponding to the "first stage of formation of the helium atom, i.e., to capture of the first electron by the doubly charged nucleus of this atom" and notes that "this close connection between the properties of two different elements, which at first glance seems so striking, must be considered as an expression of the simplicity of structure which characterizes the nuclear model of the atom." Then Bohr speaks about the "fundamental work of Moseley on the x-ray spectra of the elements" and, pointing to the great value of the discovery of Moseley's law, "which lies first of all in the fact that it led to universal acceptance of the suggestion that the socalled atomic number is just equal to the number of electrons in the atoms of a given element" emphasizes that "while the value of this aspect of Moseley's results was immediately clear, on the other hand, it was more difficult to understand the far-reaching similarity of x-ray spectra with the hydrogen spectrum, which was revealed by Moseley's data." Bohr notes that "the similarity of the structure of x-ray spectra and the hydrogen spectrum was further intensified in an extraordinarily interesting way by Sommerfeld in his arguportant theory of the fine structure of the hydrogen lines," and emphasizes that on taking into account the

dependence of the electron mass on velocity, the motion of the electron in its orbit is no longer purely periodic and can be described as a central motion made up of purely periodic motions in an orbit differing very slightly from an ellipse, and a slow uniform rotation. The stationary states for such a central motion are determined by the two quantum numbers n and k. Instead of one energy value E_n (see Eq. (8)), n different values $E_n + \Delta E_{nk}$ are obtained (see Eq. (20)). Thus, Bohr clearly connects the characterization of the electron states by two quantum numbers, instead of one, with removal of the degeneracy. Later, Bohr reminisces about the application by Sommerfeld of Eq. (20) to the doublet structure in x-ray spectra and emphasizes that, in spite of "the great formal similarity between x-ray spectra and the hydrogen spectrum," is necessary to assume the existence of a "fundamental difference" in the processes leading to these spectra. According to Bohr, "emission of the hydrogen spectrum, like the ordinary spectra of other materials, is associated with a process in which the electron is captured and bound in the atom," and "the appearance of x-ray spectra is determined not only by the direct interaction between the electrons and the nucleus of the atom, but also depends in a very intrinsic way on the mode of binding of the electrons in the finished atom which has been formed. In considering this last problem, which naturally interests us here, we have an important guiding thread in the form of the unique mode of variation of many properties of the elements with atomic number, which found expression in the so-called periodic system of the elements." Later, Bohr presents a table of all the elements in a sequence of their order numbers and with a breakdown into periods containing 2, 8, 8, 18, 18, and 32 elements (the table is terminated by six elements of the VIIth period from 87 to 92), and makes the basic suggestion: "In order to interpret this unique regularity it is natural to assume a distinct separation of the electrons in an atom into groups, such that the arrangement of the elements in the periodic system by groups can be assigned to the gradual formation of these electron groups inside the atom as the atomic number is increased."

Bohr gives a review of previous work, in which the idea of separation of the electrons in the atom into groups had already been applied, beginning with the work of Thompson (the nature of which Bohr presented above; see p. 8). He dwells in the greatest detail on the work of Kossel, and then discusses Lewis and Langmuir (see also above, p. 10). Here he emphasizes the need for "study of the possibilities of spatial distribution of the electrons in the atom," but criticizes Langmuir's work for introduction of special postulates on the structure of corresponding atoms to explain the properties of the different elements, which differs "deeply and in principle from the attempts to explain the specific properties of the different elements by means of general laws valid for interaction of the particles in any atom." Bohr concludes the first part of the first part of his paper as follows: "The main problem of this report must consist just of showing that the work on the program expressed by these aspirations is in no way hopeless; on the contrary, it is possible to penetrate the structure of the atom at a

glance by successive use of the general postulates of quantum theory, if, on the basis of these postulates, we approach the problem posed by the following question: How can an atom be formed by the successive capture and binding of individual electrons in the force field surrounding the nucleus?"

The second part of Bohr's paper is devoted to the quantum theory of spectra. He discusses spectra as a source of information on the occurrence of the processes of binding of electrons by the atom, "For an element with atomic number Z," he says, "we must consider that the binding process occurs in Z steps which correspond to the successive capture of Z electrons in the field of the nucleus. For each such capture process we must expect a characteristic spectrum, but only for the first two elements, hydrogen and helium, do we have an exhaustive knowledge of the spectra." Bohr indicates that for the remaining elements we do not yet know more than two spectra-the arc and the spark spectra. He analyzes the general structure of the spectra (neglecting for simplicity the finer structure of the spectral lines-doublet, triplet, and so forth), indicating that the frequency of the lines for many arc spectra are represented to a good approximation by the difference of two Rydberg terms of the type of Eq. (22), and for many spark spectra-the same terms with replacement of R by 4R, like the He⁺ spectrum. Arc and spark spectra respectively correspond, according to Bohr, "to the last stage in the binding of a neutral atom, and in particular to the capture and binding of the Z-th electron," and "the next to the last step in binding of the atom, and in particular the binding of the (Z - 1)-th electron." Bohr emphasizes that in the binding of all electrons except the first, each electron being bound interacts closely with the previously bound electrons, and it can be characterized by two quantum numbers n and k like an electron in a hydrogen atom, with inclusion of the dependence of the mass on velocity, with the difference that the deviation of the motion from purely periodic will be significantly greater. Later, he discusses the correspondence principle, which represents an attempt to "base the application of the quantum theory on the same point of view which gives us the hope of discussing this theory as a rational extension of our ordinary concepts" and which permits us to "reduce the problem of the possible radiation processes accompanying the various transitions of an atom from one stationary state to another, to investigation of the various harmonic components in the motion of the atom." Bohr presents examples of the application of the correspondence principle to periodic orbits and to central motion, concerning the possibilities of the various quantum transitions, i.e., in our contemporary terminology, selection rules. In the first case the single quantum number n can change by any number, and in the second case the quantum number k can change only by ± 1 (for any change of n), which leads to appearance only of completely defined spectral series. Bohr also dwells on the question of "the complex structure of spectral lines" (in contemporary terminology, multiplet structure). This structure he explains as the interaction of the last bound electron with previously bound electrons. In order to characterize the motion of a given electron, a third

quantum number is introduced, "which determines the orientation of the plane of the orbit with respect to the configuration of the previously bound electrons, so that the resulting angular momentum of the atom is equal to an integral multiple of Planck's constant divided by $2\pi''$ (i.e., $M_J = Jh/2\pi$, where J is the so-called intrinsic quantum number, analogous to Eq. (14)). Bohr here cites the work of Sommerfeld and Landé^[30]. In the remainder of the article Bohr limits himself to characterization of electron stationary states by means of the two quantum numbers n and k.

In the third part of the report, Bohr discusses the formation of electron shells of an atom by successive capture and binding of electrons by the nucleus, beginning with the first electron. He designates the possible electron orbits by the symbol n_k (see above, p. 12).

Binding of the first electron occurs into the final stationary state with n = k = 1, the singly quantized circular orbit 1_1 . Binding of the second electron, as Bohr emphasizes, is a "considerably more complicated problem." Bohr bases his solution on the arc spectrum of helium, which is broken down into two systems of lines-the spectrum of orthohelium and the spectrum of parahelium, which correspond to the fact "that the binding of the secondary electron can occur in two different modes." On the basis of the experiments of Franck and his co-workers on the helium atom by the method of electron impact, Bohr reaches the conclusion that the normal state of the helium atom is the final result of the binding process corresponding to emission of the parahelium spectrum, in which the second electron being captured, like the first, is bound into a 1_1 orbit. In contrast to this, the final result of the binding process corresponding to emission of the orthohelium spectrum is the metastable (superstable) state of the helium atom, and here the second electron is captured into a 2_1 orbit, and the strength of the bond is roughly six times less than in the 1_1 orbit (according to contemporary accurate data, 4.67 compared to 24.59 eV). Bohr speaks of "equivalent 1_1 orbits" of the two electrons in the normal state of the helium atom and emphasizes that helium is the first inert gas in the periodic system, and forms, together with hydrogen, the first period of the system of elements. "The great difference in chemical properties between hydrogen and helium", Bohr indicates, "depends intrinsically on the great difference in the strength and type of the electron bonds...'

Further on, Bohr goes into a discussion of the elements whose neutral atoms contain more than two electrons, and suggests that the first two electrons in these atoms also are in equivalent 1_1 orbits (the K layer). The question of the binding of the third electron is directly answered by study of the spectrum of lithium. The normal state of the lithium atom is an s state, corresponding to k = 1, and the ionization energy, which is equal to the work of removing from the atom an electron which is in this state, is 0.396 of the ionization energy of the hydrogen atom (5.39 instead of 13.60 eV). Therefore it is necessary to assume that the electron is bound in a 2_1 orbit with a binding energy which exceeds the binding energy of an electron in a 2_1 orbit in the hydrogen atom, hcR/4 = 3.6 eV, by roughly 1.5 times (which Bohr explains later in the example of the sodium atom). Thus, on the basis of spectral data, Bohr arrives at a picture of the formation and structure of the lithium atom (two tightly bound 1_1 electrons and one weakly bound 2_1 electron, in contemporary terminology and designations—an electron configuration $1s^22s$), "which provides a natural explanation for the great difference in the chemical properties of lithium from those of helium and hydrogen."

With respect to the next elements in the periodic system. Bohr suggests that the fourth, fifth, and sixth electrons (for beryllium, boron, and carbon) and bound into 2_1 orbits, and the seventh, eighth, ninth, and tenth electrons (for nitrogen, oxygen, fluorine and neon) in 2_2 orbits, which leads to the formation in neon of a highly symmetric spatial electron configuration of eight doubly quantized electrons (the L layer), in agreement with the conclusions of previous investigators. Like them, Bohr was guided in this matter by the periodic law, and the question of how electrons with a given n are distributed in shells with given n and k (in orbits of a definite type, for example, in 2_1 and 2_2 orbits in the cases being discussed), Bohr solved by symmetry considerations relating to the spatial arrangement of the orbits and the formation of the chemical bonds. In particular, from the fact that the carbon atom forms four equal-valued chemical bonds, he deduced that in this atom there are probably four electrons in equivalent 21 orbits (four 2s electrons; it is well known that this assumption turned out to be incorrect-it is inconsistent with the subsequently established Pauli principle (see below), and also spectral data which were obtained later).

Going to the third period of the system of elements, Bohr considers the binding of the eleventh electron in the sodium atom and reaches the conclusion that the normal s state of this atom corresponds to n = 3 for the outer electron, i.e., a 3_1 orbit. For subsequent elements of the third period, Bohr suggests the binding of three more electrons in 3_1 orbits and then four electrons in 3_2 orbits, with formation in argon of an electron configuration of eight triply quantized electrons (the M layer).

Bohr arrived at particularly important results in discussing the binding of electrons for elements of the fourth period. For potassium the nineteenth electron, as shown by the arc spectrum of this element, is bound into a 4_1 orbit. Similarly, for calcium the twentieth electron is bound into the same orbit, and the neutral atom of calcium contains two valence electrons in 4_1 orbits. "However, when we go to elements with higher atomic numbers," Bohr remarks, "it is well known that the properties of elements of the fourth period differ more and more from the properties of the corresponding elements of the third period, up to the elements of the iron family, whose properties are essentially different from the properties of the third-period elements. In the transition to still higher atomic numbers, we encounter for the first time other relationships-we meet with elements which in their chemical properties approach more and more the elements in the last part of the previous period, up to element number 36, when we again encounter an inert gaskrypton." Bohr explains these relationships by capture of electrons into a 3_3 orbit in which the binding, with increasing nuclear charge, should become stronger than in 4_1 orbits (which, with increasing nuclear charge, approach in their properties quadruply quantized orbits, calculated without inclusion of the interactions in the atom). For the nineteenth electron, its bond in a 3_3 orbit becomes more stable than in a 4_1 orbit, at the very beginning of the fourth period. This statement Bohr proves by comparison of the spark spectrum of calcium (Z = 20) with the arc spectrum of potassium (Z = 19). In both cases there is one outer (nineteenth) electron, but if the 4_1 (4s) term for the potassium atom exceeds the 3_3 (3d) term by more than a factor of two, then for the calcium ion the 4_1 term is only slightly higher than the 3_3 term and we can expect that in the next element-scandium (Z = 21) the bond in the 3_3 state will be more stable than in the 4_1 state. In the elements following scandium, the number of electrons in 3_3 orbits will decrease. In Bohr's words, in this way occurs "the formation of one of the internal electron groups of the atom", in this case a group of electrons with n = 3 (the M layer). Consideration of the properties of the elements in the last part of the fourth period shows that this group should in its final form contain 18 electrons. Bohr suggests that in the 3_1 , 3_2 , and 3_3 orbits, six electrons are finally distributed in each orbit (based on symmetry considerations, as in doubly quantized orbits). Bohr's ideas of the formation and structure of atoms of elements of the fourth period permit, as he points out, explanation in general terms not only of the chemical and spectral properties of these elements, but also of their paramagnetism and the existence of colors of the ions.

The next systems of elements are discussed by Bohr in a similar manner. In the fifth period, in rubidium and strontium, the 37-th and 38-th electrons are bound into 5_1 oribts, and the filling of the 4_3 orbits then begins. The presence in the fifth period of eighteen electrons indicates "the furthest stage of formation of electron groups in quadruply quantized orbits," for which Bohr again suggests the distribution of six electrons each in orbits of these types $(4_1, 4_2, \text{ and } 4_3)$. In the sixth period, after binding of the 55-th and 56-th electrons into 6_1 orbits in cesium and barium, filling begins of orbits with smaller n values. Bohr says of this behavior: "... We should be prepared, however, to encounter soon completely new relationships. In particular, we must expect that with increasing nuclear charge, not only will the moment arrive when an electron in a 5_3 orbit will be bound more tightly than in 6_1 orbit, but we also must be prepared for the moment when on formation of an atom the 47-th electron will no longer be captured into a 5_1 orbit and when, on the other hand, the binding of this electron will be tighter in a 4_4 orbit-to be exact, just as for elements of the fourth period the moment arrived when the nineteenth electron was bound for the first time into a 3_3 orbit instead of a 41 orbit." Bohr points out that we should expect a number of elements with almost identical properties, as in the case of the iron family, but still more complex, "since we are dealing here with successive formation of an electron configuration located deeper in the interior of the atom." We obtain "a

simple explanation of the appearance of the family of rare earths at the beginning of the sixth period of the system of elements." From the length of the sixth period we can determine directly the number of electrons, which is equal to 32, entering into "the group of electrons in quadruply quantized orbits" after its "final formation" (i.e., in the N layer). Bohr once more suggests the presence of an identical number of electrons in orbits of each type, in this case 8 electrons each in the 4_1 , 4_2 , 4_3 , and 4_4 orbits. Bohr notes that his explanation of the appearance of the rare earth family in the sixth period is confirmed by study of the magnetic properties and colors of the ions of the corresponding elements. The appearance of the platinum family is explained by Bohr in a natural way as the second stage of formation of the group of quintuply quantized orbits. Later, Bohr indicates the formation in the atom of the 86th element of an extremely symmetric electron configuration of eight electrons, as in the case of the other inert gases. Finally, after a brief discussion of the beginning of the seventh period, Bohr presents a summary table giving "a symbolic representation of the structure of the inert gas atoms" (see Fig. 5, Table I). In the conclusion of the third part of his paper, Bohr emphasizes that it is based on the correspondence principle. This principle allows us to hope, writes Bohr, "that behind the applications of the quantum theory there is an intrinsic binding of the same type as the intrinsic binding in classical electrodynamics; the latter is not capable, however, in spite of the wide field of its applicability in many physical phenomena, of explaining the stability of atomic structure, whose existence follows from the properties of the elements." Bohr maintains that, although the results contained in the table presented also cannot be considered as uniquely following in all details from the correspondence principle, nevertheless "any substantially different interpretation of the properties of the elements on the basis of the postulates of quantum theory is hardly possible." Bohr here refers not only to the optical spectra which characterize the formation of the atom and their intrinsic relation with the chemical properties of the elements, but also the x-ray spectra, whose emission depends on "the reorganization of an atom which has already been formed." Bohr devotes the fourth and last part of his paper to interpretation of x-ray spectra. This question was discussed shortly afterward by Bohr in more detail and more completely, jointly with Coster^[31], and we will analyze it somewhat later. We will note only that at the end of the paper, for a conclusion as to the correctness of the discussion, Bohr particularly emphasizes the great value of the fact "that we have used the same application of quantum theory to the conditions of stability of the atom for interpretation of the two groups of phenomena'' (formation of the atom and reorganization of the atom). In addition, Bohr points to the incompleteness of the discussion in two directions-"not only in respect to analysis of details, but also in the justifications for the general point of view", and says: "However, it is evident that there is no other path for advancement in the field of study of the atom than the path which we have followed up to this time, namely continuation of our efforts for a simultaneous development of our ideas in these two directions."

Thus, Bohr's report gave the basis of the physical interpretation of the periodic law—it developed the ideas of successive capture and binding of electrons by the nucleus and of the gradual filling of electron shells characterized by two quantum numbers, principal and azimuthal, and in this process gave a natural explanation of the appearance of the transition and rare-earth elements. The Bohr theory of the periodic system, which was set forth in this paper and later

Element Atomic number	Atomic		Number of m _k electrons													
	11	21	22	31	32	33	41	42	43	44	51	52	53	61	62	
Helium	2	2						 	_		-			-	$\ _{-}\ $	_
Neon	10	2	4	4	-		-		-		-			100.2		
Argon	18	2	4	4	4	4	-		_		-				-	-
Krypton	36	2	4	4	6	6	6	4	4		-			-	1-1	
Xenon	54	2	4	4	6	6	6	6	6	6	-	4	4			
Emanation	86	2	4	4	6	6	6	8	8	8	8	6	6	6	4	4
						ł										

Table I. Early diagram of inert gas electron configurations according to Bohr

Element A Helium Neon Argon Krypton Xenon	Atomic	Number of n _{k1} , k2 electrons														
	number	11	21	² 2, (1⊢2)	31	3 2,(1+2)	33, (2+3)	41	42, (1+2)	43, (2+3)	44, (3+4)	51	52, (1+2)	⁵ 3, (2+3)	61	⁶ 2, (1+2)
	1					l							1	1		
Helium	2	2				-		-	-	-		-	-		-	-
Neon	10	2	2	2+4	-	- 1			1 — '			1-			-	-
Argon	18	2	2	2+4	2	2+4		-					-		Į	-
Krypton	36	2	2	24	2	2 + 4	4+6	2	2+4		-		-	-	-	
Xenon	54	2	2	2-14	2	24	4+6	2	2+4	4+6	- 1	2	2+4	- 1		
Emeration	86	2	2	914	2	244	446	2	2+4	446	6.1-8	2	2+4	4+6	2	2 ± 4

Table II. Diagram of inert gas electron configurations according to Stoner

FIG. 5. Tables from Pauli's article [44] on the exclusion principle.

supplemented on its publication* and in the articles "Line Spectra and Atomic Structure"^[33] and "X-ray Spectra and the Periodic System of Elements"^[31], immediately received wide acceptance, and in particular was discussed in detail by Sommerfeld in the fourth edition of his book, Atombau and Spektrallinien (^[34] Chap. 3. Secs. 4-5) and served as a powerful stimulus for future research. The most important question was: how many electrons fill the various electron shells. Bohr's assumption, based on symmetry considerations, that the electrons are equally distributed (in a layer with a given n) among shells with different k, led to the conclusion that these shells are not completely filled at once, but continue to be added to even in the next periods; for example, according to his table (see Fig. 5) the 4_1 (4s) electron shell is filled in the fourth period by four electrons, in the fifth period two electrons are added, and in the sixth period still two more, and only then is it completely filled. Pauli, in his Nobel lecture in 1946, "The Exclusion Principle and Quantum Mechanics", recalls Bohr's statement in 1922 on the problem of the filling of shells: "It made a strong impression on me that Bohr... spoke about a general rule according to which the filling of any shell would occur and in which, in contradiction to Sommerfeld's attempt, the number 2 would be just as important as $8''^{[35]}$ (we are discussing Sommerfeld's attempt to connect the number 8 with the number of vertices of a cube, as was done also by other scientists, for example, Lewis; see above, p. 10). As we know, Pauli himself in 1925 found such a rule in the form of the exclusion principle formulated by him, which has obtained the name the Pauli Principle, and which justified the electron shell filling numbers, which are equal to 2, 6, 10, 14, ... for k = 1, 2, 3, 4, ... (i.e., for s, p, d, f,... electrons) and which were proposed in 1924 by Stoner (see below). This was a logical completion of Bohr's theory of the periodic system and a generalization of the results of research on optical and x-ray spectra, and was closely related with the more complete characterization of the electrons in an atom-the characterization of each electron by means of four quantum numbers. We will discuss briefly the development of the corresponding research, which led to establishment of the Pauli principle and to the discovery of a new, important property of the electronits spin, which is responsible for appearance of the fourth quantum number characterizing the electron, in addition to the three quantum numbers n, k, and m (see above, p. 11).

In the study of optical spectra of atoms, it has been possible to explain formally the multiplet structure of spectral terms with given n and k-their decomposition into r components (r = 2, 3, 4, ... in the case ofdoublets, triplets, quartets, and so forth; in the case of singlets, r = 1, there is only one component)-by addition of the vector M_k -the orbital angular momentum of the outer electron, and the vector $M_{\rm R}$ -the angular momentum of the core formed by the nucleus and the remaining electrons. When added, these angular momenta form the resultant (total) angular momentum of the atom, $M_J = M_K + M_R$. In order to explain the number of component multiplet terms and the observed pattern in the splitting of spectral lines in a magnetic field (the Zeeman effect), it was necessary to make a number of assumptions as to the possible values of the quantum numbers K, R, and J, which determine the values of the angular momenta M_{K} , M_{R} , and M.I according to the formulas

$$M_{K} = Kh/2\pi, \quad M_{R} = Rh/2\pi, \quad M_{J} = Jh/2\pi.$$
 (24)

Here the quantum number $K = k - (1/2) = 1/2, 3/2, 5/2, \ldots$ and is a half integer, and the core quantum number $R = r/2 = 1/2, 1, 3/2, 2, \ldots$ and is a half integer for an even number of electrons in the atom and an integer for an odd number. The intrinsic quantum number J is also a half integer for an even number of electrons and an integer for an an integer for an even number.

It should be mentioned that various workers of that period (1920-1925) made different choices of the absolute values of the quantum numbers characterizing the orbital angular momentum of the outer electron, the angular momentum of the core, and the resultant angular momentum. Sommerfeld (^[34], Chap. 8, Sec. 1) introduced the quantum numbers $j_a = k - 1 = K - (1/2)$ = 0, 1, 2, 3, . . . (it is identical with the azimuthal quantum number *l*; see Eq. (15')); j_s for the core, which takes on the values $j_s = R - (1/2) = 0, 1/2, 1,$ $3/2, \ldots$ for singlets, doublets, triplets, and so forth, and which determines the number of levels r (in contemporary terminology the multiplicity) according to the formula

$$r=2j_s+1, \qquad (25)$$

and j = J - (1/2) (the intrinsic quantum number), which takes on for these levels r values from the sum $j_a + j_s$ to the difference $|j_a - j_s|$ ("the vector sum"):

$$j = j_a + j_s, \ j_a + j_s - 1, \ j_a + j_s - 2, \ \dots, \ |j_a - j_s|.$$
 (26)

In particular, for doublet terms $j_s = 1/2$ and $j = j_a \pm (1/2)$, except the s term $(j_a = k - 1 = 0)$, for which $j = j_s = 1/2$. According to Sommerfeld j_s and j are integers for an even number of electrons in the atom and half integers for an odd number of electrons,

Only after the discovery of spin and the creation of quantum mechanics was it clear that Sommerfeld's introduction of the quantum numbers was correct. The quantum number j_S turned out to be identical with the quantum number S which determines the total spin angular momentum of the atom, and Eq. (26) for the vector sum of the angular momenta turned out to be

^{*}Bohr added to the Danish original $[^{32a}]$ and the German translation $[^{32b}]$, and later also a separate publication (see ref. 2). One of these additions was a table of the periodic system in the form of a staircase (after Julius Thomsen), which was later widely reproduced in various publications.

[†]Jointly with Coster.

[‡]This is a collection of articles devoted to the memory of Wolfgang Pauli. It contains a number of articles with material relating to the discovery of the exclusion principle and electron spin: R. Kronig, The Turning-Point Years; W. Heisenberg, Recollections of the Period of Development of Quantum Mechanics; B. van der Waerden, The Exclusion Principle and Spin. The last article is particularly interesting. Pauli's Nobel lecture is also included in the collection.

extremely general^{*}. It is valid for addition of the total orbital and total spin angular momenta of the atom, if we set $j_a = L$, $j_s = S$, and j = J, where the quantum numbers L, S, and J determine the values of the orbital, spin, and resultant angular momenta of the atom $(M_L + M_S = M_J)$ according to formulas of the type of Eq. (16). An exposition of the systematics of atomic spectra, based on addition of the various angular momenta[†], in essentially the contemporary form was first given by Friedrich Hund in his book Linenspektren und Periodisches System der Elemente.^[36]

For the quantum number j, the valid selection rules permit its change by ± 1 and by 0, in contrast to the selection rules for the quantum number k, which allow its change only by ± 1 (see above, p. 14). Thus,

$$\Delta j = \pm 1, 0, \quad \Delta k = \pm 1.$$
 (27)

These selection rules were derived on the basis of Bohr's correspondence principle (see, for example, Sommerfeld's book^[30b], pp. 699-711), and the first of these rules can be obtained also from the condition of conservation of total angular momentum in the radiation processes (but not the second rule; see ref. 2, p. 103).

For doublet terms, the structure and possible quantum transitions are shown in Fig. 6, which is taken from Sommerfeld's book^[30D] (p. 477)‡ (to the left are shown values of the azimuthal quantum number and to the right the intrinsic quantum number; the wider arrows indicate a greater intensity of the transitions, and the dashed arrows indicate transitions forbidden by selection rules). This diagram turned out to be valid not only for the optical spectra of atoms with one outer electron, but also for x-ray spectra, which was important for solution of the problem of the electron shell filling numbers (see below, p. 19).

An important piece of research was the study of the Zeeman effect, which permitted establishment of the number of states corresponding to given values of the quantum numbers K, R, and J (or, according to Sommerfeld, j_a , j_s , and j) and differing in their values of the magnetic quantum numbers $m_K = m$ (see p. 11), m_R , and m_J , which determine the values of the projections M_{KZ} , M_{RZ} , and M_{JZ} of the angular momenta M_K , M_R , and M_J (i.e., permitted establishment of the multiplicity of the degeneracy removed by the magnetic field as a result of the fact that different orientations of the angular momenta in the magnetic field correspond to different energies). These numbers of states turned out to be

$$g_K = 2K = 2j_a + 1$$
, $g_R = 2R = 2j_s + 1$, $g_J = 2J = 2j + 1$. (28)

It should be emphasized that, in spite of the great successes achieved in the years 1923-1924 in the study of the Zeeman effect, the fundamental question of the



FIG. 6. Diagram of optical levels and transitions from Sommerfeld's book [^{30b}].

anomalous magnetic moment associated with the angular momentum of the core was left unsolved: the corresponding magnetic moment turned out to be larger by a factor of two than we should expect on the basis of the well known and theoretically justified relation between the magnetic moment and the angular momentum for the orbital motion.

In addition to the substantial progress in the study of optical spectra of atoms, important results were obtained also in investigation of x-ray spectra. We have already mentioned above the complex structure of the x-ray terms (see p. 12), which consist of 2n - 1 components for a given value of n. This structure was discussed in detail in an article by Bohr and Coster^[31], from the point of view of Bohr's theory of the periodic system. At the beginning of the article there is a table of the filling of the electron shells, more complete than in Bohr's paper (see Fig. 5), and a diagram of the x-ray levels and transitions is given (Fig. 7)*. In the diagram the levels corresponding to the L, M, ... layers (n = 2, 3, ...) are denoted by successive Roman numerals (this designation, which was introduced by Bohr and Coster in this article, is preserved even today) and the values of the quantum numbers n, k_1 , and k_2 , are shown. The last two quantum numbers were introduced by Bohr and Coster instead of the azimuthal quantum number k, a comparison with the general systematics of spectra showing (^[39] and ^[34] p. 312) that $k_1 = k$, and $k_2 = j + 1/2$. The intrinsic quantum number $k_2 = k_1$, $k_1 - 1$ (see above and Fig. 6; the selection rules (27) are satisfied also for x-ray lines, see Fig. 7). However, at that time (1923) it was not possible to explain as we do today the extremely far reaching similarity of the level scheme for the x-ray spectra (see Fig. 7), which correspond to the ionized atom from whose shells one electron has been removed, with the level schemes of the neutral atom with one external electron (see Fig. 6): the number of x-ray levels with a given n, their quantum numbers (including selection rules), and their sequence are the same as for the neutral atom with one external electron, in spite of the completely different energy scales. An interpretation of this similarity could be given only on the basis of the Pauli principle, of which it was the direct consequence.

^{*}On introduction of the quantum numbers K, R, and J, the vector addition scheme becomes more complicated and is no longer general (see ref. 36).

[†]The normal coupling scheme based on addition of orbital and spin angular momenta of the individual electrons, $M_L = \sum M_{i_1}$, $M_S = \sum M_{S_i}$, $M_L + M_S = M_J$, was proposed by Russel and Saunders³⁷.

[‡]The designations have been changed and supplemented.

^{*}On the left side of the diagram, instead of the old designations used by Bohr and Coster, we have given the current designations with indication of the electron shell from which the electron has been removed.

T.



FIG. 7. Diagram of x-ray levels and transitions from the article of Bohr and Coster $[^{31}]$.

Level	K		L	_	М							
Sublevel		LI	$\widetilde{L_{11}}$		MI	м _{II}	M _{III}	<i>м</i> ₁	$\hat{v} M_{v}$			
$k_1 \\ k_2$	1 1 1	2 1 1	2 2 1	2 2 2	3 1 1	3 2 1	$3 \\ 2 \\ 2$	3 3 2	3 3 3			
Optical term	15	28	2p_2	2 <i>p</i> ₁	38	3p ₂	3p1	3d2	3d ₁			

FIG. 8. The table from Stoner's article [40].

An important step was made in 1924 by Edmund Stoner in his article "The Distribution of Electrons in Atomic Levels'^[40]*. In this paper, Stoner proceeds from the energy level classification proposed by Landé (whose work^[39] he cites) by means of principal, azimuthal, and intrinsic quantum numbers, and presents a table of classification of x-ray energy levels (Fig. 8)[†]. Stoner emphasizes the analogy of the x-ray and optical terms, which is reflected in the table, and writes that "it is valid to apply the ideas which have permitted the optical data to be systematized, to the case of x rays, and in particular with regard to assignment of the intrinsic quantum numbers." He then notes, as a "remarkable feature" of the classification adopted, that "the number of electrons in each filled level is equal to twice the sum of the intrinsic quantum numbers"-for the K, L, M, and N levels (layers), this number of electrons is respectively 2, 8 (2 + 2 + 4),

18 (2 + 2 + 4 + 4 + 6), 32 (2 + 2 + 4 + 4 + 6 + 6 + 8). He also makes the basic assumption that "the number of electrons associated with each sublevel individually is also equal to twice the intrinsic quantum number." This leads him, taking into account that a given azimuthal quantum number $k = k_1$ corresponds to two sublevels with $k_2 = k_1$, $k_1 - 1$ (except for the value $k_1 = 1$, which corresponds to one level with $k_2 = 1$), to filling numbers of the electron orbits $n_1, n_2, n_3, n_4, \ldots$ (i.e., of the ns, np, nd, nf, ... shells) of 2, 2 + 4 = 6, 4 + 6= 10, $6 + 8 = 14, \ldots$ electrons. The electron distribution in the shells as obtained by Stoner differs from that obtained by Bohr in that the electron shells filled in a given period no longer change in the following periods, i.e., complete filling is attained immediately (see Fig. 5). It is important that the number of electrons in a sublevel with a given value of intrinsic quantum number is equal to the number of different energy values in a magnetic field (and this is emphasized by Stoner)-the number of values $2k_2 = 2j + 1$ of the magnetic quantum number $m_{k_2} = m_j$, i.e., the multiplicity of the degeneracy. "We can suppose that for the intrinsic sublevel, .. the number of possible orbits," writes Stoner, "is equal to twice the intrinsic quantum number, and these orbits differ in their orientation with respect to the atom as a whole. Electrons can enter the composition of a group as long as all possible orbits are not occupied, and then the atom will have a symmetric structure." An important observation by Stoner relates to the statistical weight of the electron states in the atom: "If the electrons in the atom are distributed according to a given scheme, then the interesting idea suggests itself that all electrons bound in the atom and entering into the composition of completed groups must be considered as having the same statistical weight, namely unity (or h^3), since then we will have one electron in each possible equally probable state."

Stoner discusses the various data which permit us to draw conclusions about the electron distribution in the sublevels—the intensity of x-ray lines, absorption of x rays, magnetic properties, chemical properties, optical spectra—and reaches the conclusion that these data all taken together give serious arguments in favor of the scheme proposed by him, which "alone is simple and consistent." In addition, he emphasizes that his scheme "permits all of the essential features included in the Bohr picture of the atom to be preserved and, thus, is to an equal degree in agreement with the general chemical and spectroscopic data, differing, however, in the distribution in the completed groups and in indicating a somewhat simpler mode of buildup."

Stoner's work was immediately regarded as very important. Sommerfeld, in the foreword to the fourth edition of his book (October, 1924) wrote: "Stoner's modification of the Bohr system is a great step forward..." ($^{[34]}$, p. VI). Pauli later said: "At this time (the autumn of 1924—M. E.) there appeared the work of the English physicist Stoner, which contained, along with an improvement in the classification of electrons in the subgroups, the following important remark: for a given value of the principal quantum number, the number of energy levels of the solitary electron in the spectra of the alkali metals in an external magnetic

^{*}The work was carried out at Rutherford's laboratory and at the end of the article Stoner expresses his gratitude "for helpful criticism and discussion" to Rutherford's closest associate, theoretician Ralph Fowler, who often visited Bohr in Copenhagen.

[†]In this table we have changed Stoner's designations. The designations of the optical terms are given in accordance with Fig. 6.

field is equal to the number of electrons in the closed shell of the inert gases corresponding to the same value of the principal quantum number. Then, on the basis of my previous results on classification of spectral terms in a strong magnetic field, the general formulation of the exclusion principle was also clarified for me" (^[35], pp. 231 and 359). Let us consider now the work of Pauli himself. In the 1923 article "Regularities of the Anomalous Zeeman Effect"^[41] which he later evaluated as "having the decisive role in the discovery of the exclusion principle" (^[35], pp. 232 and 259), Pauli discussed the relation between the normal Zeeman effect in strong magnetic fields and the "anomalous" Zeeman effect in weak magnetic fields. He generalized the results obtained earlier by Heisenberg^[42] (in those days, theoretical physicists were vigorously occupied with the theory of spectra), and although he did not succeed in solving the problem of the "anomalous Zeeman effect," he experienced its difficulties.

Next, and very important, was Pauli's work at the end of 1924 (published in the beginning of 1925) "The Influence on the Zeeman Effect of the Dependence of the Electron Mass on Velocity"^[43]. In this paper Pauli calculates the influence of the mass dependence of an electron in the K layer on the Zeeman effect, on the assumption that the electrons of this layer produce resultant angular momenta different from zero-both the mechanical moment and the related magnetic moment. He obtained a result in contradiction with experiment and reached the fundamental conclusion that for filled shells the resultant magnetic and mechanical moments are zero (which had been suggested by Sommerfeld) and that, therefore, in the case of atoms of the alkali metals with one outer electron, all the mechanical and magnetic moments are determined only by this electron; consequently, even the anomaly in the magnetic moment (see above, p. 18) is not associated with the core, but is a property of the electron itself. Pauli formulated his conclusion as follows: "Closed electron configurations should not contribute to the magnetic moment and to the mechanical angular momentum of an atom. In particular, for the alkali metals we must consider the values of angular momentum of the atom and the changes in the energy of the atom in an external magnetic field mainly as the result of the action of only the optical electron; the latter must also be considered as the source of the magnetomechanical anomaly. According to this point of view, the doublet structure of the alkali metal spectra, as well as the violation of Larmor's theorem, arise from the peculiar doublevaluedness of the quantum properties of the optical electron, which cannot be described classically."

Finally, in March of 1925, Pauli published his famous paper "On the relation of the filling of the electron groups in the atom to the complex structure of the spectra"^[44], in which he gave a general formulation of the exclusion principle, about which he later said: "The main idea can be expressed as follows: the complex numbers of electrons in closed subgroups reduce to the simple number 1, if the classification of the group is carried out by means of four quantum numbers with the condition that any degeneracy is removed. In general a nondegenerate level is already "filled,"

if it is occupied by only one electron; states which are inconsistent with this postulate are forbidden'' (^[35], p. 360). We have seen above that Stoner closely approached this thought, in speaking of the statistical weight of electrons, which is 1 (see p. 19). However, Pauli made the decisive step as a result of the fact that he began to characterize each electron in the atom by means of four quantum numbers and abandoned the thought that the intrinsic quantum number is necessarily associated with the existence of an interaction with the core. Pauli begins Sec. 1 of his paper with a characterization of the stationary states of the optical electron of the alkali metal atoms by means of the three quantum numbers n, k_1 , and k_2 (the same quantum numbers used by Bohr and Coster to characterize the xray terms), where ' k_1 determines the magnitude of the interaction of the optical electron in a central field with the core of the atom," and " k_2 is equal to $k_1 - 1$ and k_1 for the two terms of the doublet (for example, p_1 and p_2)," and by means of a fourth quantum number m₁, "which determines the component of angular momentum parallel to the external field." Noting that the maximum value of the quantum number m_1 is $j = k_2$ -1/2, Pauli points out that "the number of stationary states in the magnetic field for given values of k_1 and k_2 is $2j + 1 = 2k_2$, and the number of states for the two doublet terms together for a given k_1 is $2(2k_1 - 1)$ ", which with our current designations gives 2(2l + 1) $= 2, 6, 10, 14, \ldots$ for $l = 0, 1, 2, 3, \ldots$ In addition, for the case of strong fields (the Paschen-Back effect) Pauli introduces instead of k_2 a second magnetic quantum number m_2 , which determines "the component of the electron magnetic moment parallel to the field." Then the state of an electron in a strong magnetic field is determined by the four quantum numbers n, k_1, m_1 , and m2, instead of n, k1, k2, and m1. Later, Pauli defines for the entire electron assembly "total components," which are parallel to the field and equal to

$$\overline{m}_1 = \Sigma m_1, \quad \overline{m}_2 = \Sigma m_2. \tag{29}$$

Although the definitions of these components do not agree with our current definitions $m_L = \Sigma m_l$ and $m_S = \Sigma m_S$ for the projections of the orbital and spin angular momenta of the electrons, the method of discussion used by Pauli is correct in principle and was later used by Hund*.

The exclusion principle itself is formulated by Pauli in Sec. 2, on the basis of Stoner's results. He presents Bohr's and Stoner's schemes for filling the electron shells (see Fig. 5) and emphasizes that according to Stoner the numbers of electrons 2(2k - 1)in filled shells with a given $k = k_1$ "are identical with the numbers of stationary states of alkali metal atoms in an external field for a given value of k" and a similar agreement exists for subshells with given k_1 and k_2 . "Now," writes Pauli, "this representation of Stoner's can be proved and generalized by applying to the case where equivalent electrons exist in the atom the concept, discussed in the preceeding paragraph, of the complex structure of spectra and the anomalous

^{*}In definition of the possible multiplet terms for two or several equivalent electrons with inclusion of the Pauli principle (see ref. 38).

Zeeman effect." He gives the following formulation "of a more general rule for the appearance of equivalent electrons in an atom":

"In an atom there can never be two or more equivalent electrons for which the values of all of the quantum numbers n, k_1 , k_2 , and m_1 (or, equivalently, n, k_1 , m_1 , and m_2) in strong*) fields are identical. If an electron exists in an atom, for which these quantum numbers (in an external field) have definite values, then this state is occupied."

Later, Pauli discusses the consequences of this principle which he has formulated. Of course, Stoner's results are obtained from it directly and, consequently, the lengths of the periods are 2, 8, 18, 32,... For a given k_1 and k_2 (i.e., in contemporary language l and j) there cannot be more electrons in an atom than $2k_2$, corresponding to the number of possible values of m_1 , and "in closed groups just one electron corresponds to each value of m₁." For two equivalent s electrons (the normal state of alkaline earth metal atoms), k_1 = $k_2 = 1$, Pauli immediately finds that J = 0. Actually, for the two electrons m_1 cannot simultaneously have the same value and either for the first electron m'_1 = 1/2 and for the second $m_1'' = -1/2$, or vice versa, and $\overline{m} = m'_1 = 0$. Consequently, the total angular momentum is also zero (in agreement with experiment, only a singlet state is possible). Here Pauli notes the important fact that interchange of two equivalent electrons does not give a new state. A significant discussion is given by Pauli of closed groups from which one electron has been removed. Pauli shows that in this case the same terms are obtained as for one electron (the same number of terms with the same values of J), and in this way the similarity of the x-ray term diagram and the alkali metal atom term diagram is explained (in Fig. 7 on the left we have indicated exactly in their presentday designations electron configurations with one missing electron and the symbols of the corresponding terms, which agree with the symbols of the alkali metal atom terms, see Fig. 6). As Pauli notes, this result is a particular case of a general law of reciprocity, according to which to each electron configuration there corresponds an additional associated configuration in which the occupied positions are replaced by vacant positions (holes), and vice versa. For the two associated configurations the sum of the numbers of occupied positions is equal to the number of electrons in the filled group, and the term systems are identical in number of terms and in the values of the quantum numbers. Pauli discusses an example of this reciprocity law-the electron shells p^2 and p^4 , which contain two and four p electrons (k = l + 1 = 2)and which complete each other up to the filled shell p^6 .

In the conclusion of the article Pauli writes: "The problem of a more fundamental justification of the general rule which we have adopted here on the appearance of equivalent electrons in an atom could be successfully solved only after further development of the basic principles of quantum theory." It is well known that the exclusion principle was later derived from the more general principle of antisymmetry of wave functions, which is associated, as Pauli himself showed, with the properties of particles with half-integer spin.

The characterization of an electron by means of four quantum numbers instead of three, corresponding to the three degrees of freedom of its orbital motion, indicated the existence in the electron of a fourth degree of freedom. This degree of freedom turned out to correspond to an intrinsic angular momentum (a mechanical angular momentum and the magnetic moment associated with it) of the electron-the electron spin, apparently due to rotation of the electron around its own axis. The hypothesis of electron spin was proposed in 1925 independently by Uhlenbeck and Goudsmit, on the one hand, and by Kronig, on the other hand, (^[35], pp. 245, 250, and 30) and was first published by Uhlenbeck and Goudsmit^[45] and only later by Kronig^[46]. This hypothesis, as is well known, was universally confirmed experimentally, in particular by the large mass of spectroscopic data, and later was justified by relativistic quantum mechanics. The doubled magnetomechanical ratio for the spin in comparison with the orbital angular momentum turned out to be a characteristic property of the electron. The idea of electron spin became an integral part of the physical theory of the periodic system and of quantum chemistry.

The discovery of spin permitted an improvement of the characterization of an electron by four quantumnumbers, and the formulation of the Pauli principle which was given in Pauli's basic paper (see above, p. 20). The quantum numbers s and m_S were introduced (s = 1/2 and $m_S = 1/2$, -1/2), which determined the intrinsic mechanical angular momentum of the electrons M_S and its projection M_{SZ} according to the formulas

$$M_s = sh/2\pi, \quad M_{sz} = m_s h/2\pi.$$
 (30)

The quantum number j turned out to define the total angular momentum of the electron M_i as the sum of the orbital angular momentum M_l and the spin angular momentum M_s , $M_j = M_l + M_s$ (where $M_l = lh/2\pi$, $l = j_a = 0, 1, 2, ...$). An electron in a weak magnetic field, when the coupling of M_l and M_s (which determines the spin-orbit interaction) is preserved, can be characterized by the four quantum numbers n, l, j, and m (m = m_j = m_1 = j, j - 1, j - 2, ..., -j; a total of 2j + 1 values for given n, l, and j), and in a strong field, when this coupling is broken, by the four quantum numbers n, l, m_l, and m_s (m_l = l, l - 1, l - 2, ..., -l; $m_s = 1/2, -1/2, a \text{ total of } 2(2l+1) \text{ values for given } n$ and l). The Pauli principle can be formulated in a shortened form as follows (^[38], p. 115): "For each set of four quantum numbers n, l, j, and m or n, l, m_l , and m_s in an atom there is no more than one electron" To this is added, "Situations which are transformed into each other by interchange of two electrons give only one term.'

The development which we have described of spectral research, completed by the establishment of the Pauli principle and the discovery of spin, represented, from the point of view of a physical interpretation of the periodic system, the completion of the program

^{*}The term strong fields here means both magnetic fields in which the anomalous Zeeman effect is observed, and magnetic fields in which the Paschen-Back effect is observed.

contemplated by Bohr at the end of his report in 1921 (see p. 16), under the heading "Analysis of Details". The completion of this program with regard to "justification of the general point of view" was accomplished by the creation of quantum mechanics (in which Bohr's participation, as head of the Copenhagen school as made up at this time, 1924-1926, was exceedingly important). We will not dwell in detail on the widely known and well described basic postulates of quantum mechanics and the applications of quantum mechanics to atomic and molecular structure, including the well developed theory of the chemical bond. We will note only certain aspects. In quantum mechanics, Bohr's model of electron motion in an atom in definite orbits according to the laws of Newtonian mechanics was replaced by characterization of the electrons in the atom by means of wave functions. Strictly speaking, the electrons in an atom, in view of the interaction between them, cannot be distinguished from each other, and therefore it is impossible to assign to each electron an independent wave function. However, this can be done approximately (and the degree of approximation in the various cases can be estimated) by characterizing each electron by means of "orbitals," which depend on the principal quantum number n and azimuthal quantum number *l*-the orbitals 1s, 2s, 2p, 3d, 4p, and so forth.

Obviously, each orbital corresponds to a definite distribution of "electron density" in the atom. The concepts of electron shells and their filling are retained, and the Pauli principle is formulated in more general form as the principle of antisymmetry of the wave functions of the electron system. The concept of orbitals can be applied also to electrons in molecules and plays an important role in the theory of the chemical bond. For molecules, as for atoms, we can introduce the concept of electron shells and determine by means of the Pauli principle the filling numbers of the shells, which turn out to be 2, 4, and 6. The various physical and chemical properties of atoms and molecules are calculated on the basis of approximate quantum-mechanical methods, and the periodicity of these properties finds here its quantitative expression.

It should be especially emphasized that the physical interpretation of the periodic law, given by Bohr and other scholars and based on regularities in spectra, is completely retained and has acquired a more fundamental justification. In addition, it must be noted that a particularly import role was played by spectroscopy in this period when Bohr was creating his quantum theory of the atom and interpreting the periodic law on this basis. At the present time, although spectroscopy is widely and successfully applied to study of the structure of atoms and molecules and to investigation of the elementary processes in which they take part, its applications involve more specific problems, and not the general and fundamental problems, which it had already been possible previously to solve by means of spectroscopy.

In conclusion, evaluating Mendeleev's great discovery, we can say that at the present time the significance of the periodic law of the chemical elements has been completely demonstrated as one of the remarkable generalizations of science. This law, which played a tremendous role in creation of the quantum theory of atoms and molecules, is now one of the firm bases of the development of contemporary physics and chemistry.

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