Rydberg and the periodic system of the elements

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It is not so well known as it should be that Rydberg's occupation with spectral lines had its origin in his interest in the periodic system of the elements, an interest which accompanied him through his whole life.

After an early attempt (1885) to discover new laws by a Fourier analysis of the famous Lothar Meyer curve for the atomic volumes of the elements, already in 1889 in his first larger paper (1) on the emission spectra of the chemical elements he clearly formulated the idea, that these spectra should give the clue to the understanding of the periodic system. The connexion between spectra and chemical properties had been empirically well established by Kirchhoff and Bunsen, but the attempts at a theoretical explanation of this connexion were very vague. Rydberg said rather generally that the periodic system of elements shows us "that the effective force between the atoms must be a periodic function of the atomic weight". This he considered to be a hint that periodic motions of the atoms have something to do with it, which lead to the analysis of the spectra. Therefore he concluded that the spectral analysis will lead nearer to the goal of a mechanics of the atoms and of an understanding of the periodic system than "investigations of any other physical property".

I quote here Rydberg's own words*: "Durch Mendelejeffs Entdeckung des periodischen Systems der Elemente ist ein neuer Ausgangspunkt aller einschlägigen Arbeiten gewonnen worden und doch hat man sich dessen selten bedient. Um solche Untersuchungen wenigstens in Schub zu bringen, habe ich in einer früheren Abhandlung (Bihang till K. Svenska Vet.-Akad. Handlingar, *10*, no 2) mit etwas grösserer Genauigkeit die periodische Beziehung zwischen dem spezifischen Gewichte und dem Atomgewichte der Elemente zu bestimmen versucht. Ich habe dort gefunden, dass man annähernd diese Beziehung durch eine Sinusreihe mit veränderlichen Koeffizienten darstellen kann. Daraus habe ich ferner geschlossen, dass die Periodizität sehr vieler physikalischer Konstanten davon abhängen muss, dass die wirksame Kraft zwischen zwei Atomen eines und desselben oder verschiedener Elemente eine periodische Funktion des Atomgewichtes sei. Steigt man noch weiter vor, so gelangt man zu der sehr wahrscheinlichen Annahme, dass Kohäsion, Adhäsion und chemische Affinität

* Ostwalds Klassiker, Nr. 196, p. 9 f.

im Grunde auf periodische Bewegungen der Atome zurückzuführen seien. Es läge somit am nächsten, die periodischen Bewegungen überhaupt zu untersuchen, und da die Spektren der chemischen Elemente auf Bewegungen dieser Art beruhen, werden wir in den Bereich der Spektralanalyse hingewiesen. Zwar können wir nicht wissen, ob diese periodischen Bewegungen dieselben sind, die wir anfänglich aufsuchten, aber eine Untersuchung dieser Schwingungen wird uns jedenfalls wertvolle Erkenntnisse vermitteln über die Beschaffenheit der Atome und wird uns unserem Ziele mehr nähern als eine Untersuchung irgendeiner anderen physikalischen Eigenschaft."

I think, one has to admit that Rydberg's speculations were sometimes rather wild, but on the other hand they were always controlled again by his study of the empirical material. In a paper of 1897 (2) he expressively stated (Chapt. XI): "In investigations on the periodic system the ordinals (Ordnungszahlen) of the elements instead of the atomic weight should be used as independent variables". His argument for it was that the atomic numbers simply run through all integers.

At that time no suffficient attention had been paid to Rydberg's claim and only later the work of Julius Thomson and others on the periodic system of the elements followed.

In this same paper Rydberg finds an interesting simple rule for the relation between mass-number M and atomic number Z. Today we must add, that the rule concerns the mass of the most frequent isotope of this Z value. The rule is:

if Z is odd (odd chemical valence) $M = 2Z + 1$
" Z is even $M = 2Z$.

Rydberg was aware that nitrogen ($Z = 7$, $M = 14$) is an exception, but it is true that otherwise this rule holds until about Ca. Rydberg trusted this rule so much that he always assumes holes and shifts the atomic numbers upwards, till the rule fits. In this way he has the general tendency to assume too many holes in the periodic system and too high values for the atomic numbers.

After the lecture of Professor Bohr I only briefly mention Rydberg's idea of a relation between the parity of multiplicity of the spectral lines and the parity of the chemical valence. If the one is even the other is odd and vice versa. However, Rydberg was not sure of this idea being unable to give a general proof of it. The reason for it was first that the order and the resolution of more complicated spectra (as for instance copper) was not sufficiently advanced at that time to determine correctly this multiplicity. Secondly the difference between spark spectra and arc spectra made complications, as it was not known at that time that the first are emitted by ions. Only much later it became clear that the rule holds without exception if the chemical valence is replaced by the number of electrons in the emitting atom. This exact rule of alternation ("Wechselsatz") was called after Rydberg by Sommerfeld.

A further progress in the order of the periodic system was made by Rydberg in his paper "Elektron, der erste Grundstoff" of 1906 (3). Here (p. 11) he said for the first time that the 3 numbers 2, 8, 18 for the periods in the system of the elements are represented by 2.1^2, 2.2^2, 2.3^2. There was still some uncertainty about the number of the rare earths, which Rydberg assumed to be 36 instead of 32. His atomic numbers were still too high but not as high as in his earlier papers.

In a big paper "Untersuchungen über das System der Grundstoffe" of 1913 (4) he goes one step further. After the quotation of the earlier formulas $2 = 2.1^2$, $8 = 2.2^2$ and $18 = 2.3^2$ he goes on (§ 3): "the continuation would be $2.4^2 = 32$, $2.5^2 = 50$ etc." This is the famous formula $2p^2$ (p integer) which Sommerfeld called "cabbalistic" in his book "Atombau und Spektrallinien" and which impressed me very much as a student. Definitely he says now about "the group G_4" ($p = 4$, rare earths) that it consists of 32, not of 36 elements.

There is an important difference of interpretation between Rydberg's paper of 1913 and the one usual today. He called the numbers $2p^2$, which determine the distance between two noble gases, "a half group" and its double 4.1^2, 4.2^2 ... $4p^2$ "a whole group". He was lead to this interpretation by the fact, that the periods 8 and 18 occur twice in the system. And he was convinced, that the same holds for the first group corresponding to $p = 1$, which he believed to consist of four, not of two elements. The value 4 for the atomic number of He seemed to him supported by spectral lines in the nebulae and in the corona, which he ascribed to two hypothetical new elements which he called Nebulium and Coronium.

All this can be seen in Figure 1 taken from Rydberg's paper (4) of 1913, showing his representation of the periodic system in spiral form. The "half" and the "whole" group correspond here to the proceeding of 180° and 360° respectively. All holes in the system are entirely correct now, so that Rydberg's atomic numbers differ from He on from the true ones only by the constant difference of two, due to his mentioned assumption of the two elements Nebulium and Coronium between H and He. Now we know, that the lines in question are all due to ionized atoms of known elements, the nebulium lines to ionized oxygen and nitrogen, the corona lines to very highly ionized iron.

Rydberg got Moseley's famous paper in manuscript before it was printed and was glad about the confirmation of his old idea (1897) of the importance of the atomic number and of the details of his representation of the periodic system. But in a note (5) about Moseley's paper in 1914 he still maintained the mentioned difference of two and his hypothesis of two new elements between H and He.

With this note Rydberg's publications seem to have been terminated. As I heard, his health did not permit him to follow anymore the subsequent development until his death in 1919. So this brief historical survey naturally comes to a conclusion with the dawn of the new era in our understanding of the spectra, inaugurated by Bohr's work of 1913, which contained his famous revolutionary postulates of the quantum theory of atomic structure. But Rydberg was not anymore influenced by it.

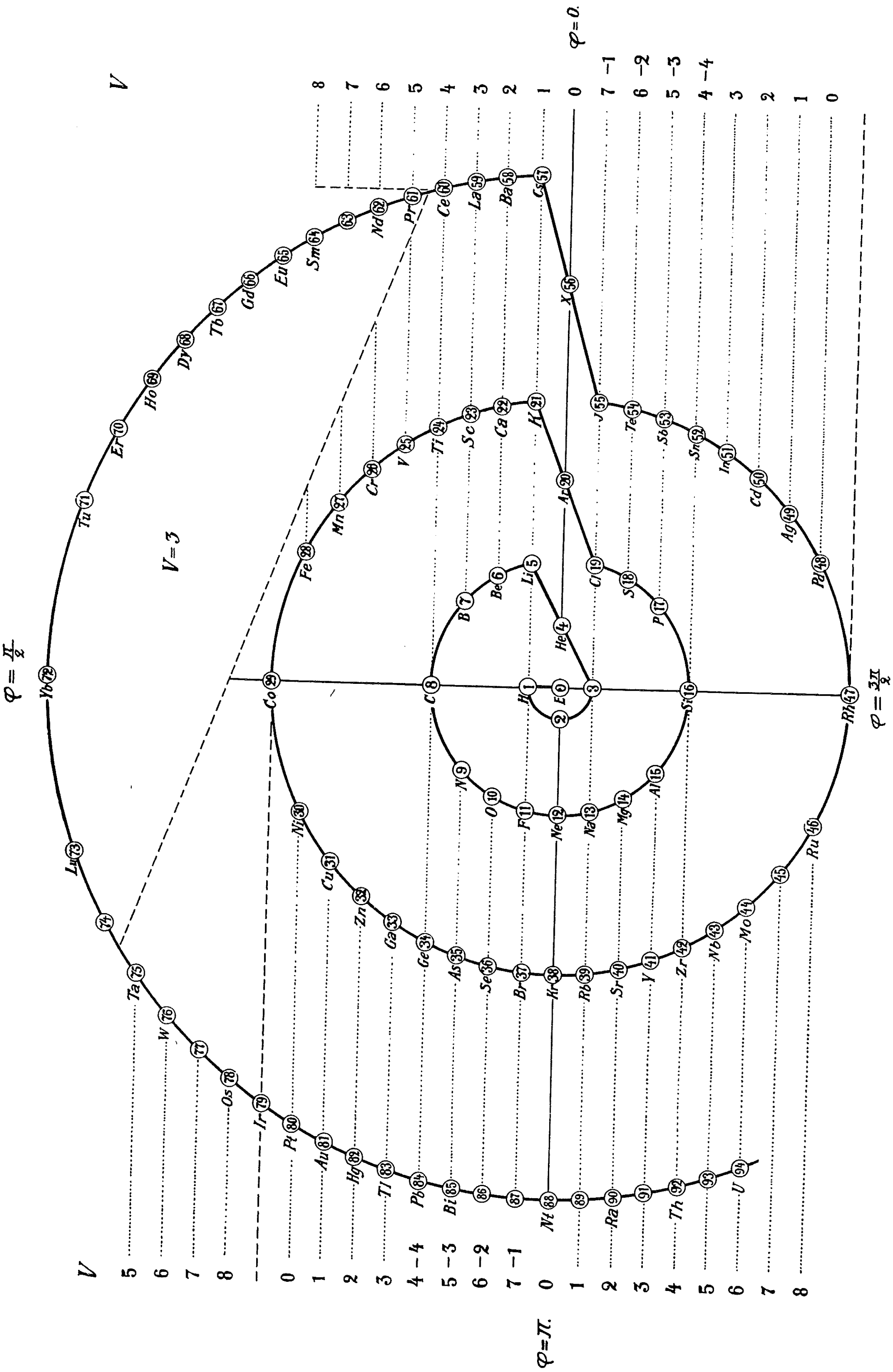

Fig. 1.

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2. "Studien über Atomgewichtszahlen", ZS f. anorg. Chemie *14*, 66 (1897).
3. "Elektron, der erste Grundstoff", Lund 1906.
4. "Untersuchungen über das System der Grundstoffe", Lunds Univ. Årsskrift, Bd *9*, No. 18, 1913. In French: "Recherches sur le système des éléments", Journ. de chimie phys. *12*, 585 (1914).
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