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ON A NEW LAW OF SERIES SPECTRA

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This communication is intended to show how we may derive from the known spectral series of an element, new series which represent accurately, without the inclusion of any new constant, nearly all of the series and lines recently discovered by Lenard, Konen, Hagenbach, Saunders, Moll, Ramage, and Bergmann. The new principle of combination also finds application to other spectra, particularly to helium and the earth alkalies. Closer relationships to the atomic weight than have been known hitherto are also furnished.

In its most convenient form, the series formula proposed by me reads:[1]

$$\nu = A - \frac{N}{[m+\alpha+\beta(A-\nu)]^2}, \qquad (1)$$

where ν is the wave-number referred to a vacuum, N is a universal constant, m the numeral, and A the limit of the series; α and β are constants. For small values of m, ν may become negative, which must be taken into account in the term $\beta(A-\nu)$. The constants α and β characterize the course of the series: they are identical for two series with constant differences.

We also have approximately

$$\nu = A - \frac{N}{\left[m+\alpha+\frac{\beta N}{m^2}\right]^2}. \qquad (2)$$

We use for abbreviation

$$m, \alpha, \beta = \frac{N}{[m+\alpha+\beta(A-\nu)]^2}. \qquad (3)$$

Let the constants α and β have the values d and δ for the pairs of the first subordinate series for instance ("diffuse series" according to Rydberg's notation); for the second subordinate series (Rydberg's "sharp series") let the values be s, σ; for the principal series, let

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[1] *Annalen der Physik*, **12**, 264, 1903. Inaugural Dissertation.

the values be p_1, π_1, and p_2, π_2; for the alkalies $\pi_1=\pi_2$ very approximately.[1]

If the first subordinate series has a satellite, a different set of values, d', δ', applies to the second principal line, where again $\delta=\delta'$, approximately.

The statement of three series may now be written (*loc. cit.*, p. 291): Principal series:

$$\pm\nu=(1.5, s, \sigma)-(m, p_i, \pi_i)\ , \qquad i=1, 2;\ m=2, 3, 4 \ldots\ldots, p_1>p_2\ .$$

Second subordinate series:

$$\pm\nu=(2, p_i, \pi_i)-(m, s, \sigma)\ , \qquad i=1, 2;\ m=1.5,\ 2.5,\ 3.5 \ldots\ldots$$

First subordinate series:

$$\pm\nu=\begin{cases}(2, p_i, \pi_i)-(m, d, \delta)\ , & m=3, 4, 5 \ldots\ \text{(first principal line and satellite).}\\ (2, p_2, \pi_2)-(m, d', \delta')\ , & m=3, 4, 5 \ldots\ \text{(second principal line).}\end{cases}$$

The constant separation of the doublet is $\nu_1=(2, p_1, \pi_1)-(2, p_2, \pi_2)$. On the basis of the observed data now available, the following points may be shown:[2]

1. In the equation of a principal series, if we replace 1.5 by the larger numbers 2.5, 3.5, ... ; and in the equation of a subordinate series, if we replace 2 by the larger numbers 3, 4, 5, ... , new lines will result which have been observed in many cases. This was already suspected by Rydberg.

2. For every symbol (m, α, β) there exists a minimum number m (namely, 3 for the first subordinate series; 1.5 for the second subordinate series, according to the notation of my dissertation already cited), which is a fundamental number; if we assign still smaller values to m, we should expect a stronger line, but in practice this line has not been observed. I have already shown[3] that in no spectrum does an actual line correspond to the numeral $n=2$ of the first

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[1] *Loc. cit.*, p. 291.

[2] The reader will find further particulars in a paper to appear presently in the *Physikalische Zeitschrift.*

[3] *Annalen der Physik*, **25**, 660, 1908; *Physikalische Zeitschrift*, **9**, 244, 1908.

subordinate series, in so far as the observations are adequate on this point.

3. If we form from these symbols the new combination $(1.5, s, \sigma)-(3, d, \delta)$ we obtain new lines which have been observed in case of *He*, *K*, *Rb*, but which are lacking in *Na* and *Li* thus far; for the earth alkalies they fall in the infra-red. The observed value for *He* is $\nu=26244.86$, the observed value is 26244.78.

4. In case of *Li* and *Na*, there has been also observed the combination $(2, p_1\pi_1)-(m, p_1\pi_1)$; $(2, p_2\pi_2)-(m, p_2\pi_2)$; $m=3, 4 \ldots.$

5. If we form $(3, d, \delta)-(m, p_1-p_2, \pi_1-\pi_2)$; $m=4, 5, \ldots.$ then we get the infra-red series found by Bergmann[1] for *K*, *Rb*, *Cs*, and the corresponding lines for *Li*, *Na*, *He*, which were unknown.

For *Rb* and *Cs*, the first subordinate series has a satellite, so that we have further a second series $(3, d', \delta')-(m, p_1-p_2, \pi_1-\pi_2)$, which runs along in the neighborhood of the first, and has a constant difference with respect to this, as was observed by Bergmann, and even earlier by Saunders in case of *Cs*, while for *Rb* the lines could not be separated. The fundamental number for this newly formed symbol $(m, p_1-p_2, \pi_1-\pi_2)$ is $m=4$.

6. The following combinations also exist:

$$(2, p_i, \pi_i)-(m, p_1-p_2, \pi_1-\pi_2)\,, \quad i=1, 2;\ m=4, 5, \ldots.$$

The pair shading toward the violet of *Na*, the corresponding pair of *Cu*, and the series of lines which have been found in *Li* and *Na*, by Lenard, Konen, and Hagenbach, belong here.

$$(4, p_1-p_2, \pi_1-\pi_2)-(m, p_1-p_2, \pi_1-\pi_2)\,.$$

7. Extended investigations, such as exist for the alkalies, are lacking for the earth-alkalies in the infra-red region; and the principal series have not been observed, showing that the test of the principle of combination, in the sense hitherto used, cannot be made at present. The following circumstances, however, indicate that it is also valid here: in the first subordinate series of the series of triplets, with two satellites, we have to introduce the new symbols (m, p_3, π_3), (m, d'', δ'') with $p_1>p_2>p_3$. In the first approximation we may neglect

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[1] Inaugural Dissertation, Jena, 1907; also C. Runge, *Physikalische Zeitschrift*, 9, 1, 1908.

$\pi_1-\pi_2$, $\pi_2-\pi_3$, and compute p_1-p_2, p_2-p_3, from the limits of the subordinate series, in spite of the fact that the principal series have not been observed; p_1-p_2 will be about twice as large as p_2-p_3, and the two differences of the vibration number (designated by Rydberg as ν_1 and ν_2) are

$$\nu_1=(2,\,p_2,\,\pi_2)-(2,\,p_1,\,\pi_1)\ ;\qquad \nu_2=(2,\,p_3,\,\pi_3)-(2,\,p_2,\,\pi_2)\,.$$

There frequently occur double lines, with the distance ν_1, and triplets with the distance ν_1, ν_2, outside of the series. This is to be expected on the principle of combination only, and only when $(2,\,p_i,\,\pi_i)$ are associated with any quantity $(m,\,\alpha,\,\beta)$. These doublets and triplets must therefore belong to series which end at the same point $(2,\,p_i,\,\pi_i)$ as the subordinate series already known, but of which only a few terms of sufficient intensity are to be perceived.

It was further possible to find the equation of the second subordinate series for the strong ultra-violet pairs for *Ca*, *Sr*, *Ba*, for which the difference of the vibration-numbers ν' is to be twice as large as ν_1, and from the elements of these double lines to form the corresponding differences of the constants p, on the assumption that $\pi_1-\pi_2=0$. The distance differs from that of the series of triplets by only about 15 per cent.; in the same exact computation, the two quantities would probably become equal to each other, which would correspond to the principle of combination.

Finally, subordinate series of close triplets have recently been found for *Ca* and *Sr*, by Fowler and by Saunders, from the limits of which again the differences $p'_1-p'_2$, $p'_2-p'_3$, can be formed. Within the limits of accuracy of these, it appears that they are the same as those computed from the satellites and principal lines of the first subordinate series $d-d'$, $d'-d''$, so that a new combination exists here.

It further appears of advantage, in respect to the relations with the atomic weight, to introduce the constants of the formula in place of the wave-numbers, in spite of the fact that this can only be regarded as an approximation. It is well known, for instance, that the quotient of ν_1 and the square of the atomic weight μ does not vary much within a group of chemically related elements; but on the contrary it varies greatly from group to group, from 31.6 for *Cs*, to 187.0 for *Tl*. We introduce $\frac{p_2-p_1}{\mu^2}$ in place of $\frac{\nu_1}{\mu^2}$ and the variation becomes much less.

The discrepancies which still remain are probably due in part to the incompleteness of the series formulae, but particularly to the neglect of $\pi_1-\pi_2$, which certainly is not admissible in the case of *Al, In*, and *Tl*. A knowledge of the principal series of these elements would enable us to decide about this.

Element*	*Na*	*K*	*Rb*	*Cs*	*Cu*	*Ag*	*Mg*	*Ca*
$\frac{\nu_1 103}{\mu^2}$	32.3	37.8	32.3	31.6	61.8	79.0	68.8	66.1
$\frac{p_2-p_1}{\mu^2}10$....	14.2	18.9	18.0	18.6	18.6	24.2	14.6	17.7

Element*	*Sr*	*Zn*	*Cd*	*Hg*	*Al*	*In*	*Tl*	*He*
$\frac{\nu_1 103}{\mu^2}$	51.5	91.0	93.2	115.4	152.8	172.1	187.0	63.8
$\frac{p_2-p_1}{\mu^2}10$....	15.7	17.2	18.6	22.3	24.8	29.2	32.7	20.4

* According to the summary by Rydberg, *Rapports du Congrès de Physique*, Paris, 1900. Tome 2.

It is known that with increasing atomic weight the series fall off with increasing rapidity, so that only those lines are observed which correspond to the lowest numbers of the order. At the same time the number of the different series increases (even *Mg* shows series of double lines and of simple lines in addition to the series of triplets) and the number of combinations increases. Thus we finally reach a spectrum in which we may perceive a large number of characteristic constant differences, but no series. It seems to me very probable that the so-called spectra of the second class which exhibit this behavior are spectra with very many combinations and with very slightly developed series.

The computation of a quantity (m, a, β) assumes a knowledge of the elements of a series in the formula of which it enters. This element may be determined with great accuracy, except when only a few diffuse lines are observed; it is also somewhat independent of the outstanding uncertainty as to the exact form of the equation of the series. In the cases cited under (1), (3), (4), we have indeed to compute exclusively differences and sums of observed wave-numbers; the accuracy is naturally still greater here. But on the other hand the constants entering into the symbol $(m, p_1-p_2, \pi_1-\pi_2)$ may be varied by 20 per cent. without making the difference between computation and observation much worse. On account of their smallness the influence of the constants p_1-p_2, $\pi_1-\pi_2$, is relatively slight compared to that of m, and the series run along nearly parallel with Balmer's series, particularly for *Li*, *Na*, and *He;* for greater atomic weight the observations are hitherto too inaccurate to give us any certainty on this point.

In a paper which recently appeared[1] I have shown that we may cite systems of the simplest sort of which the energy is purely electromagnetic and which observe Balmer's formula, the laws of series and the analogous Zeeman effect, etc. The vibration

$$v=N\left[\frac{1}{4}-\frac{1}{m^2}\right]$$

is produced by the magnetic field of $m-2$ elementary magnets turned toward each other, which are identical among themselves: in addition to this magnetic series the electron is subject to only rigid combinations. Similar facts hold good for other spectra. Higher numbers of the order thus correspond in a certain degree with higher magnetic polymerizations, which constantly become less stable, so that the lines become broader with an increasing number of the order, and also become constantly weaker. Violent motions, such as occur in an electric spark, are also unfavorable to stability, whence the series in the spark cease at lower numbers of the order than in the arc.

The magnetic field in an atom may be regarded in all spectra as produced by two poles of opposite sign, which separately may occupy different positions in the atom. In case of hydrogen, these points lie at equal distances on a straight line. It would appear that we may more generally state the principle that the simple lines refer to or depend upon the positions of these poles in the atom. In (m, a, β) $-(n, a', \beta')$ each of the terms represents the influence of one pole;

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[1] "Magnetische Atomfelder und Serienspektren," *Annalen der Physik*, 25, 660, 1908.

and, as we have shown before, the possible positions of the separate poles permit the most varied combinations of the poles in pairs.

As to a certain minimum prescribed in the number of the order m—which occurs in the case of no known processes of vibration—this mode of representation only affirms that the magnet poles are held by the structure of the atom at a certain minimum distance from the electron vibrating within an atom, an idea which is quite plausible.

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