LUND UNIVERSITY

On the emission spectra of the chemical elements

Rydberg, Johannes (Janne) R

1967

Link to publication

2 On the Emission Spectra of the Chemical Elements†

J. R. RYDBERG

15. The Series of Differences of Wave Numbers

As the numbers n (a) differ from the oscillation numbers only by a constant factor (see above), we can use them instead of these without affecting the form of the functions. It then appears immediately, when these numbers have been arranged in series in the same way as the corresponding wavelengths, that a consider- able improvement has been achieved. Since the beginning of the work, after having tried arranging the lines in series, I always calculated the differences between successive lines, in order to see whether there was any regular variation with increasing ordinal number of the lines. Here I calculated in the same way, but whereas in the former case no relation was detectable between these differences in the various series, either for the same element or for analogous elements, it was here immediately apparent that there is a regularity which can serve as a guide in finding cor- responding lines of different elements. To see this, it is sufficient to examine Table I (b) (Chapter VI), which gives the wave-number series of the alkali metals. We find, for example, that the differ- ences between these numbers for the Li and Na series are in exact agreement:

† Sections 15 and 16 from *Den Kongliga Svenska Vetenskaps Akademiens Handlingar* 23 (11), 1889. Translated by J. B. Sykes.

| Sharp series | | | Diffuse series | | |
| Li | Na | | Li | Na | |
	Series 1	Series 2		Series 1	Series 2
3290·2	3165·6	3159·0	5338·3	5386·7	5386·8
1694·5	1647·0	1655·6	2476·7	2484·9	2477·0
			1349·5	1357·9	1363·9

The analogy is still more striking for the group of elements Mg, Zn, Cd, Hg, where the values of the first two differences are as follows:

First sharp series

Mg	Zn	Cd	Hg
10679·5	11764·0	11090·7	11616·1
4017·2	4312·5	4115·3	4256·3

First diffuse series

Mg	Zn	Cd	Hg
6241·8	5812·3	5871·1	5800·8
2775·3	2636·4	2632·7	2631·8

Thus the difference of the wave numbers of corresponding lines are almost the same for elements of the same group. In order to examine these relations more closely I have calculated the relevant differences, which I denote by Δn, for all the series known to me. It appears that there are numbers of all magnitudes but that the values of Δn in one series are all either larger or smaller than those of the corresponding terms of another series. This will be most clearly seen by means of the following table, which gives the values of Δn for successive lines in most of the series which are known over a fairly wide interval. The series are placed in order of decreasing Δn in the second term, since the first term is not known for all the series. The notation for the series is described in Chapter V. (c)

An examination of the table shows that the terms in all the series decrease quite rapidly with increasing ordinal number, while the values of Δn in a given series as well as in different series become closer. But on comparing the series term by term we find, as already stated, that the difference is always in the same

VALUES OF Δn

Series	Ordinal number of difference							
	1	2	3	4	5	6	7	8
Li[P1,2]	16026·8	5542·4	2556·6	1364·4	824·6	533·8	369·5	258·9
Na[D1]	—	5386·7	2484·9	1357·9	813·9	523·5	—	—
Ca[D1]	—	4996·7	2323·9	1246·3	723·4	—	—	—
Na[P1]	13314·9	4751·4	2280·2	1233·5	—	—	—	—
Tl[S2]	12278·3	4395·1	2089·6	1213·0	732·4	465·6	350·1	250·2
K[P1]	11685·9	4303·8	2050·3	1158·0	723·0	451·8	322·5	245·5
Mg[S1]	10679·5	4017·2	1957·5	1116·5	685·6	—	—	—
Ca[S1]	8943·7	3507·8	1759·3	1015·0	620·6	—	—	—
Na[S1]	7484·8	3165·6	1647·0	962·6	600·1	407·6	—	—
K[D1]	—	2842·7	1507·5	881·2	550·5	385·8	256·9	—
Mg[D1]	6241·8	2775·3	1476·7	868·4	561·4	—	—	—
Zn[D1]	5812·3	2636·4	1416·8	862·7	—	—	—	—

direction. If, therefore, we start from the value 16026·8 and follow the first column downwards, then the remaining columns down to 245·5, we can see that all the values of Δn form a single series of steadily decreasing numbers. There are, however, some exceptions, namely 723·4 in the Ca[D1] series, which is less than the following number 732·4, and the numbers 561·4 (apparently too large) and 256·9 (apparently too small). These anomalies, each occurring in the last term of a series, which is always somewhat uncertain, are well within the limit of error, and probably arise from the inaccuracy of the measurements. Instead of 256·9, for example, the parallel series K[D2] gives 266·9; the two should be equal, and the latter value agrees perfectly with the Δn in adjoining series. To give an idea of the effect of errors of observation, I will quote here the series Zn[D1] as given in the table according to the observations of Hartley and Adeney, and as given by Living and Dewar:

	H.A.	L.D.	Diff.
	5812·3	5792·1	20·2
	2636·4	2621·9	14·5
	1416·8	1409·4	7·4
	862·7	830·6	32·1

The difference is thus greatest in the last term, no doubt because the weakest lines are measured less accurately than the others. With these examples in front of us, we need not be deterred by

the slight anomalies which occur, and can consider that the numbers in the table confirm the following law:

If the series of Δn derived from known series of wave numbers are arranged in order of magnitude of any term, all the other terms in the series will be in the same order. This is true even when any series is shifted relative to the others by increasing or decreasing the ordinal number of each term of the series by a fixed whole number.

This law may also be stated as follows:

All differences between corresponding terms of any two series of Δn have the same sign.

If these series of Δn are imagined to be plotted graphically with the ordinal numbers m of the terms as abscissae and the values of Δn as ordinates, and the resulting points to be joined by continuous curves, the above property simply means that these curves will not intersect at a finite distance; for if they did, the terms of one series would be greater on one side of the point of intersection, and on the other side they would be smaller, than the corresponding terms of the other series, which contradicts the above-mentioned law. A displacement of the series as described above corresponds geometrically to a translation of the curves parallel to the axis of abscissae by an amount equal to a whole number of units of m. After such a translation there are again no points of intersection between different curves. But if this is true for all the curves, it may be regarded as very probable that they also do not intersect during the translation, and that when one curve passes another they coincide exactly. For, if we consider Fig. 2.1, we see the series Zn[D1] in two positions (a and b) differing in the values of m, which in the latter case are one more than in the former. If we suppose that the curve reaches the second position by a translation parallel to the m axis, the table shows it has passed through all the other curves, of which three are shown in the diagram. A glance at these curves will surely show the plausibility of the assumption that all the curves can be made to coincide by translations parallel to the m axis, since, so far as can be judged from the diagram, the difference of abscissae for any two
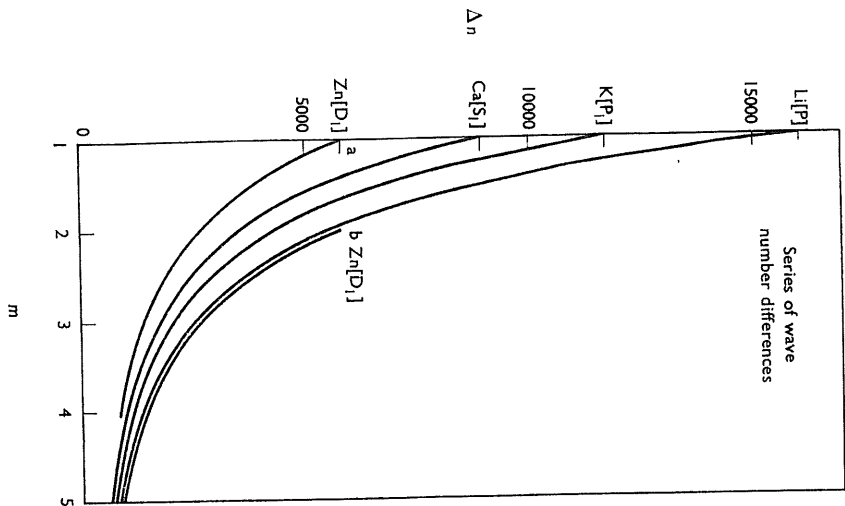
FIG. 2.1

curves is constant for all values of the ordinate. If, contrary to expectation, this assumption is not strictly true, it will at least give a very satisfactory approximation.

Let us therefore suppose that the curves are all of the same shape and differ only in position. If the equation of any one curve is

$$\Delta n = F(m)$$

the other curves will have equations of the form

$$\Delta n = F(m+\mu)$$

where μ is a constant which takes different values for different series, and which shows the distance through which the curve in question must be moved in order to coincide with the first. Thus the general expression for a series of differences becomes

$$\Delta n = F(m+\mu) \qquad (5)$$

where Δn is the wave-number difference of two consecutive terms in a series of lines, m the ordinal number of the difference and μ a characteristic constant of the series. Hence it follows that *the form of the function F and of all the constants except μ is the same for every series.* It must be remembered, however, that our conclusions are drawn from a consideration of the properties of series, and are therefore subject to the same uncertainty as the measurements of the lines forming these series.

16.   The Series of Wave Numbers

We can now return without difficulty to the original series, which consist of the wave numbers of spectral lines. The wave numbers n always increase with the ordinal numbers of the lines, and we have generally

$$n_m = n_{m+1} - \Delta n$$

n_m, being the wave number of the mth line of a series, or, replacing Δn by its value from equation (5) and continuing the series,

$$n_m = n_{m+1} - F(m+\mu)$$
$$n_{m+1} = n_{m+2} - F(m+1+\mu)$$
$$n_{m+2} = n_{m+3} - F(m+2+\mu)$$
$$\cdots \qquad \cdots$$

We have already assumed in section 13,[a] when considering the

series of n, that the value of n continually approaches, at $m = \infty$, a finite limit which we call n_0, and the form of the series of Δn and of the corresponding curves compels us to suppose that the limit of Δn or of $F(m+\mu)$ is zero at $m = \infty$. Adding the respective sides of the foregoing equations, we therefore have

$$n_m = n_0 - \sum_m^\infty F(m+\mu) \qquad (6)$$

where the sum is always finite if n_0 is.
Another series gives similarly

$$n'_m = n'_0 - \sum_m^\infty F(m+\mu')$$

where n'_0, μ' are the constants corresponding to n_0, μ in the previous equation, and n'_m the value of the mth term of the series. The two sums in these equations have the same number of terms, and we know from the previous discussion that any term in one of the sums differs from the corresponding term in the other sum only by the value of μ. Thus one sum is changed into the other if μ is replaced by μ', and so it follows that they are simply two different values of the same function of μ. Putting

$$\sum_m^\infty F(m+\mu) = f(m+\mu)$$

the equation for the wave numbers of a series of spectral lines can be written

$$n = n_0 - f(m+\mu) \qquad (7)$$

where n is the wave number of any line, m its ordinal number, and n_0 and μ two characteristic constants of the series, the form of the function and any other constants involved being the same in all the series.

The form of the curves which represent the series of n shows that they probably have two asymptotes, one parallel to the n axis as already described (the line $n = n_0$), the other parallel to the n axis. For $n = n_0$ we thus have $m = \infty$ or

$$f(m+\mu) = 0 \qquad \text{for} \qquad m = \infty$$

The asymptote parallel to the n axis must have the form

$$m + \mu + C = 0$$

C being a constant which, from the preceding discussion, has the same value for every series. Since the absolute magnitude of the constant μ is undefined, we can include the constant C in it, and the equation of the asymptote parallel to the n axis will be

$$m + \mu = 0$$

whence

$$f(m+\mu) = \infty \qquad \text{for} \qquad m + \mu = 0$$

The simplest function which meets these conditions is

$$f(m+\mu) = C_0/(m+\mu)$$

where C_0 should be a constant common to all the series. The resulting equation for n, namely

$$n = n_0 - C_0/(m+\mu) \qquad (8$$

is just equation (2) of section 13,

$$(n - n_0)(m+\mu) = C_1$$

where $\mu_1 = \mu$ and $C_1 = -C_0$. We have already considered this formula, which does not fulfil the condition of always giving the same value of the constant C_1; this may be seen by comparing the values of this constant in the series given as examples in section 13. The considerable differences which exist between theory and observation have shown that this formula is invalid.

Let us therefore consider the next simplest formula,

$$n = n_0 - N_0/(m+\mu)^2 \qquad (9)$$

where N_0 is a constant. I was just in the course of examining this equation when I saw Herr Balmer's calculation of the hydrogen spectrum. I then examined the formula used by Balmer, namely

$$H = hm^2/(m^2 - 4)$$

where H is the wavelength, m the ordinal number of the line and h

a constant. If we replace wavelengths by wave numbers, putting

$$H = 10^8/n, \quad h = 10^8/n_0,$$

we find

$$n = n_0(m^2 - 4)/m^2$$

or

$$n = n_0 - 4n_0/m^2$$

This is clearly the same equation as (9) if $N_0 = 4n_0$, $\mu = 0$, which shows that Balmer's formula is a particular case of equation (9). Since Balmer's formula is known to give an entirely satisfactory description of the elementary spectrum of hydrogen, we have reason to think, *a priori*, that our equation (9) will be more suitable than the previous equation (8).

Notes

(*a*) n denotes the wave number, which is related to the oscillation number or frequency ν by the expression $n = \nu/c$. In Part 1 we use the symbol $\bar{\nu}$ for wave number.

(*b*) Table I is not reproduced here. It consists of a list of the wave numbers of the spectral lines of the elements. Modern data of this kind can be readily found from tables of term values (Charlotte Moore, *Atomic Energy Levels*, Vols. 1, 2, 3, 4, National Bureau of Standards, U.S.A.). Many books on atomic spectra (e.g. Kuhn, Bibliography to Part 1) give simplified tables of term values for a number of elements.

(*c*) Rydberg's notation for series is no longer used. The modern equivalents with subscripts omitted where Rydberg did not distinguish fine structure components are:

Rydberg notation	Modern notation	Rydberg notation	Modern notation	Rydberg notation	Modern notation
Li[P$_{1,2}$]	Li:$2^2S_{1/2}$–n^2P	Tl[S$_2$]	Tl:$6^2P_{1/2}$–$n^2S_{1/2}$	Na[S$_1$]	Na:$3^2P_{3/2}$–$n^2S_{1/2}$
Na[D$_1$]	Na:$3^2P_{3/2}$–n^2D	K[P$_1$]	K:$4^2S_{1/2}$–$n^2P_{3/2}$	K[D$_1$]	K:$4^2P_{3/2}$–n^2D
Ca[D$_1$]	Ca:4^3P_2–n^3D	Mg[S$_1$]	Mg:3^3P_2–n^3S_1	Mg[D$_1$]	Mg:3^3P_2–n^3D
Na[P$_1$]	Na:$3^2S_{1/2}$–$n^2P_{3/2}$	Ca[S$_1$]	Ca:4^3P_2–n^3S_1	Zn[D$_1$]	Zn:4^3P_2–n^3D

In Rydberg's paper the number given to a member of a series is not the principal quantum number, as in the modern notation for terms, but is merely an identification number.

(*d*) Section 13 is not included in this extract, but this passage is self-explanatory.