NOTES ON BAND SPECTRA BY W. RITZ[1]

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I. MECHANISM OF EMISSION OF BAND SPECTRA

In the paper[2] in which Ritz studies a simple electromagnetic mechanism emitting series spectra, he states on p. 673 (*Œuvres*, p. 112):

> These theories are not applicable to band spectra. I will only say in this connection that they might perhaps be ascribed to closed rings or polygons consisting of the elementary magnets under consideration, on the assumption that such formations play an important rôle in the construction of the atom, and that they must first be touched off by the electrical or chemical processes producing the light before a series spectrum can come into existence.

Among the papers left by Ritz there has been found a small sheet bearing some equations and a rough draft of the theory of this mechanism of emission of band spectra, which I shall attempt to expand.

Let us recall that the organ of emission of *series spectra*, conceived first by him as formed of magnetic and non-magnetic rods, juxtaposed in a straight line, may be realized in different ways. Ritz preferred to regard[3] the small magnetic rods as produced by solids of revolution charged with electricity at their surface and having a rapid rotational motion around their axis. He had taken into account particularly that for any solids of revolution there can be found a superficial distribution of electricity which renders them equivalent to systems of two magnetic poles situated on the axis. When the magnetic poles approach the surface, the electric density increases indefinitely in their vicinity and the surfaces carrying the electricity become practically equivalent to point charges. These solids are alternately positive and negative, and endowed

[1] Note added to the *Œuvres de W. Ritz*, published by the Société suisse de physique, (Gauthier-Villars, 1911). Translated from the MS from M. Weiss.

[2] "Magnetische Atomfelder und Serienspektren," *Annalen der Physik*, **25**, 660, 1908; *Œuvres de W. Ritz*, chap. vii, p. 98.

[3] *Op. cit.*, p. 670.

with rotations in opposite directions. They are fixed each to the other, in the form of a linear chain, by their electrostatic attraction. Ritz had thought that the non-magnetic rods, required also by the theory of series spectra, might be bodies similarly charged but deprived of rotation, and then, going a step farther, that the vibrating electron and the free electric pole at the extremity of the file of rods are one and the same thing.

Disregarding now the non-magnetic rods, let us consider a file of magnetic rods. We may assume that when it is subjected to a tension α^2 it is capable of vibrating in a manner analogous to that of a cord, or rather that of a chain.

There prevails along this cord a magnetic field H directed lengthwise, and it carries equidistant electric charges. Let us assume that these charges set up circular vibrations around the axis under the combined influence of the tension α^2 and the field H. (Ritz's notes say nothing in regard to the reason why the effect of the field on the adjacent positive and negative charges does not neutralize them. We may perhaps invoke for this purpose a difference of configuration of the positive and negative charges, which has been assumed elsewhere. Those occupying a more extended place would be, for example, partially outside the field.)

The vibratory state is then expressed by

$$\left.\begin{aligned} y&=A\sin\frac{\mu\pi x}{a}\sin\nu t \\ z&=A\sin\frac{\mu\pi x}{a}\cos\nu t \end{aligned}\right\} \qquad (1)$$

where a is the distance between two consecutive knots for the fundamental vibration, and $\nu:2\pi$ the frequency. The equations of motion of an element of cord, dx, of mass μdx, and of charge ϵdx, will contain the term of inertia and the forces proceeding from the magnetic field and from the tension of the cord:

$$\left.\begin{aligned} \mu\frac{\delta^2 y}{\delta t^2}+\epsilon H\frac{\delta z}{\delta t}-\alpha^2\frac{\delta^2 y}{\delta x^2}&=0 \\ \mu\frac{\delta^2 z}{\delta t^2}-\epsilon H\frac{\delta y}{\delta t}-\alpha^2\frac{\delta^2 y}{\delta x^2}&=0 \end{aligned}\right\} \qquad (2)$$

from which, substituting (1), twice the same equation:

$$\mu\cdot\nu^2+\epsilon\cdot\nu\cdot H-\frac{\mu^2\pi^2}{a^2}\alpha^2=0 \tag{3}$$

in which H can also be replaced by $-H$, then

$$\nu=\pm\frac{\epsilon H}{2\mu}\pm\frac{\epsilon H}{2\mu}\sqrt{1+\frac{4m^2\pi^2\mu}{\epsilon^2H^2a^2}\alpha^2}\,. \tag{4}$$

The solutions corresponding to the two positive signs and to the two negative signs are alone acceptable. In placing $\frac{4\pi^2\alpha^2\mu}{\epsilon^2H^2a^2}=k^2$, a number which is small when the tension of the cord has a subordinate rôle with respect to the field, we have

$$\nu=\frac{\epsilon H}{\mu}\left[1+\frac{m^2k^2}{4}-\frac{m^4k^4}{16}+\ldots\right]. \tag{5}$$

For $m=0$, we find the frequency of a charge describing a circle in the field H. If we stop with the second term, we have Deslandres' law, with $\nu_0=\frac{\epsilon H}{\mu}$ for the head of the band. If we retain the third term, ν increases less rapidly, as experiment requires.

Ritz is here brought to choose between a rectilinear file and a closed ring. He gives the preference to the latter in the following terms: "If there are two extremities, the lines would have to be first simple ($m=1$, 2 . . . .), for as m increases, the different vibrations will correspond accordingly as we are at the extremities or the center. Consequently, circular ring."

Since ν increases with m, the band has the head on the red side. To obtain decreasing values, it is necessary to assume α^2 negative. The ring, instead of being extended, is compressed in the direction of the periphery.

The separation between two consecutive lines is given from the complete formula (4) by

$$\frac{d\nu}{dm}=\frac{\nu_0}{2}\frac{mk^2}{\sqrt{1+m^2k^2}}\,.$$

It increases more slowly than Deslandres' law indicates, and that is in accord with the experiment. But the separation does not cease increasing. The formula does not give then the maximum of separation of the experiments of Kayser and Runge[1] on the spectrum of cyanogen.[2]

Among some other notes of Ritz there is the trace of numerous attempts to find the best empirical formula with three constants representing these experiments of Kayser and Runge. These notes seem to be prior to his ideas on the electromagnetic origin of spectra and are accordingly only indirectly related to the above. He tries particularly

$$\nu = a + bm^2\sqrt{1+cm^4}$$

and the first three terms of its development

$$\nu = a + bm^2 + cm^6,$$

and finds that the term in m^6 varies too rapidly. He tries

$$\nu^2 = a + bm^2 + cm^4$$

and

$$\nu = a + bm^2 + cm^4.$$

He finds this last formula preferable to the others, and notes in this connection that "*from the 16oth line the functions $\nu = f(m)$ and $\nu^2 = f(m)$ behave in a manner not regular.*"

We shall revert to this point. He tries further

$$\nu^2 = \frac{a+bm^2}{1+cm^2},$$

and the error is a little larger than formerly.

In a conversation Ritz expressed an idea which relates to the mechanism of emission what he calls "the irregular character of the function ν for the lines of high order." He expressed himself about as follows:

There are in certain bands a considerable number of lines whose position is determined with exactness; but, whatever the empirical law by which we

[1] *Wiedemanns Annalen*, **38**, 80, 1889.

[2] The same notebook also contains the following information, referring to another possible solution of the problem, in which the tension α^2 is not involved: "Beyond the constant magnetic field which it produces for its whole length, a ring can still be submitted to exterior magnetic fields, variable from point to point, and weak with respect to the first."

seek to represent the distribution of the lines in these bands, there comes a time when for a number of high order of lines this law fails. If we have recourse to a graphical representation, the curve turns short with an abruptness which the usual formulae do not give.

Let us assume that the part of the atom whose vibrations emit band spectra has a structure analogous to that of a chain composed of links of known length. One would understand then very well that the vibrations are produced for the greatest part of the phenomenon as if the chain were a continuous structure, while for wave-lengths of nearly the same length as the link (or for certain particular values in relation with it) the numbers of vibrations are influenced by the finite length of the element.

II. STRUCTURE OF THE BANDS

To the question, "Is it not established that the bands have sometimes two 'heads,' one on the side of large wave-lengths and the other on the side of small wave-lengths?" (hypothesis of Thiele[1]), Ritz replied merely, "That idea is not tenable."

The tables of numbers found in his notes show that this conviction is based also on the study of the bands of cyanogen observed first by Kayser and Runge,[2] and later by Jungbluth,[3] with heads at λ 3883.56, 3871.53, 3861.85, and 3854.85.

In a few words the status of the matter is this: King,[4] having discovered new heads directed from the side of short wave-lengths, has believed it possible to consider them as "tails" corresponding to the "heads" previously known, and has associated them by making the bands overlap each other. As a proof of this coordination, he gives numerical relations between the wave-lengths of the heads and tails. They are contained in the following table:

T_n	Q_n	T_n/Q_n	T_n	Q_n	T_n/Q_n
3590.52	3203.84	1.12069	3883.60	3465.69	1.12059
3585.99	3180.58	1.12746	3871.59	3433.17	1.12770
3584.10	3160.32	1.13409	3861.91	3405.04	1.13417

The value of this table as a demonstration seems to me small. According to Deslandres' law, which is applicable to the heads of

[1] *Astrophysical Journal*, **6**, 65, 1897.

[2] *Wiedemanns Annalen*, **38**, 80, 1889.

[3] *Astrophysical Journal*, **20**, 237, 1904.

[4] *Ibid.*, **14**, 323, 1901.

bands of a series, as well as to the lines of a band, the distances between the successive heads, measured on a scale of frequencies, form an arithmetical progression. Suppose that we associate two series of bands turned in opposite directions, and both obeying this law, but entirely independent as to their origin. If the ratios of the two arithmetical progressions are close, as frequently happens,[1] the distances between the heads and tails will also form an arithmetical progression (criterion of dependence quoted by Jungbluth). It will be the same whatever two bands are taken to start with; and this will happen according as the ratios will be of the same or of contrary sign, when the first bands are displaced in the same or in contrary sense.

In the first approximation, the quotient of the frequencies will vary, in the same cases, in arithmetical progression. This is what King finds. In regard to the great similarity of the series of successive bands, we should not know how to attach any importance to the fact that this quotient passes twice approximately through the same three values.

This argument appears, nevertheless, to have had sufficient weight in the conviction of Kayser,[2] who considers it certain that King has found the tails corresponding to the heads, and that consequently the hypothesis of Thiele is correct.

Jungbluth proposes to test this hypothesis by making new measures on a part of the bands formerly known. To discuss them (Fig. 1),[3] he uses as abscissas the wave-lengths, and as ordinates the difference of wave-lengths of two successive lines. The curves which he thus obtains for four of the bands of cyanogen proceed from their heads T_1, T_2, T_3, and T_4 in an approximately parabolic manner, which corresponds to Deslandres' law $\nu = A + (Bm+C)^2$, where ν is the frequency and m a whole number; but for the lines of high orders the curve is distinctly below the parabola and the separation of the consecutive lines passes even through a maximum. These experimental curves are continued in dots and

[1] Ch. Fabry, *Journal de physique*, **4**, 245, 1905.

[2] *Handbuch der Spectroscopie*, **2**, 487.

[3] The figure given here is Jungbluth's redrawn on the basis of the tabular values contained in his paper.

seem to end naturally, in the original drawing by Jungbluth, for the last three bands with tails Q_2, Q_3, Q_4 indicated by King. For the first, there being no head according to King in the region where Jungbluth expects it, he carries the curve on and thus determines

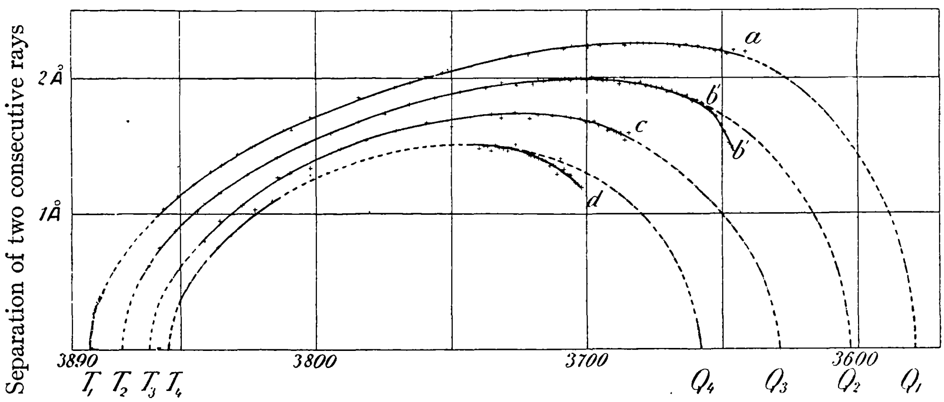

FIG. 1

the position of the tail Q_1 in a region where it is not observable on account of the presence of an intense band.

Omitting this, we have:

Heads according to Jungbluth	Heads according to King	Assumed Tails
T_2 3871.53	4152.93	Q_2 3603.12
T_3 3861.85	4158.22	Q_3 3628.98
T_4 3854.85	4165.54	Q_4 3658.27

The co-ordination of the heads and tails according to Jungbluth is therefore in direct contradiction to that of King. Moreover, according to Jungbluth, the complete bands of King overlapping each other are replaced by bands fitting one within the other (Fig. 2).

FIG. 2

Jungbluth, who expressly notes this circumstance, does not fear to add that, taken in connection with the numerical relations of King, it brings a new confirmation to King's views.

To discover exactly what is the import of the experiments of Jungbluth, I have marked on the drawing (Fig. 1) the points observed. The experimental part, in heavy line, ends for the four bands in *a*, *b*, *c*, *d*. For two of the bands, at *b*, and at *d*, it is separated from the part extrapolated by Jungbluth, represented by a dotted line, by a greater curvature, seeming to confirm the idea of Ritz, and rendering impossible the assignment of the tails made by Jungbluth.

But if we compare the experiments of Jungbluth with that of Kayser and Runge, the agreement which is good as far as b' ceases. It is easily seen that Jungbluth has at b' passed inadvertently to the lines of a neighboring band, which are placed in respect to those that he has followed to that point somewhat as the lines of a vernier are to those of the principal scale. Moreover, Jungbluth suppressed in his drawing the portion $b'b$. Definitively for the four bands, the correlation between the heads and tails is admissible rigorously for two of them (T_2-Q_2; T_3-Q_3).

Ritz's idea of the irregular nature of the function ν for the lines of high order which rests on the sharpness of the turn at b' has in part as its origin an error of Jungbluth.

It seems, nevertheless, that as a result of the paper by Jungbluth the conviction has become general that the hypothesis of Thiele is correct. In 1905 A. Hagenbach[1] expressed this in a monograph on band spectra. It has not been remarked that in reality the *conclusions* of Jungbluth at the end of his paper are much less affirmative than his *curves*.

We find in Ritz's notes the following: "The tails according to King, particularly the one at λ 3603, are impossible, because they are composed of lines relatively intense with almost *constant differences*, while the differences ought to increase very rapidly toward the head of the band."

This remark is very probably suggested by an examination of the plate of Kayser and Runge[2] on which it is easy to recognize the appearance described by Ritz. It is possible to measure the distance of the lines to about 0.5 Å, which carries the arc of the

[1] *Wüllner-Festschrift*, 133, 1905.

[2] *Akad. Berlin. Phys. Abh. nicht zur Akad. gehör. Gelehrter*, 1, 44, 1889.

corresponding curve well outside the limits of the figure. The same is visible on the plate of Jungbluth (*op. cit.*).

This argument seems definitively to destroy what remains of probability in the assumptions made by Jungbluth. We have already done justice incidentally to the argument which Jungbluth deduces on the ground that the *lengths* of the bands vary in arithmetical progression. Let us mention that, on the contrary, Ritz notes carefully, as an important fact, the arithmetical progression, pointed out by Jungbluth, of the maxima separations of the lines of the four bands (2.25; 2.00; 1.75; 1.5 Å). This fact retains its value independently of every hypothesis as to the existence of one head or of two heads.

We may then conclude that the hypothesis of Thiele is strengthened by:

1. The existence of heads directed in the two senses.
2. The existence of a maximum in the separation of the lines.

But we have not been able to continue the demonstration of this hypothesis up to the present time, either by the possibility of co-ordinating without confusing the heads and tails, or by pursuing the decrease of the distance of the lines in an interval sufficiently extended beyond the maximum. The separation of the lines in the region of the tail at λ 3603 disproves it strictly.

Ritz's idea is not in contradiction with the facts. But the indications in his favor which remain with regard to the four bands of cyanogen are slightly diminished after suppressing the faulty part, $b'b$, of Jungbluth's.

It would be of great interest to make new determinations on bands composed of a large number of lines and, perhaps, to resume the discussion of the data already found.

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