THE MATHEMATICAL STRUCTURE OF BAND SERIES II.

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SYNOPSIS.—In the first article of this series, the author proposed a hyperbolic formula, for the accurate representation of long band series. The present paper initiates a more general discussion of this formula, and of the experimental results which the author has since obtained.

Detailed analytic work has shown the new formula accurate, within limits of experimental error, for those band series showing the most radical deviations from the simple Deslandres' law. Preliminary work indicates that the hyperbolic formula is equally satisfactory in the case of series showing positive deviations from Deslandres' law, instead of the customary negative deviations.

A complete investigation of any band series is greatly facilitated by a preliminary study of its deviations from Deslandres' law. New methods have accordingly been developed for making this comparison in a rapid, yet accurate manner. In particular, there is developed a new Least Squares' formula, giving directly the value of the only desired constant in a Deslandres' formula, thus avoiding the more extended calculations necessary when all three constants are simultaneously evaluated.

A comparative study of band and line series formulæ suggests for band series a modified hyperbolic formula. This modified formula has been tested on several series and has been found very satisfactory. New line series formulæ are also suggested, but are not seriously recommended at this time.

INTRODUCTION.

IN the first paper on this subject,[1] there was proposed a new formula for band series, together with the detailed quantitative results for the main (A_1) "singlet" series of the 3883 CN. band. It was shown also that preliminary work indicated that the formula would hold equally well for the other series of this band. In particular, the singlet series from the third head (C_1 series) exhibits the most radical deviations from Deslandres' law of any known band series. It therefore forms a crucial test for any new formula. This series has since been extended at both ends, the new lines having been identified from the author's own spectrograms. The complete quantitative results for this series were presented to the American Physical Society at the October, 1917, meeting.[2]

Certain remarkably systematic irregularities in the C_1 series, brought out by these computations, made it seem desirable to study also the B_1 series. This work has now been completed, much of the actual computing

[1] Astrophysical Journal, 46, 85–103, 1917. In the future, it will be referred to as I.
[2] PHYS. REV., (2), 11, 136, 1918.

having been done by an assistant, for whose services the author is indebted to the Rumford Committee of the American Academy of Sciences. At the same time, a general survey was made of practically all band series which seemed to show large deviations from Deslandres' law. A very considerable amount of material, both quantitative and qualitative, has now been collected, and it has seemed desirable to present a general review of the progress of the work to date. Such detailed results as appear of sufficient importance will be published later.

The present communication includes:

1. A discussion of methods of handling band series formulæ, in particular, Deslandres' parabolic formula.

2. A new viewpoint as to the original hyperbolic formula, together with a possible alternative formula in which the necessity of making a summation is avoided.

In the next paper there will be presented a review of typical band series, especially of those showing radical deviations from Deslandres' law, in a positive, as well as in a negative sense.

The Mathematical Analysis of Band Series.

It is well known[1] that all band series seem to conform to Deslandres' law[2] for at least an initial portion of their extent. The investigations of the author have convinced him that *no* band series strictly obeys Deslandres' law over *any* portion of its extent. But for short series (*i. e.*, series covering a small frequency interval) the deviations from this law may easily be far less than the experimental errors.[3] The first step however in the examination of any given series consists in determining how closely it conforms to the simple Deslandres' formula. Various methods for doing this have been used by previous investigators, but no general discussion of the matter has yet been published.

Deslandres' formula, in its original form,[4] states that the frequencies of successive lines of a band series are given by the parabola

$$\nu = \nu_0 + am + bm^2 \tag{1}$$

or

$$\nu = A + B\,(m + c)^2, \tag{1'}$$

[1] For the most complete summarized description of all bands discussed in this series of articles, see Konen, "Das Leuchten der Gase und Dämpfe," pp. 199–278.

[2] Deslandres, Comptes Rendus, 103, 375, 1886.

[3] It may be remarked in passing that the amount of deviation from Deslandres' law seems to have no connection with the spectral extent of the series, nor with the number of terms in the series. Some series of 100 or more terms show a scarcely perceptible deviation, others of the same length a most radical deviation. Many series of few terms (30 or less) but of large spectral range also show radical deviations.

[4] For discussion see I., pp. 86–87.

where m takes successive integral values 0, 1, 2, 3, etc.[1] The successive first frequency differences are then given by the straight line

$$\Delta\nu = a + 2bm = 2B(m + c), \tag{2}$$

where m has the successive *fractional* values 0.5, 1.5, 2.5, etc., while the second frequency differences are given by the constant

$$\Delta\rho = 2b = 2B. \tag{3}$$

Any series for which the second frequency difference is constant therefore, per se, obeys Deslandres' law, and the first obvious method of testing this law is to compute these second differences.

But because of experimental errors, true perturbations, etc., these differences will never be constant, and in many cases it is difficult to tell from mere inspection whether they exhibit any definite trend from constancy. A far more delicate method of detecting any such trend, if present, is to plot the first frequency differences against m, on a fairly large scale. (50 × 50 cm. is recommended.) This curve, by Deslandres' law, should be a straight line, of slope $2b$ (*i. e.*, secondary frequency difference), and intercept ($\Delta\nu = 0$) $m = -a/2b = -c$. The author has called it the "slope" form, and has found it to be actually an hyperbola.

In practically all long series the slope curve exhibits a very definite trend from linearity. Yet in instance after instance investigators have analytically fitted the series to a Deslandres' formula, and have concluded that the agreement was satisfactory, when the slope curve (*if* it had been plotted) would instantly have shown the falsity of such a conclusion.

But let us assume that a casual inspection of the $\Delta\nu : m$ curve does not indicate any definite non-linearity. This condition is more likely to arise when the experimental errors are rather large (over 0.02 A). A case in point is the main series of the 3371 Nitrogen band, which Lewis[2] extended, by using self-induction in the circuit, until it entered the next band at 3159 A. The $\Delta\nu : m$ curve for this band is apparently a straight line and the equation given by Lewis is the best obtainable when the simplified Deslandres' formula

$$\nu = A + Bm^2 \tag{4}$$

[1] Comparing (1) and (1′) $b = B$; $c = a/2b$; $\nu_0 = A + Bc^2$. There seems to be some confusion as to just what is to be considered the "head" of a band. The ordinary idea, stated implicitly if not explicitly, is that this head is given by the line corresponding to $m = 0$, in any satisfactory formula. The author has tried in I. to follow consistently this usage. But (1′) is often written $\nu = \nu_0 + B(m + c)^2$. This makes ν_0 (the head) correspond to $m = -c$. I doubt if anyone actually thinks of the head in that way, and so the form is objectionable. Of course when $c = 0$, the two view-points become identical.

[2] Astrophysical Journal, 40, 148, 1914.

is used. As has been remarked[1] (4) is *not* Deslandres' law, and its use is permissible only when the inaccuracy of the data makes the true determination of the intercept ($-a/2b = -c = -$ "the phase") impossible. In this case, the data *are* rather inaccurate, but a slight improvement can be made by using (1′) rather than (4).

The problem now becomes,—what is the best analytical method of handling the experimental data, in order to determine whether or not the Deslandres' formula holds, *i. e.*, whether a straight line is really the best simple smooth curve that can be passed through the experimental points of the $\Delta\nu : m$ plot, and if so, what is the slope of this curve? This problem is identical with that of determining the constancy of the acceleration of gravity, and its value, if constant, given the position of a series of crests on an Atwood's Machine curve, but with the time and point of initial descent not known. For this latter problem we have

$$s = s_0 + \nu_0 t + 1/2gt^2 \tag{5}$$

or

$$s = (s_0 - \nu_0^2/2g) + g/2(t + \nu_0/g)^2, \tag{6}$$

i. e.,

$$s = \alpha + \beta(t + \lambda)^2, \tag{6'}$$

where λ = the "phase," *i. e.*, the fractional part of a second before $t = 0$ at which descent began.[2] In the case of Deslandres' law, (1) and (1′) correspond to (5) and (6′) respectively.

If a study of the actual plotted data, together with a knowledge of the experimental conditions, indicates that the deviations of the data from any simple smooth curve are due solely to chance experimental errors, then the method of Least Squares leads to the "most probable" values of the constants of the equation of the curve. In the case of spectral series, the conditions necessary for the legitimate application of Least Squares are actually present,—*i. e.*, in a well-measured series, using the new International standards, there is practically no opportunity for unsuspected systematic errors of any appreciable amount.

The full details of the method of Least Squares, as applied to the Deslandres' formula, are given by V. Carlheim-Gyllensköld.[3] The necessary calculations are, however, rather extended, especially in the case of long series. Moreover we do not, at the outset, wish to assume the truth of Deslandres' law. Instead, we wish to investigate whether or not the

[1] I., p. 89.

[2] I. e., we assume $t = 0$ for the nearest even second to the time of starting, just as in band series we choose m so as to make c (the "phase") some fraction less than 0.5. This may possibly be the analogy Thiele had in mind when he called c the "phase." The question of the origin of the term has recently been raised. (Proc. Phys. Soc. of London, 30, 130, 1918.)

[3] Svenska Vet. Ak. Handl., 42 N : r 8, 1907.

best smooth $\Delta\nu : m$ curve has a constant slope or a varying slope. But in the case of a long band series, such as the 3371 N series, the method of Least Squares can be applied, with great advantage, to this problem as well. For we may break up the $\Delta\nu : m$ curve into several sections, and determine, by Least Squares, the most probable value of the slope for each section. With 30 or more lines to a section, the probable error of this procedure is far less than that of any graphical method,—a fact which is frequently overlooked, but which the present series of investigations has repeatedly demonstrated.

The author has tried also various approximate methods for computing the second difference and of testing its constancy, but has come finally to the conclusion that the Least Squares solution is the only really feasible procedure in a case like that under consideration, where a plotted $\Delta\nu : m$ curve does not definitely indicate any curvature. Fortunately however it has been possible to very considerably reduce the amount of necessary calculations, so that the Least Squares method becomes but slightly longer than various approximate methods.

In equation (1) we have three undetermined coefficients, but in this particular case, we are interested only in the value of b. Moreover, the variable m takes on the regular series of values 1, 2, 3, etc. Now in the case of the simpler equation

$$y = A + Bx \tag{7}$$

it is possible to compute directly, by Least Squares, the value of B, when $x = 1, 2, 3, \ldots, n$. In fact[1]

$$B = \frac{(n-1)(y_n - y_1) + (n-3)(y_{n-1} - y_2) + ,\ \text{etc.}}{1/6n(n^2-1)}. \tag{8}$$

The "physical meaning" of (8) is that we are to combine the first and last observations, the second and next to last, etc., and each difference thus obtained is to be multiplied by a factor equal to the length of the interval (in terms of the corresponding change in x). Finally, we divide the numerator by the total number of corresponding changes in x. Thus for 6 observations, (8) can be written

$$B = \frac{5(y_6 - y_1) + 3(y_5 - y_2) + (y_4 - y_3)}{5^2 + 3^2 + 1^2}. \tag{8'}$$

In the case of equation (1), it is to be expected that a similar formula for the value of b can be derived. But so far as the author has been able to ascertain, no such formula has been published. Accordingly this work has been carried out, and the desired expression obtained. As is to be

[1] See Kohlrausch, "Physical Measurements," p. 17 (English translation of 7th German edition).

expected, the necessary reductions and the final result are much more complicated than in the case of (7) and (8). This result is

$$b = \frac{30}{n(n^2-1)(n^2-4)}\Sigma\{(y_r+y_{n+1-r})(A+[r-1]B+6[r-1][r-2])\}, \quad (9)$$

where $A = (n-2)(n-1)$,

$B = 6(2-n)$,

n = number of observations (y) [$y = \nu$ of (1)],

$r = \begin{cases} 1, 2, 3, \ldots\ n/2 \text{ for } n \text{ even.} \\ 1, 2, 3, \ldots\ (n+1)/2 \text{ for } n \text{ odd.}[1] \end{cases}$

Thus for $n = 6$, we have

$$b = \frac{5(y_6+y_1)-(y_5+y_2)-4(y_4+y_3)}{56}. \quad (9')$$

For $n = 5$

$$b = \frac{2(y_5+y_1)-(y_2+y_4)-2(y_3)}{14}. \quad (9'')$$

The "physical meaning" of (9) is this: The coefficients of the first and last observations, the second and next to last, etc., are the same. Hence the readings may be combined in pairs, as in the case of (8). (But note that the pairs of observations are added while in (8) they are subtracted.) The successive coefficients of these pairs of observations follow a parabolic law, in which the second difference is constant (= 12). Hence the calculation of the coefficients is very simple. In (9) A is the initial coefficient, and B the initial first difference. Thus formula (9) may be written

$$b = \frac{30}{n(n^2-1)(n^2-4)}\{A(y_1+y_n) + (A+B)(y_2+y_{n-1}) + (A+2B+12)(y_3+y_{n-2}) + (A+3B+36)(y_4+y_{n-3}) + \text{, etc.}\}. \quad (10)$$

In applying (9) to the N3371 series, the 84 observed frequencies (all weighted equally) were divided into two equal sets. For the first 42 (small m's) we obtain $b = 3.681$; for the second 42 (large m's) $b = 3.605$.[2] The mean is 3.643, very close to Lewis' value of 3.634, using the simplified equation (4).

Because of the large number of observations, the probable error in these results is very small. There is thus clear evidence of a variation

[1] Note that for *n odd*, the last term in the summation contains but *one y, i. e.*, $y_{n+1/2}$ with the coefficient $(1-n)(1+n)/2$.

[2] The best approximate methods which the author has been able to devise give for the first 42, $b = 3.645$ or 3.660; for the last 42,—3.585 or 3.555,—showing the uncertainty of the methods.

of slope of about 2 per cent. But since 3.681 is the probable slope at the center of the first half of the series, while 3.605 applies to the center of the second half, we have a probable total variation, over the entire extent of the observations, of about 4 per cent. It is thus evident that the second difference *decreases*, and that the series shows deviations from Deslandres' law in the *negative* sense. Moreover, we have thus detected this 4 per cent. variation in a case where a really good analytic fitting of Deslandres' formula reveals practically no trace of systematic deviations. Even when such deviations *do* appear in the analytic work, they are difficult to interpret. This 3371 series has been used for illustration because it is the only really long series, among those studied, which from the plotted $\Delta\nu : m$ curve *seemed* to obey the parabolic law.

In the case of more complex formulæ, such as the hyperbolic law proposed by the author, it is practically necessary to use the ordinary methods of calculation. After plotting the data and drawing the best smooth curve through the results, a number of points on this curve, equal to the number of arbitrary constants in the assumed formula, are chosen and the theoretical curve is made to pass through these points, by solving the simultaneous equations of condition. The Obs-Calc value for each observation is then calculated and plotted (as ordinate). A smooth curve is drawn through the results (the so-called "Residual Plot" [1]). The object is then to "warp" the x-axis until it fits this smooth curve as well as possible. With practice one can predict roughly whether it is possible to so warp the axis as to give a really good agreement. The criteria depend entirely upon the form of equation used, and general rules cannot be given. Each warping means, of course, the determination of a new set of constants. In the case of the hyperbola, four trials are usually sufficient, if the data are all equally trustworthy. For the B_1 and C_1 series of the 3883 CN band, many more trials were necessary, since the systematic deviations, to be discussed later, made it difficult to determine, at first, just what would constitute the best agreement. Much time was thus lost trying to do (in the light of future knowledge) quite impossible things.

Also, the hyperbolic formula refers to the $\Delta\nu : m$ curve. The Obs-Calc values are however calculated and plotted for the $\nu : m$ curve. The warping of the x-axis of the Residual Plot then consists in giving it a definite new *slope* (*i. e.*, a definite new $\Delta\nu$) at selected points, and solving, instead of giving it a definite new *ordinate*. The judging of the proper slope is far more difficult than the judging of the proper ordinate, and this is the one real objection to the use of the "slope" form of the equa-

[1] Goodwin, Precision of Measurements, p. 60.

tion. But the greater simplicity of this form more than compensates. The fact that, for the proposed hyperbolic formula, the $\nu : m$ equation is a summation, instead of an integral, is an objection to this particular formula but not to the use in general of the $\Delta\nu : m$ curve, rather than the $\nu : m$ curve.

The Hyperbolic Formula, and a Possible Alternative Form.

As shown in Fig. 2, page 92 of I., the $\Delta\nu : m$ curves[1] for the A_1, B_1, and C_1 series of the 3883 CN band look very much like hyperbolæ, instead of the straight line demanded by Deslandres' formula. These three series have now been found to fit accurately hyperbolic curves, save for certain systematic perturbations (previously known) and for small systematic irregularities, newly discovered. These latter amount to a change of frequency of only one part in 300,000 as a *maximum*, and so are inconsequential as far as the general form of the curve is concerned. Aside from the real periodic irregularities, the observed and computed curves agree to at least 0.005 A throughout a series 200 A long, *i. e.*, on a $\nu : m$ curve extending ten feet in each direction, the agreement is to less than 0.1 mm. throughout, indicating the great accuracy of the hyperbolic formula.

The deviations from Deslandres' law in all of these series are in a *negative* sense, in that the successive frequency differences increase *less* rapidly than demanded by the law, *i. e.*, the second differences *decrease*. Series of this type will be referred to as *negative series*, and bands containing them as "bands of the negative type." The phrase "negative bands" is already in use, with a distinctly different meaning. In I. the statement was made that in only one band are series known in which the deviations are in a contrary sense, *i. e.*, the 2370 band of air. This statement is quite incorrect. At the time of discovery, these 2370 series *were* the only known examples of what we shall call *positive series*. Since then a number of similar series have been found. It is these series which the author has been particularly studying. In the 2370 band there are four

[1] In all detailed quantitative work, the author has used the frequency in vacuo, but for the qualitative work to be described in the following paper the reduction to vacuo is not necessary and has not been made. Wave-lengths should never be used, except incidentally. In this connection it might be added, since it seems not known everywhere, that there is published a table of reciprocals (Cotsworth's Reciprocals,—McCorquodale and Co., London.) giving to seven figures the reciprocals of all numbers to 100,000. By linear interpolation to hundredths one can obtain the reciprocal of any 7 figure quantity to seven figures. The maximum error is one unit in the last figure, the probable error considerably less than half a unit. The rule for interpolating the seventh figure, as given in the tables, is obviously incorrect. The author has found it more convenient to use a slide rule for all interpolations. When a succession of adjacent frequencies is desired, as in a band series, each can be obtained in a very few seconds,—quite as rapidly, in fact, as by the use of the best calculating machines.

positive series, and four negative series. We shall call such a band a "*neutral band.*" At present the 2370 band is I believe the only known example.

In the only detailed study of this band,[1] a very good drawing but no data on the observed wave-lengths are recorded. (Schniederjost[2] resolves only a few lines of this band.) The only data given are the Obs-Calc values for every fifth line, for four of the series, together with the equations used. With this data it is possible to work back to the observed frequencies, for every fifth line, and thus to determine roughly the form of the $\Delta\nu : m$ curves. These curves show but slight deviations from a straight line, the maximum variation in slope being about 9 per cent. (for the II_2 and IV_2 series). That is, the final slope (highest m) is about 109 per cent. or 92 per cent. respectively, of the initial slope (at $m = 0$). The $\Delta\nu : m$ curve for the A_1 series of the 3883 band has been given in Fig. 2 of I. (page 92) and for convenience in comparing other series the slope at various points, in terms of the initial slope (*i. e.*, the relative second frequency differences) is given herewith.

$m =$ 0	100 per cent.	$m =$ 101	76.5 per cent.
21	98 per cent.	121	61.5 per cent.
41	95 per cent.	141	29.0 per cent.
61	91 per cent.	151	14.0 per cent.
81	85.5 per cent.	156.5	0 per cent. (max. $\Delta\nu$)

In respect to the magnitude of the departure from Deslandres' law, the 2370 series are thus not in a class with the 3883 series, or with many others studied, and the fitting of them to a six constant equation, such as that proposed by the author, would be a simple matter. The striking point about these 2370 series is however the fact that four of them show positive deviations, and four negative, and the deviations in corresponding series are *equal.* This shows that if the *negative* series are hyperbolic (and the $\Delta\nu : m$ curves look quite similar to the initial portion of the A_1 3883 curve) the *positive* series are *also* hyperbolic. It also suggests a new point of view on the entire subject.

We have assumed in I. that the hyperbolic law is due to the fundamental field of force of the molecule (all spectroscopists now agreeing that band series are due primarily to molecular structure, rather than to atomic). Let us assume however that the *tangent to the* $\Delta\nu : m$ *curve at* $m = 0$ represents this fundamental field of force, *i. e.*, a Deslandres' law, and that the deviations from this straight line indicate disturbing effects. Let us denote any $\Delta\nu$ on the straight line by $\Delta\nu_s$ and any $\Delta\nu$

[1] Deslandres and Kannapell, Comptes Rendus, 139, 584, 1904.

[2] Zeitschrift für wiss. Photographie, 2, 265, 1904.

on the hyperbola by $\Delta\nu_n$. Let $\Delta\nu_s - \Delta\nu_n = D$. Then if the $\Delta\nu_n : m$ curve is truly an hyperbola, the $D : m$ curve will also be an hyperbola (and conversely) since we have made only a linear transformation of variables in which the derivatives $ab - 4c^2$ remains invariant. (The transformation is mathematically the same as that from fixed to moving axes.) Moreover, the curve in $-D$ and m is also an hyperbola, by symmetry, and thus the curve in $\Delta\nu_s - (-D) = \Delta\nu_p$ is an hyperbola. (The converse transformation of variables.) Thus the four *positive* series ($\Delta\nu_p : m$ curves) are hyperbolæ, if the four *negative* series ($\Delta\nu_n : m$ curves) are. Also, we can state that the systematic deviations (D) from the fundamental field of force of the molecule (assumed to be such as to give a Deslandres' law) are of such nature as to yield hyperbolic $D : m$ curves, instead of saying that the field of force is such as to yield hyperbolic $\Delta\nu : m$ curves. The two statements are actually only different ways of viewing the phenomena, for the physical facts are the same, in either case.

The chief use that has been made of the above ideas is in the handling of positive series. It is difficult to recognize the hyperbolic form, in such series, and I have therefore drawn the tangent at $m = 0$, reversed the deviations (D) from this line, and drawn the resulting curve, thus obtaining the corresponding negative $\Delta\nu : m$ curve. This curve, in all cases, has appeared to be hyperbolic, as nearly as could be judged by mere inspection. This procedure also gives a simple method of judging, in the case of positive series, how radical are the departures from Deslandres' law. In only one series (one of those in the 3064 water band) does the corresponding negative $\Delta\nu : m$ curve extend past the point of maximum $\Delta\nu$. In this one case it has about the extent of the A_1 3883 curve. Thus no positive series shows anything like the deviation of the C_1 3883 series.

The so-called positive series are thus found (qualitatively, at least) to be no exception to the hyperbolic law, but to represent simply *positive* hyperbolic deviations from Deslandres' law, instead of *negative* deviations. Needless to say, the structure of *positive* band series is somewhat different from that of *negative* series. The former has no point of maximum $\Delta\nu$ and no "tail." The remarks on page 101 of I. should therefore be considered as applying only to *negative* series.

The hyperbolic law proposed by the author has the form

$$\Delta\nu^2 + B\Delta\nu . m + Cm^2 + D\Delta\nu + Em + F = 0, \qquad (11)$$

where $F = 0$ for the A_1 3883 series.

Solving for $\Delta\nu$ we have

$$\Delta\nu = -Bm/2 - D/2 \pm \sqrt{\left(\frac{B^2-4c}{4}\right)m^2 + \left(\frac{BD}{2} - E\right)m + \frac{D^2}{4} - F}, \quad (12)$$

where $m = 0.5, 1.5, 2.5$, etc., and the negative sign before the radical is to be used. Then

$$\nu_n = \nu_0 + [\Sigma\Delta\nu]_{m=0.5}^{m=n-0.5}. \quad (13)$$

Since $\Delta\nu$ is given by an hyperbola we might write (13) as

$$\nu = \nu_0 + \Sigma \text{ hyperbola}. \quad (14)$$

As explained in I., pages 100–101, the best convergent series that approximates this function is probably

$$\nu = a + bm^2 - cm^4 + dm^6, \text{ etc.}, \quad (15)$$

which Kilchling[1] uses as an empirical formula, but which Ritz[2] derived on theoretical grounds.

The formal analogy between line and band series has frequently been pointed out. The approximate formula for line series (Rydberg) is

$$\nu = \nu_\infty - \frac{N_0}{(m+\mu)^2}, \quad (16)$$

or

$$\frac{N_0}{\nu_\infty - \nu} = (m+\mu)^2. \quad (17)$$

The approximate formula for band series is

$$\nu = A + B(m+\mu)^2 \quad (1')^3$$

or

$$\frac{\nu - A}{B} = (m+\mu)^2. \quad (18)$$

(18) and (17) have the same functional form, and hence the formal analogy, previously stated by various authors. The following suggestions however are believed to be mainly original.

There seem to be two possible methods of modifying the $f(m)$ occurring in (17) and (18), in order to obtain more accurate formulæ. (1) Compute successive differences, in (17) and (18). This gives

$$\Delta\left(\frac{N_0}{\nu_\infty - \nu}\right) = 2(m+\mu), \quad (19)$$

$$\Delta\left(\frac{\nu - A}{B}\right) = \frac{\Delta\nu}{B} = 2(m+\mu). \quad (20)$$

[1] Zeitschrift für wiss. Photographie, 15, 293, 1916.

[2] Ritz (Weiss) Comptes rendus, 152, 585, 1911, or Astrophysical Journal, 35, 75, 1912.

[3] Here, as explained, A is *not* exactly equal to ν_0 (the true head) but differs from it by Bc^2. In giving the formal analogy between line and band series, equation (1′) is usually written with ν_0 in place of A. But to avoid inconsistency, this has not been done here.

But the author has found that $\Delta\nu$ = hyperbola, instead of $\Delta\nu$ = straight line. By analogy we might expect for line series

$$\Delta\left(\frac{N_0}{\nu_\infty - \nu}\right) = \text{hyperbola}. \tag{21}$$

The other method is (2) Compute the square roots of (17) and (18). This gives

$$\sqrt{\frac{N_0}{\nu_\infty - \nu}} = m + \mu, \tag{22}$$

$$\sqrt{\frac{\nu - A}{B}} = m + \mu. \tag{23}$$

In the case of line series, this second procedure has always been followed. The $\sqrt{N_0/\nu_\infty - \nu}$ instead of being a straight line, is actually a much more complex $f(m)$. Nicholson[1] concludes that it must be some $f(m + \mu)$. Ritz uses $f(m) = m + a + b/m^2$. Hicks uses $m + a + b/m$. Nicholson,[1] in order to get accurate agreement for even the simple Helium series, has had to use

$$m + \mu + \frac{a}{m + \mu} + \frac{b}{(m + \mu)^2} + \frac{c}{(m + \mu)^3}.$$

But *possibly* this $f(m)$ is an hyperbola. By analogy we would have, for band series,

$$\sqrt{\frac{\nu - A}{B}} = \text{hyperbola}, \quad \text{or} \quad \nu = A + (\text{hyperbola})^2, \tag{24}$$

where B has been incorporated into the hyperbola. By comparing (24) with (14) it is seen that we have thus replaced the summation by a square, and have thus greatly simplified the necessary calculations.

Formula (24) has been carefully tested on the A_1 and C_1 series of the 3883 band. It *seems* to fit these series almost as well as does (14). More trials might possibly result in an equally good agreement. If either the A_1 or C_1 series were slightly longer, it would be possible to decide definitely between the two formulæ. The C_1 series extends much further (in terms of curvature) than the A_1, but because of the greater size of the perturbations and other irregularities of the C_1 series, there is a greater uncertainty as to the best position of the theoretical curve. The two formulæ can be made to give practically identical results for small values of m, but not for larger values.

The methods of handling the two formulæ are quite different, but only the following brief statement will be made at this time. With formula (24) it is possible to handle the data directly in terms of ν and m.

[1] Proc. Roy. Soc., (A), 91, 255, 1915.

But since the computations necessary in solving six simultaneous equations are several times as extended as those necessary for five, the author has preferred to work with the hyperbola, *i. e.*, with the curve in $\sqrt{\nu - A}$ and m. Now the experimental values of $\sqrt{\nu - A}$ are indeterminate, since A is as yet unknown. In the case of line series [compare (22) with (23)] it is possible to determine ν_∞ with great accuracy, regardless of the type of function used. The same thing is roughly true for A in band series. Any simple formula, such as Deslandres', applied to the known smaller values of m, will give an approximate value of A. It is moreover known that the curve in $\sqrt{\nu - A}$ and m must approach linearity, with decreasing m, since all band series approach Deslandres' law in this region, and this curve is very sensitive to small changes in A, when m is small. It is thus possible to determine accurately the value of A, necessary to get even approximate linearity. All computations can be made with a 20-inch slide rule. It is not necessary to have a good agreement between the observed and computed $\sqrt{\nu - A} : m$ curves, for m small, since in this case a relatively large change in $\sqrt{\nu - A}$ produces a relatively small change in $\nu - A$. The converse is true for large values of m, so that in this region the observed and computed $\sqrt{\nu - A} : m$ curves must agree very exactly.

By using the above method, the time required to determine a given set of constants is the same for the two formulæ. But for the new formula the time required for testing the constants is far less, and this constitutes, with the old formula, the major portion of the work. Since either of the formulæ give practically satisfactory results for the 3883 series, it is immaterial which form is used, in testing other simpler series. But since the original form allows the data for the hyperbolic curve $(\Delta\nu : m)$ to be computed directly from the observations, this form has been used in all the general work to date. Each form has six coefficients, or five, if the hyperbola cuts the origin.

In lines series, by analogy, we would have instead of (22)

$$\nu = \nu_\infty - \frac{N_0}{(\text{hyperbola})^2}. \qquad (25)$$

The author has plotted the experimental curves, for certain well-known line series, in terms of $\Delta(N_0/\nu_\infty - \nu)$ and m, and also in terms of $\sqrt{N_0/\nu_\infty - \nu}$ and m. The hyperbolæ (if either of the curves are such) are reversed, compared to band series, approaching linearity for large values of m, while the vertex occurs near the origin.[1] Unfortunately, line series do not

[1] The limiting slope ($m = \infty$) equals *two*, for the first form, or *unity*, for the second, regardless of the equation used, and thus should be the same for all line series, if N_0 is truly a universal constant. (Rydberg Constant). In band series one finds a great diversity of nitial slopes and there is no such corresponding universal constant.

yield themselves to graphical methods, for if an error of 0.01 A in term $m = 2$ is represented by, let us say, 0.01 mm., an equal error in $m = 30$ may be represented by about 5 mm. or more.

The author is not prepared, at the present time, even to suggest the use of either (21) or (25) for line series. The present trend of line series work is to derive formulæ directly from theoretical considerations. Because of the recent success of such efforts, by the use of various modifications of the Bohr atom,[1] it does not seem desirable to introduce any new purely empirical formula. In the case of band series, we should expect, from theoretical considerations, a formula of the type of (14) rather than of (24), since any application of the quantum idea must involve a summation, implicitly if not explicitly.

Addendum.

The author has just received a reprint of a long paper by T. Heurlinger entitled "Untersuchungen Uber Die Struktur der Bandenspektra" (Lund, 1918). A small portion of Heurlinger's work duplicates work (unpublished) of the author. In general however the ground covered is different. Heurlinger is not primarily interested in a new type of formula. He uses simply the power series (15), or a modification, and compares the numerical constants, for the various series. His main object is to relate together all the series in any one band, or group of bands, and to thus formulate general rules regarding band structure. The paper contains several ideas on band structure, radically new, but very suggestive, and apparently supported by a large amount of experimental evidence. The author intends to discuss these ideas more fully in a future paper.

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[1] See particularly H. S. Allen, Proc. London Phys. Soc., 30, 127, 1918. Vegard, Phil. Mag., 35, 293, 1918. Ishiwara, Proc. Math. Phys. Soc. of Tokio, (2), 8, 106, 1915; (2), 8, 173, 1915; (2), 8, 540, 1916; (2), 9, 20, 1917; (2), 9, 160, 1917.