

The Theory of the Band Spectra of PH and NH

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The theoretical formulae for the effect of molecular rotation on spin multiplets are considered for triplet cases. The form of the "swelling" term in D is found for the limiting case a , and its importance is evident in the explanation of the experimental observations on PH and NH. Formulae are given, from which the molecular constants A , B and D can be calculated. This has been done for the

two examples mentioned, moreover for PH the Λ -type doubling has been calculated from the theoretical formulae derived by Hebb, and is found to agree well with experiment. The explanation of the observations on NH necessitated considering an appreciable ρ -type tripling in the ${}^3\Sigma$ level, which has not been observed before.

1. INTRODUCTION

THE rotational distortion of spin multiplets was first considered by Kemble,¹ using the methods of the old quantum theory. The next step was taken by Hill and Van Vleck,² who started from Hund's case b type³ of coupling, and, with the new quantum mechanics, found the energy formulae and amplitudes for the general case which has a type of coupling intermediate to cases a and b . A later development by Van Vleck⁴ took case a as the unperturbed system and for doublet and triplet states, obtained formulae identical with the formulae of Hill and Van Vleck. They have been applied with considerable success to the explanation of doublet spectra, but little has been done towards the explanation of triplet spectra. This is largely because the formulae are not put in suitable form for direct comparison with experiment. The energy values, which are the roots of a cubic equation, have been given in the form of expansions, but these are valid only for certain regions of convergence, and do not provide a very satisfactory test of the theory. These energies can be evaluated by a numerical method, provided the molecular constants are first determined with considerable accuracy.

In this paper expressions are obtained from the coefficients of the equation, which is cubic in the energy value, which give the molecular constants B , D and A , for all values of the rotational

quantum number J . In calculating these constants we do not take into account the terms which give rise to the Λ -type doubling. The best test of the theory occurs in the determination of the constant A . The expression which is derived for A is peculiarly sensitive to errors in the values of B and D , and in the case of NH it showed the necessity of taking account of a slight splitting of the Σ levels.

2. THE MATRIX OF THE D TERM

It can be shown from simple classical considerations⁵ that the total rotational energy for a case b type of coupling, can be written in the form

$$W_r = BN^2 + DN^4 + \quad (1)$$

where N is the nuclear angular momentum. The value of N is given in terms of the rotational quantum number K and the quantized component Λ of the orbital angular momentum along the electric axis, by

$$N = (K(K+1) - \Lambda^2)^{\frac{1}{2}}. \quad (2)$$

We take W_r as the form of the unperturbed energy, when the coupling between the spin angular momentum and the electronic orbital angular momentum of the molecule conforms to case b . In future we shall take a factor B out of the matrices, including those matrices which were given by Hill and Van Vleck, and Van Vleck, and we shall write

$$\lambda = A/B, \quad \mu = D/B. \quad (3)$$

The unperturbed energy for case b will therefore give a diagonal matrix

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¹ E. C. Kemble, *Phys. Rev.* **30**, 387 (1927).

² E. Hill and J. H. Van Vleck, *Phys. Rev.* **32**, 250 (1928).

³ An account of the different coupling cases is given in the article by Hill and Van Vleck, reference 2; cf. also R. S. Mulliken, *Rev. Mod. Phys.* **2**, 105 (1930).

⁴ J. H. Van Vleck, *Phys. Rev.* **33**, 467 (1929).

⁵ R. S. Mulliken, *Rev. Mod. Phys.* **2**, 99 (1930).

$$H_{r,b} = N^2 + \mu N^4. \quad (4)$$

The perturbing matrix H_p , has been given by Hill and Van Vleck. We shall not require the explicit values of its elements, but simply observe that they will have λ as a constant factor. The solution of the problem in the general case will then be given by the solution of the set of linear equations

$$W(r; r)S(r; r') - \sum_l iH_b(l; r')S(r; l) = 0; \quad (5)$$

where
$$H_b = H_{r,b} + H_p; \quad (6)$$

and
$$\sum_l S(r; l)S^*(r'; l) = \begin{cases} 0 & \text{if } r' \neq r \\ 1 & \text{if } r' = r. \end{cases} \quad (7)$$

Van Vleck has set up the matrix corresponding to a case a type of coupling, and has shown that (5) transforms over to this case for doublet and triplet states, when $A \rightarrow \infty$. We shall write this matrix for case a

$$H_a = H_{r,a} + H_0. \quad (8)$$

H_0 comes from the interaction of the spin and electronic angular momentum and has the form

$$H_0 = \lambda \Lambda \Sigma. \quad (9)$$

The matrix $H_{r,a}$ is independent of λ . If we let S_1

be the matrix which carries (4) over into case a , and \tilde{S}_1^* be the transpose of the conjugate of S_1 , then

$$H_a = S_1 H_b \tilde{S}_1^*. \quad (10)$$

Using the expressions (6) and (8) in Eq. (10) and equating the terms in λ to zero, we find

$$H_0 - S_1 H_p \tilde{S}_1^* = H_{r,a} - S_1 H_{r,b} \tilde{S}_1^* = 0. \quad (11)$$

The expression on the left equated to zero serves to define S_1 . Then substituting the value of $H_{r,b}$, given by (4), into the second of the Eqs. (11), we obtain

$$\begin{aligned} H_{r,a} &= S_1 N^2 \tilde{S}_1^* + \mu S_1 N^4 \tilde{S}_1^* \\ &= H + \mu H^2; \end{aligned} \quad (12)$$

where we use H to denote the matrix $S_1 N^2 \tilde{S}_1^*$ whose elements have been given by Van Vleck. The addition to that theory is found in the presence of the matrix μH^2 , which occurs when the effect of the terms in D is taken into account. This result serves to show that the main contribution of these terms to the energy, for case a type of coupling, is of the diagonal form $DJ^2(J+1)^2$, corresponding to the fact that the main contribution of the terms in B is of the form $BJ(J+1)$.

3. FORMULAE FOR ${}^3\Pi$ STATES

We first give the elements of the matrix H_a for a ${}^3\Pi$ state. In order to simplify the algebra later, we subtract from the diagonal elements the value of

$$\frac{1}{3} \text{Spur } H_a = J(J+1) - \frac{1}{3} + \mu \{ J^2(J+1)^2 + 4J(J+1) + 5/3 \}; \quad (13)$$

we then find,

$$\begin{aligned} H_a(\Pi_0; \Pi_0) - \frac{1}{3} \text{Spur } H_a &= -\lambda + 4/3 + 2\mu J(J+1), \\ H_a(\Pi_1; \Pi_1) - \frac{1}{3} \text{Spur } H_a &= 4/3 + 4\mu \{ J(J+1) - 1 \}, \\ H_a(\Pi_2; \Pi_2) - \frac{1}{3} \text{Spur } H_a &= \lambda - 8/3 - 6\mu \{ J(J+1) - \frac{2}{3} \}, \\ H_a(\Pi_1; \Pi_0) = H_a(\Pi_0; \Pi_1) &= [1 + 2\mu \{ J(J+1) + 1 \}] \{ 2J(J+1) \}^{\frac{1}{2}}, \\ H_a(\Pi_2; \Pi_1) = H_a(\Pi_1; \Pi_2) &= [1 + 2\mu \{ J(J+1) - 1 \}] \{ 2J(J+1) - 4 \}^{\frac{1}{2}}, \\ H_a(\Pi_2; \Pi_0) = H_a(\Pi_0; \Pi_2) &= 2\mu \{ J(J+1) - 2 \}^{\frac{1}{2}} \{ J(J+1) \}^{\frac{1}{2}}. \end{aligned}$$

The existence of terms proportional to $\mu = D/B$ in the diagonal elements of H_a shows that in the limiting case a the effect of the D terms on the energy is not simply $DJ^2(J+1)^2$ for all three components, as usually assumed in the literature. Instead this effect is not quite the same for all components, the difference being of the order $DJ(J+1)$, and the apparent triplet separation is accordingly modified to this extent by centrifugal expansion.

The energy levels for the general intermediate case between cases a and b , will be given by the roots of the equation⁴

$$|(W/B)\delta(\Sigma; \Sigma') - H_a(\Sigma; \Sigma')| = 0, \quad \Sigma, \Sigma' = -1, 0, 1. \quad (14)$$

The constants B and D

Using Eqs. (14) and (13), we find

$$\text{Spur } W(J) = B \text{ Spur } H_a = -(B-5D) + 3(B+4D)J(J+1) + 3DJ^2(J+1)^2. \quad (15)$$

$$\text{Therefore, writing } \Delta_2(J) = \text{Spur } \{W(J+1) - W(J-1)\} = \text{Spur } W(J+1) - \text{Spur } W(J-1), \quad (16)$$

$$\text{we obtain } \Delta_2(J)/6(2J+1) = B+4D+2D(J^2+J+1). \quad (17)$$

The values of $\Delta_2(J)$ can readily be found from the experimental data by using the difference combinations for the Π_0, Π_1, Π_2 levels,

$$\begin{aligned} W_A(J+1) - W_A(J-1) &= Q_1(K+1) - O_1(K+1) = S_3(K-1) - Q_3(K-1), \\ W_B(J+1) - W_B(J-1) &= R_2(K) - P_2(K). \end{aligned} \quad (18)$$

The values of B and D can then be found by plotting $\Delta_2(J)/6(2J+1)$ against $J(J+1)$, and interpreting the slope and the intercept of the straight line according to Eq. (17). As has been mentioned in the introduction, Eq. (17) will have some small additional terms which give rise to the Λ -type doubling and consequently the results will be slightly different according as the A or the B levels are considered. This is not of much consequence in the cases considered subsequently.

The coupling constant A

After making the transformation

$$E = W/B - 1/3 \text{ Spur } H_a, \quad (19)$$

Eq. (14) becomes

$$-E^3 + \alpha E + \beta = 0; \quad (20)$$

where

$$\begin{aligned} \alpha &= \lambda^2 - 4\lambda + (4/3) + 4J(J+1) + 8J(J+1)\{2J(J+1)+1\}\mu \\ &\quad - 4\{2J(J+1)-1\}\lambda\mu + 16J^2(J+1)^2\{J(J+1)+1\}\mu^2, \\ \beta &= -(4/3)\lambda^2 + (4/3)\lambda + 16/27 + (8/3)J(J+1) + (\text{terms in } \mu). \end{aligned}$$

The values of E can be found from the differences

$$E_i = (1/B)(W_i - \frac{1}{3} \text{ Spur } W) = (1/B)(Q^{i_1, 2, 3} - Q^{i_1, 2, 3}). \quad (21)$$

We here use the suffixes i and j , which have the values 1, 2, 3, to designate the energies or term values of the Π_0, Π_1 , or Π_2 states.

Analogous relations can be obtained from the other branches. This would give a method for determining the constant A , as Eq. (17) is quadratic in λ . It is, however, possible to determine λ by a simpler method, which is probably more accurate, as it does not depend upon the readings of so many term values. This is to use the identity

$$\frac{3}{4}(E_1 - E_3)^2 + \frac{1}{4}\{(E_1 - E_2) - (E_2 - E_3)\}^2 \equiv (\text{Spur } E)^2 - 3 \sum_{i, j=1, 2, 3} E_i E_j = 3\alpha, \quad (22)$$

which gives the relation

$$\begin{aligned} \frac{3}{4}B^{-2}(W_1 - W_3)^2 + \frac{1}{4}B^{-2}\{(W_1 - W_2) - (W_2 - W_3)\}^2 &= 3(\lambda - 2)^2 - 8 + 12J(J+1) \\ + 24J(J+1)\{2J(J+1)+1\}\mu - 12\{2J(J+1)-1\}\lambda\mu &+ 48J^2(J+1)^2\{J(J+1)+1\}\mu^2. \end{aligned} \quad (23)$$

The terms on the left-hand side of this equation can be calculated from the experimental data. $W_1 - W_2$ and $W_2 - W_3$ are the separations between the Π_0 and the Π_1 components, and the Π_1 and the Π_2 components, respectively, for a given value of J . $W_1 - W_3$ is the sum of these separations, and is therefore what is known as the over-all spin-multiplet width. These differences are given by

$$\begin{aligned} W_1(J) - W_2(J) &= P^1(J+1) - P^2(J+1) = Q^1(J) - Q^2(J) = R^1(J-1) - R^2(J-1), \\ W_2(J) - W_3(J) &= P^2(J+1) - P^3(J+1) = Q^2(J) - Q^3(J) = R^2(J-1) - R^3(J-1). \end{aligned} \quad (24)$$

The value of μ has previously been determined, and so $(\lambda - 2)^2$ can be evaluated for different values of J . The term in $\lambda\mu$ in Eq. (23) is small, and hence an approximate value of λ can be introduced without causing much error. We naturally expect to find the values of $(\lambda - 2)^2$ constant, if the particular molecule considered has a type of coupling intermediate to cases *a* and *b*.

When the constants λ and μ have been calculated in the manner indicated, a good check on the agreement with experiment can be obtained by calculating the values of E from Eq. (20). This can readily be done by a numerical method.

4. COMPARISON WITH EXPERIMENT

The $\lambda 3400$ band of PH

This band was analyzed by Pearse⁶ and shown to consist of nine branches, representing $^3\Pi \rightarrow ^3\Sigma$ transitions. The graph in Fig. 1, drawn according to Eq. (17) gives the values, $B = 8.024$ and $D = -5.42 \cdot 10^{-4}$. The values of A calculated for different values of J from Eq. (23) were found to remain nearly constant. The average value was taken to be $A = -115.4$. In Table I are given, the values of E calculated from Eq. (20), with the values of the constants given above, and also the values of E found from the experimental data by the relations (21). The agreement of the values of E determined from experiment and theory is good for all values of J , although the terms in μ in the coefficients α and β in Eq. (20), and terms giving rise to the Λ -type doubling, have not been taken into account.

TABLE I. Comparison of experimental and theoretical results.

J	EXPERIMENTAL RESULTS			THEORETICAL RESULTS		
	E_1	E_2	E_3	E_1	E_2	E_3
2	16.59	0.81	-17.41	16.46	0.96	-17.42
3	17.33	0.72	-18.04	17.22	0.84	-18.06
4	18.24	0.61	-18.85	18.19	0.70	-18.88
5	19.33	0.48	-19.81	19.31	0.55	-19.86
6	20.54	0.38	-20.91	20.57	0.42	-20.98
7	21.72	0.27	-22.12	21.98	0.29	-22.27
8	23.23	0.18	-23.41	23.40	0.18	-23.58
9	24.68	0.10	-24.78	24.93	0.08	-25.02
10	26.19	0.03	-26.21	26.53	0.00	-26.53
11	27.71	-0.03	-27.67	28.17	-0.08	-28.10
12	29.36	-0.14	-29.22	29.86	-0.14	-29.72

⁶ R. W. B. Pearse, Proc. Roy. Soc. A129, 328 (1930).

The Λ -type doubling for PH has been calculated according to the formulae given by Hebb in the preceding article. In Fig. 3 the full lines join the calculated values for different values of $J(J+1)$, and the experimental values are represented by points. The agreement is good, and particularly striking is the manner in which the

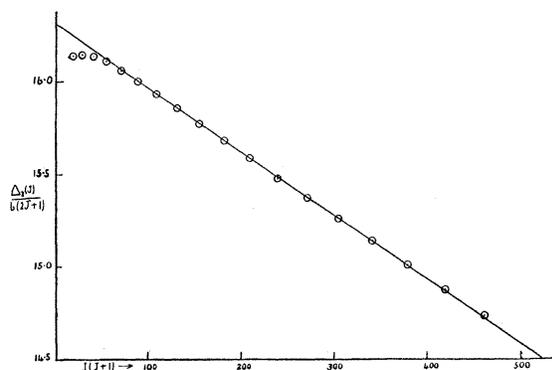


FIG. 1. Graph of Eq. (17) for PH.

TABLE II. Λ -type doubling. Comparison of experimental and theoretical values.

	EXPERIMENTAL			THEORETICAL		
	Π_0	Π_1	Π_2	Π_0	Π_1	Π_2
0	+0.12					
1	+0.07	0.07				
2	+0.09	0.18	0.08	+0.14	0.14	0.00
3	-0.02	0.29	0.18	+0.06	0.26	0.02
4	-0.02	0.32	0.02	-0.03	0.37	0.04
5	-0.12	0.37	0.09	-0.10	0.47	0.09
6	-0.16	0.53	0.10	-0.16	0.55	0.10
7	-0.25	0.59	0.30	-0.21	0.60	0.25
8	-0.24	0.57	0.35	-0.22	0.62	0.36
9	-0.21	0.62	0.54	-0.21	0.61	0.50
10	-0.10	0.57	0.63	-0.20	0.57	0.66

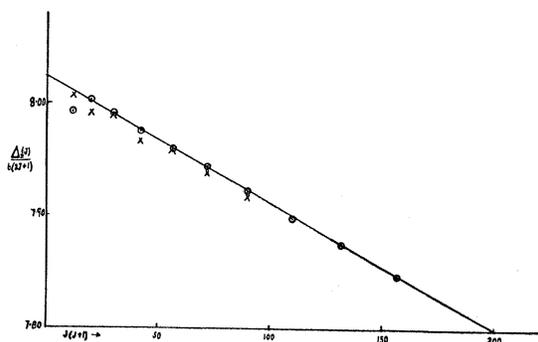


FIG. 2. Graph of Eq. (17) for NH.

maxima and minima occur in the ${}^3\Pi_1$ and ${}^3\Pi_0$ levels. The values of the three constants, which occur in the manner indicated by Hebb, were found to be:

$$C_0 = 0.12 \text{ cm}^{-1}, \quad C_1 = -0.125 \text{ cm}^{-1}, \\ C_2 = 0.0090 \text{ cm}^{-1}.$$

The $\lambda 3360$ band of NH

The experimental data given here were obtained by Pearse.⁷ Batsch⁸ has also observed these bands, but his data do not extend near to the origin of J , and he has observations only for the P and R branches. Pearse obtained observations for the three components of the P , Q and R branches. Batsch, however, has not given any observations for a Q branch, but he observed, in addition to the P and R branches, a number of faint lines which were separated from them by distances varying from about 4 to 6A. He attributed these lines to transitions for which the change in the spin quantum number is $\Delta S = \pm 1$, whereas the P , Q and R branches correspond to transitions for which $\Delta S = 0$. This is a reasonable explanation if the faint lines exist; however, Batsch apparently assumes that the observed separation of from 4 to 6A is caused by the Λ -type doubling. This could not be the case, but a possible explanation is that it is caused by the tripling of the Σ levels, caused by the spin structure. This cannot be shown directly to be the case, since the observations of the faint lines made by Batsch are not reliable enough to take for this purpose, but it can be shown

⁷ Unpublished work kindly communicated to the writer by Dr. Pearse.

⁸ H. Batsch, Ann. d. Physik 18, 81 (1934).

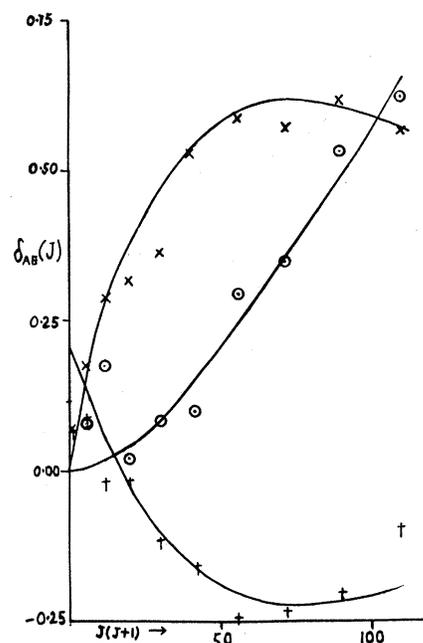


FIG. 3. A-type doubling for PH. The full lines join the calculated values of the doubling and the observed values of $\delta_{AB}(J)$ are represented by, + for the ${}^3\Pi_0$ level, \times for the ${}^3\Pi_1$ level, \circ for the ${}^3\Pi_2$ level. The experimental results are obtained from the relation,

$$\delta_{AB}(J) = \frac{1}{2}[F_A(J+1) + F_A(J)] - \frac{1}{2}[F_B(J+1) + F_B(J)].$$

that there is an appreciable separation in the Σ levels, in the manner indicated in the following paragraphs.

The data could be made to fit the theory, on the assumption that the nine branches given by Pearse were $P_1, P_2, P_3, Q_1, Q_2, Q_3, R_1, R_2, R_3$ branches. The values of B and D were first calculated according to Eq. (17). The graph is shown in Fig. 2, and the experimental points are found to be represented well by a straight line except for very low values of J . The latter deviations are presumably caused by inaccuracies in the observations, or some small effect which has not been taken into account as, for example, the perturbations caused by other excited levels of the molecule. The values of the constants were found to be $B = 16.322$ and $D = -17.3 \times 10^{-4}$.

The structure of the Σ level was then investigated, as far as was possible from the limited data at hand. We write $W'(K)$ for Π levels with $J = K$, and $W''(K)$ for Σ levels with a given value of K . Then we take the following differences:

$$\begin{aligned} P_1(K+1) - P_3(K+1) &= W_1'(K) - W_3'(K) - \{W_1''(K+1) - W_3''(K+1)\}, \\ R_1(K-1) - R_3(K-1) &= W_1'(K) - W_3'(K) - \{W_1''(K-1) - W_3''(K-1)\}. \end{aligned} \quad (25)$$

Subtracting Eqs. (25) we get

$$\begin{aligned} P_1(K+1) - P_3(K+1) - \{R_1(K-1) - R_3(K-1)\} \\ = -\{W_1''(K+1) - W_3''(K+1)\} + \{W_1''(K-1) - W_3''(K-1)\} = 4\gamma, \quad (\text{say}). \end{aligned} \quad (26)$$

If there were no ρ -type tripling the result of taking the difference on the left of Eqs. (26) would be zero. We find, however, for different values of J that this gives a value which is always negative and nearly constant and equal to -0.20 , which leads to the value $\gamma = -0.05$. Consider now the second of the Eq. (26). This is a difference equation whose solution will be

$$W_1''(K) - W_3''(K) = -2\gamma K + \text{constant}. \quad (27)$$

This is the result we get from the usual theory of ρ -type tripling. γ is the constant, which on the conventional theory arises from the interaction of the resultant spin S^* with the field produced in the direction K^* by the forced rotation of the electron system around this axis. The same result is also obtained from the alternative theory of

ρ -type tripling in $^3\Sigma$ states, given by Hebb.

We now calculate the value of $(\lambda-2)^2$ given by Eq. (23). It was found that the result was particularly sensitive to the value of D chosen, and also to the small term in γ . The effect of taking into account the various terms arising through the presence of these constants, when calculating $(\lambda-2)^2$, is well shown in Fig. 4. The terms in γ are introduced into the expression for $(\lambda-2)^2$ in the following manner:

$$\begin{aligned} (W_1 - W_3)^2 &= [(W_1' - W_3') - (W_1'' - W_3'')]^2 \\ &\approx (W_1' - W_3')^2 - 2(W_1' - W_3')(W_1'' - W_3''), \end{aligned} \quad (28)$$

neglecting the term in $(W_1'' - W_3'')^2$. Therefore, if we use Eq. (27), the first term on the left of Eq. (23) becomes

$$\begin{aligned} (W_1 - W_3)^2 &= (W_1' - W_3')^2 \\ &\quad - 2B(W_1' - W_3')(-2\gamma K + C). \end{aligned} \quad (29)$$

The effect of the separation in the Σ level, on the second term on the left of Eq. (23), is negligible. In the calculation the best value of γ , chosen to make $(\lambda-2)^2$ a constant, was found to be $\gamma = -0.06$. This value is very close to the value $\gamma = -0.05$ which was found directly from a consideration of the Σ levels.

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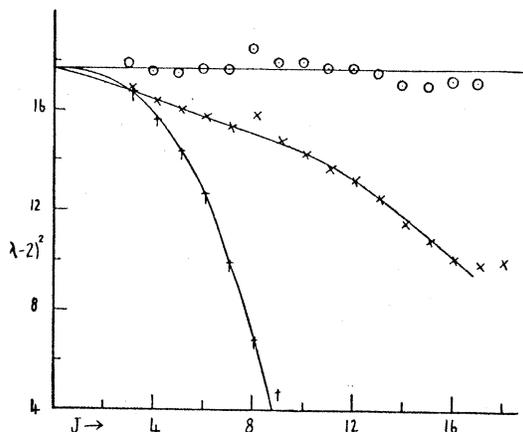


FIG. 4. $(\lambda-2)^2$ calculated for NH. The variation with J is shown by, (+) when terms containing D and γ are neglected, (x) when terms containing γ are neglected, (o) when the terms in D and γ are taken into account. The latter calculation gives the nearly constant value of $(\lambda-2)^2 = 17.7$.