

## On the Zeeman Effect in Diatomic Molecular States Having $L$ -Uncoupling

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A theoretical investigation is given of the Zeeman effect in molecular states intermediate between Hund's case  $b'$  and case  $d'$ , which are the limiting cases for small and large  $L$ -uncoupling, respectively. Zeeman patterns for the  $3d$  and  $4d$  complexes of the helium molecule are calculated and curves obtained for the variation of overall widths with  $K$  which are compared with experiment. For small  $K$  the energies are near the case  $b'$  curves, but as  $K$  increases a breaking away occurs which results in their approaching

the case  $d'$  curves. When the state in the limiting case  $d'$  has the electronic angular momentum quantized antiparallel to the nuclear rotation, a crossing over of the magnetic energy curves takes place with the passage through a state in which the molecule is relatively insensitive to the field. This crossing over occurs between  $K$  equal to 4 and 8 for the  $\Delta$  states of the helium molecule considered (magnetic field 30,000 gauss). A crossing over which occurs in one of the  $\Pi$  states is discussed.

THE experimental work of Millis<sup>1</sup> on the Zeeman effect in ortho-helium bands has shown that a wide variety of patterns is obtainable of a shape intermediate between the shapes of those patterns predicted by Hund's limiting cases for a molecule with electrons having orbital angular momentum. In Hund's case  $b'$  the angular momentum vector  $L$  is tightly coupled to the axis of figure connecting the nuclei; its component along that axis is quantized and can be designated by the quantum number  $\Lambda$ . On the other hand in case  $d'$  the coupling forces between  $L$  and the axis of figure are negligible;  $\Lambda$  no longer has meaning as a quantum number. It is now the mechanical angular momentum of the revolving nuclei which is quantized and to which can be assigned the quantum number  $R$ . In both cases, spin being absent,  $K$  represents the quantum number for the total angular momentum of the molecule. The phenomenon of the passage from case  $b'$  to case  $d'$  as the rotation of the molecule increases is closely related to  $\Lambda$ -doubling and is called  $L$ -uncoupling. It has been treated by Hill and Van Vleck, Kronig, Van Vleck, Dieke, Kronig and Fujioka and others.<sup>2</sup> The effect of an external magnetic field has been discussed for the two limiting cases by many authors.<sup>3</sup> In the intermediate case the effective magnetic moment of

the molecule varies with  $K$ , because of the uncoupling, in a way that causes the patterns to depart from both of the limiting shapes. It is the purpose of this paper to present a theoretical investigation of this subject.

### THE PERTURBATION FUNCTION

We shall start with case  $b'$  as the unperturbed system and neglect all the effects of the spin. In the bands examined by Millis the spin is unresolved and it is quite satisfactory to regard the triplet systems as singlets. This merely means that at quite low fields the Paschen-Back effect becomes total in all the triplet states and therefore the selection rule  $\Delta M_s = 0$  is rigorously obeyed. The patterns fall on top of each other since the term positions are built up around 0 and  $\pm 2\Delta\nu_n$  for all such triplets.

Our perturbation function is the sum of two parts.<sup>4</sup> The first part,  $H_1$ , is that due to the rotational distortion of the molecule and serves to remove the degeneracy which comes from the fact that  $\Lambda$  can be parallel or antiparallel to the axis of figure. The perturbing Hamiltonian consists of certain terms in the Schrödinger equation for the rotating molecule which are usually neglected in separating the electronic and rotational parts of the wave function. We take the value of the matrix elements of this Hamiltonian from Van Vleck<sup>2</sup> or Kronig.<sup>5</sup> It is

<sup>1</sup> Millis, *Phys. Rev.* **37**, 1005 (1931); **38**, 1146 (1931). See also Crawford, *Rev. Mod. Phys.* **6**, 112 (1934).

<sup>2</sup> Hill and Van Vleck, *Phys. Rev.* **32**, 267 (1928); Kronig, *Zeits. f. Physik* **50**, 347 (1928); Van Vleck, *Phys. Rev.* **33**, 467 (1929); Dieke, *Zeits. f. Physik* **57**, 71 (1929); Kronig and Fujioka, *Zeits. f. Physik* **63**, 168 (1930); Fujioka, *Zeits. f. Physik* **63**, 175 (1930).

<sup>3</sup> For a general discussion see the article by Crawford, reference 1.

<sup>4</sup> For a similar computation dealing with spin-uncoupling in molecules in a magnetic field, see Hill, *Phys. Rev.* **34**, 1507 (1929).

<sup>5</sup> Kronig, *Band Spectra and Molecular Structure*, Cambridge, University Press, 1930.

$$H_1(\Lambda, K; \Lambda \pm 1, K) = 2(BL_\eta)(\Lambda, \Lambda \pm 1)[(K \mp \Lambda)(K \pm \Lambda + 1)]^{\frac{1}{2}}, \quad (1)$$

all other elements being zero. In this expression

$$(BL_\eta)(\Lambda, \Lambda \pm 1) \equiv \int_0^\infty P_{\Lambda \pm 1}^*(r) \left[ \frac{L_\eta(\Lambda, \Lambda \pm 1) \hbar^2}{8\pi^2 c M r^2} \right] P_{\Lambda \pm 1}(r) r^2 dr, \quad (2)$$

where  $P(r)$  is the vibrational wave function of the molecule,  $M$  is the reduced mass of the nuclei,  $L_\eta(\Lambda, \Lambda \pm 1)$  is a matrix element of one of the components of the orbital electronic angular momentum operator  $L$  perpendicular to the axis of figure. We can take  $L_\eta(\Lambda, \Lambda \pm 1)$  as equal approximately to  $\frac{1}{2}[L(L+1) - \Lambda(\Lambda \pm 1)]^{\frac{1}{2}}$ , which multiplied by a kind of a mean value of the rotational constant  $B$  gives us the approximate value of the above integral.

For the part due to the external magnetic field, we take the Hamiltonian function

$$H_2 = \Delta v_n L_z, \quad L_z = L_\eta \sin \theta + L_\zeta \cos \theta, \quad \Delta v_n = H e / 4\pi m c^2. \quad (3)$$

Here  $z$  is the direction of the field  $H$ ,  $(\xi\eta\zeta)$  is a set of Cartesian axes fixed in the molecule with the origin at the center of gravity of the nuclei. The  $\zeta$  axis coincides with the internuclear line, the  $\xi$  axis lies in the  $xy$  plane, and  $\theta$  is the polar angle between the internuclear line and the direction of the field.  $L$  is the electronic orbital angular momentum operator of quantum mechanics mentioned above. To obtain the matrix elements of this Hamiltonian, we utilize the integrals given by Reiche and Rademacher<sup>6</sup> for the symmetrical top. We have for the non-zero elements

$$\begin{aligned} H_2(\Lambda, K; \Lambda, K) &= 2\beta\Lambda^2, \\ H_2(\Lambda, K; \Lambda + 1, K) &= -\beta[L(L+1) - \Lambda(\Lambda+1)]^{\frac{1}{2}}[(K-\Lambda)(K+\Lambda+1)]^{\frac{1}{2}}, \\ H_2(\Lambda, K; \Lambda, K+1) &= \frac{\Delta v_n \Lambda}{K+1} \left[ \frac{(K-M+1)(K+M+1)(K-\Lambda)(K+\Lambda+1)}{(2K+1)(2K+3)} \right]^{\frac{1}{2}}, \\ H_2(\Lambda, K; \Lambda + 1, K+1) &= [L(L+1) - \Lambda(\Lambda+1)]^{\frac{1}{2}} \frac{\Delta v_n}{2(K+1)} \left[ \frac{(K-M+1)(K+M+1)(K+\Lambda+1)(K+\Lambda+2)}{(2K+1)(2K+3)} \right]^{\frac{1}{2}}, \end{aligned} \quad (4)$$

where  $\beta = \Delta v_n M / 2K(K+1)$ .

The unperturbed energies for case  $b'$  are given by the expression

$$W_\Lambda^0 = f(\Lambda) + B[K(K+1) - \Lambda^2 + L(L+1) - \Lambda^2], \quad B = h/8\pi^2 c M r_0^2, \quad (5)$$

where  $f(\Lambda)$  is the coupling energy of an  $L$ -complex. If one makes the hypothesis of pure precession,  $f(\Lambda)$  becomes  $A\Lambda^2$ , where  $A$  is the coupling constant.

#### CALCULATION OF ENERGIES

We shall neglect the terms which are not diagonal in  $K$ . If the rotational states involved are not close together, in doing this we are neglecting a second order effect in the field which is small. In computing overall widths of Zeeman patterns this second order effect would cancel out because it only gives a shift of the pattern and a distortion of its shape. Classically we are neglecting the effect of that component of the vector  $L$  which is perpendicular to the vector  $K$ .  $K$  precesses around the direction of the field and while  $L$  precesses rapidly around  $K$ , still the effect of its perpendicular component does not average out completely for large fields. Actually we cannot expect the rotational energy differences to be always large compared to the Zeeman displacements. However, for extreme magnetic levels ( $K$  parallel and antiparallel to the field), the effect of the perpendicular component

<sup>6</sup> Reiche and Rademacher, *Zeits. f. Physik* **39**, 444 (1926); **41**, 453 (1927).

is a minimum since this component is then approximately perpendicular to the field. The truth of this fact is borne out on examining those elements of our perturbation function which are not diagonal in  $K$ . They are seen to be smallest for  $M = \pm K$ . Thus even when the effect of the non-diagonal terms is not small, we see that it can be expected that, excepting under unusual conditions such as two levels very near each other, their effect is not to change greatly the energy differences of levels corresponding to extreme values of  $M$ , that is the overall widths, but to distort the shape of the energy patterns.

For  $L=1$  the secular equation is a cubic which can be solved exactly. The three roots are

$$\begin{aligned} W_{\pm} &= A/2 + B(K^2 + K + 1) + \beta \pm B[\alpha^2/4 - \alpha\gamma + \gamma^2(2K + 1)^2]^{\frac{1}{2}}, \\ W &= A + B(K^2 + K) + 2\beta, \end{aligned} \quad (6)$$

where  $\alpha = A/B$ ,  $\gamma = 1 - \beta/B$ ,  $A = f(1)$ . If  $\alpha > 0$ , we have a normal  $p$ -complex and  $W_-$  corresponds to the  $\Sigma$  state and  $W$  and  $W_+$  to the two  $\Pi$  states. For zero fields these expressions reduce to those given by Hill and Van Vleck for  $\Lambda$ -doubling. The correlation with case  $d'$  is easily found by expanding in inverse powers of  $2K + 1$  and is given in the papers by Hill and Van Vleck and by Dieke.

In the case of  $L=2$ , which is of interest in the helium bands, the secular equation is a quintic which can be factored into the following quadratic and cubic determinants

$$\begin{vmatrix} (W_2^0 + 8\beta - W) & H_p(21) \\ H_p(21) & (W_1^0 + 2\beta - W) \end{vmatrix} = 0, \quad \begin{vmatrix} (W_2^0 + 8\beta - W) & H_p(21) & 0 \\ H_p(21) & (W_1^0 + 2\beta - W) & 2H_p(10) \\ 0 & H_p(10) & (W_0^0 - W) \end{vmatrix} = 0, \quad (7)$$

where  $H_p = H_1 + H_2$ . The quadratic we can solve at once. For the cubic approximate solutions are obtainable which are good for extreme values of the parameters and which reduce to those given by Dieke<sup>7</sup> for zero field if one makes the hypothesis of pure precession. Since these formulas are rather clumsy, we shall not give them here. However if in these expressions we retain only second order terms in the  $L$ -uncoupling and first order terms in the field, we obtain the simplified approximate solutions given below in Eqs. (8) and (9). More directly, we can use the simple perturbation theory. Thus for  $\alpha$  large,  $K$  and  $\beta/B$  small, that is near case  $b'$ , we have ( $\alpha > 0$ ,  $K \geq 2$ )

$$\begin{aligned} W\Delta_a &= 4A + B(K^2 + K - 2) + 4(K^2 + K - 2)B^2/3A + 8\beta[1 - 4(K^2 + K - 2)/3\alpha] = W\Delta_b, \\ W\Pi_a &= A + B(K^2 + K + 4) + 8(2K + 1)^2B^2/3A + 2\beta[1 - 8(2K + 1)^2/3\alpha], \\ W\Pi_b &= A + B(K^2 + K + 4) - 4(K^2 + K - 2)B^2/3A + 2\beta[1 + 4(K^2 + K - 2)/3\alpha], \\ W\Sigma_a &= B(K^2 + K + 6) - 12(K^2 + K)B^2/A + 24\beta(K^2 + K)/\alpha. \end{aligned} \quad (8)$$

For near case  $d'$ ,  $K$  large,  $\alpha$  and  $\beta/B$  small, we likewise have

$$\begin{aligned} W\delta_2 &= A + B(K - 2)(K - 1) + B(12\alpha - 3\alpha^2)/4(2K + 1) + 4\beta(K + 1) - \frac{3}{4}\beta\alpha^2/(2K + 1), \\ W\delta_{-2} &= A + B(K + 2)(K + 3) + B(12\alpha - 3\alpha^2)/4(2K + 1) - 4\beta K + \frac{3}{4}\beta\alpha^2/(2K + 1), \\ W\delta_1 &= 5A/2 + B(K - 1)K + B(36\alpha - 9\alpha^2)/8(2K + 1) + 2\beta(K + 3) - (9/8)\beta\alpha^2/(2K + 1), \\ W\delta_{-1} &= 5A/2 + B(K + 1)(K + 2) - B(36\alpha - 9\alpha^2)/8(2K + 1) - 2\beta(K - 2) + (9/8)\alpha^2/(2K + 1), \\ W\delta_0 &= 3A + BK(K + 1) - B(12\alpha - 3\alpha^2)(2 - \alpha)/2(2K + 1)^2 + 6\beta + 6\beta\alpha^2(3 - \alpha)/(2K + 1). \end{aligned} \quad (9)$$

Here we are using the subscript  $a$  to indicate the higher energy component of a  $\Lambda$ -doublet in the normal case and  $b$  for the lower energy component. The cubic gives the higher components as well as the  $\Sigma$  level to which we have also given the subscript  $a$ .  $\delta$  in Eq. (9) means that it is a  $\delta$ -complex

<sup>7</sup> See Dieke, reference 2.

( $L=2$ , case  $d'$ ) and the subscript indicates the quantized value of  $L$  along the direction of nuclear rotation. These expressions reduce to the Zeeman expressions for the two cases for limiting values of  $\alpha$ .

It should be pointed out that we can just as well begin with case  $d'$ , in which case we assume the interaction Hamiltonian to contain the square of the cosine of the angle between the  $L$  vector and the axis of figure. The matrix elements are readily obtained from the relations given in the articles by Van Vleck and Hill. On neglecting the elements not diagonal in  $K$ , we obtain the same secular equation as by the above method.

In the case of the cubic we have the following simple way of obtaining values for the magnetic energy levels from the zero-field levels. In order to use the data given by Fujioka, we take the unperturbed (case  $b'$ ) energies as approximately

$$W_{\Lambda}^0 = A_{\Lambda} + B(K + \frac{1}{2})^2 - \beta'(K + \frac{1}{2})^4, \quad \Lambda = 0, 1, 2. \tag{10}$$

Then if  $W_0, W_1, W_2$  are the zero-field roots of the cubic and if we neglect the squared and cubed terms in  $\beta$ , we can write our secular equation in the form

$$-(W_0 - W)(W_1 - W)(W_2 - W) = 2\beta[(W_0^0 - W)(W_2^0 - W) + 4(W_0^0 - W)(W_1^0 - W) - 48B^2K(K+1)\alpha_{10}^2 + 12BK(K+1)\alpha_{10}(W_2^0 - W) + 4B(K^2 + K - 1)\alpha_{12}(W_0^0 - W)]. \tag{11}$$

To obtain the energies corresponding to  $W_0$ , we substitute  $W_0$  for  $W$  throughout excepting in the first bracket on the left and then solve the resulting linear equation. The  $\alpha$ 's are constants, nearly unity, introduced and evaluated by Kronig and Fujioka in their zero-field secular determinant so as to get the best fit with experiment. They allow for the fact that  $(BP_{\eta})(\Lambda, \Lambda+1)$  in the first part of our perturbation function is not accurately equal to  $\frac{1}{2}B[L(L+1) - \Lambda(\Lambda+1)]^{\frac{1}{2}}$ .

APPLICATION TO THE HELIUM BANDS

Experimentally we find that half of the rotational states are missing. This is because  $\text{He}_2$  is a homonuclear molecule the nuclei of which obey Bose statistics and therefore the allowed states are symmetrical in the nuclei. Since the states we are interested in are also odd ( $u$ ), they are all negative under reflection in the origin and we must omit the positive ones. It is easy to see just which the negative ones are. For  $\Sigma_u^+$  states<sup>8</sup> the terms are alternately positive and negative beginning with a positive term for  $K=0$ . The two rotational terms of a given  $K$  for  $\Pi$  and  $\Delta$  states are always one positive and one negative, any one series in  $K$  being alternately positive and negative. Discarding the

positive terms, we have remaining three states for  $K$  odd and two for  $K$  even. These correspond

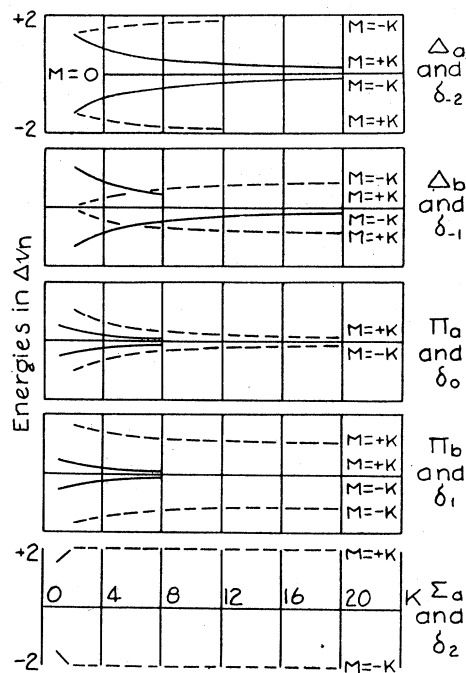


FIG. 1. Magnetic levels of a  $d$ -complex for the limiting cases drawn around the zero-field energy ( $M=0$ ). Only  $M=0, \pm K$  levels are plotted. The solid curves are case  $b'$  and the broken curves case  $d'$ . The correlation between the states is that for  $\alpha > 0$ . The energy scale is in units of  $\Delta\nu_n$ .  $K$  is the quantum number associated with the total angular momentum of the molecule.

<sup>8</sup> See Weizel, *Handbuch der Experimental Physik, Band-spektra*, p. 136.

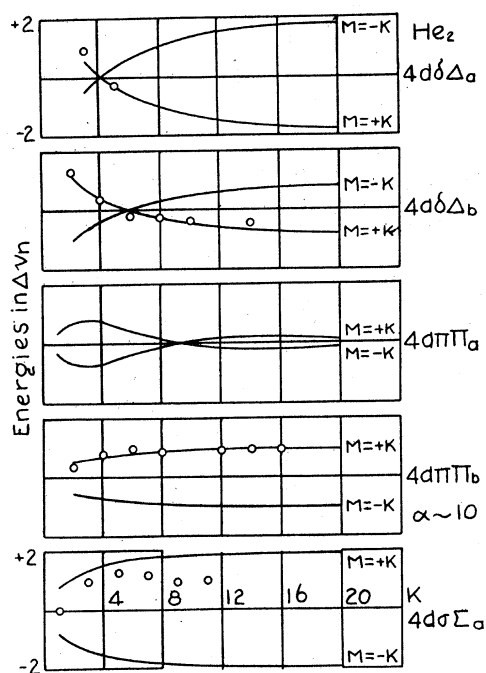


FIG. 2. Magnetic levels of the  $4d$  complex of the helium molecule calculated from the present theory using Kronig and Fujioka's constants.  $\alpha$  is approximately 10. The crossing over of the levels is due to the passage from quantization of the orbital angular momentum of the electron along the internuclear axis to quantization along the axis of nuclear rotation. During this process the component of the magnetic moment along  $K$  passes through zero thus passing through a state in which the molecule is very insensitive magnetically. The circles give the observed widths. In this figure and in Fig. 3,  $\Delta\nu_n$  is  $2.415 \text{ cm}^{-1}$  which corresponds to a field strength of 30,000 gauss.

to our cubic and quadratic given above because, our Hamiltonian being symmetrical, states of unlike symmetry cannot perturb each other.<sup>9</sup>

In Fig. 1 is given for comparison the overall widths of the magnetic energy levels for the two limiting cases, drawn using the expression

$$E = 2\beta\Lambda^2 \quad (12)$$

for case  $b'$  and

$$E = \beta[K(K+1) + L(L+1) - R(R+1)] \quad (13)$$

for case  $d'$ . In Fig. 2 are the calculated curves for the  $4d$  complex of molecular helium and in Fig. 3 those for the  $3d$  complex. All the curves show clearly the rapid change which takes place in passing from case  $b'$  with low  $K$  to case  $d'$

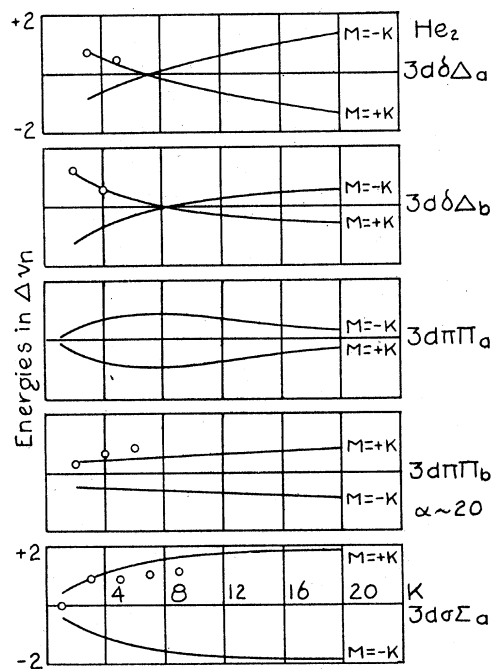


FIG. 3. Magnetic levels of the  $3d$  complex of the helium molecule calculated using Kronig and Fujioka's constants.  $\alpha$  being about 20, the binding to the internuclear axis is tighter than it is for the states in Fig. 2 and the transition to case  $d'$  is therefore slower.

with high  $K$ . The change is more rapid for the  $4d$  complex since its angular momentum vector is less tightly bound to the axis of figure. The crossing over of the extreme levels occurs when the component of the magnetic moment along  $K$  changes its direction with respect to  $K$ . The circles represent experimental points obtained from Millis' data by interpreting them in the light of the present theory. The values for the overall widths so obtained are not all self-consistent; we have tried to select those values which were the most reliable from the experimental point of view. The differences which exist are perhaps due to intensity distributions and failure to obtain well resolved patterns in some cases.

The  $\Pi_a$  states, for which unfortunately there are no experimental data, are of special interest since they are the only states for which the calculated curves do not lie between the limiting curves. An understanding of this behavior is to be found in examining the solutions for small and large  $K$  using Eqs. (8) and (9). The equation for

<sup>9</sup> In Mulliken's notation the states  $\Delta_a$ ,  $\Delta_b$ ,  $\Pi_a$ ,  $\Pi_b$ ,  $\Sigma_a$  considered in this paper are designated by  $\Delta_e$ ,  $\Delta_d$ ,  $\Pi_d$ ,  $\Pi_c$ ,  $\Sigma_e$ , respectively. Rev. Mod. Phys. 3, 94 (1931).

$\Pi_a$  shows that for small  $K$  the calculated curve for  $M=K$  will lie below the limiting case  $b'$  curve ( $\alpha > 0$ ) and that the difference between the two will increase rapidly with  $K$ . The equation for  $\delta_0$ , which is the limiting case for a  $\Pi_a$  state with uncoupling, shows that for  $\alpha > 3$  the calculated curve lies below the limiting curve but that the difference decreases rapidly with increasing  $K$ . For  $M=K$  both limiting curves lie for all  $K$  above the curve for  $M=0$ . The calculated curves start out for small  $K$  below the first limiting curve and then approach the second limiting curve from below. For the  $4d\pi\Pi_a$

state the extreme levels cross over at about  $K=10$ . For  $\alpha$  slightly greater than 20, the extreme levels would cross over first for small  $K$  and a second time for very large  $K$ .

Curves of a similar nature could be drawn for the magnetic levels of the three states of a  $p$ -complex using Eq. (6). The  $\Pi$  state correlated to the  $\delta_{-1}$  state would show a crossing over of the levels for suitable  $\alpha$  and  $K$  in a manner very similar to that shown in the cases described above.

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### On Perturbed Series, Especially in C III, B I and O IV

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Consideration of possible extra-configurational perturbations in atomic spectral series shows that often some series are preferable to others for the determination of series limits. In particular: In C III, several  $2snd\ ^3D$  terms are recalculated, but Edlén's series limit value is verified in spite of perturbations; in B I, the term values are increased by  $90\text{ cm}^{-1}$  or  $0.011$  volt, so that B I  $2s^2 2p\ ^2P_{3/2}$  - B II  $2s^2\ ^1S_0 = 66,930\text{ cm}^{-1} = 8.257$  volts; and in O IV, the old  $5s\ ^2S_1$  term is replaced by a new one at  $85,440\text{ cm}^{-1}$ ,  $?4p\ ^2P$  and  $?6f\ ^2F$  are repudiated, and  $?7f\ ^2F$  and  $?8f\ ^2F$  are verified.

ALTHOUGH the term values in most of the spectra of the lightest elements have recently been determined with a high degree of accuracy and completeness by Edlén,<sup>1</sup> there are a few instances in which series limits may be slightly altered and term assignments reconsidered after a study of the influence of extra-configurational perturbing terms.<sup>2, 3</sup> The purpose of this note is to point out the general preferability of some series over others in the determination of series limits, and to make minor alterations in three of Edlén's spectra.

An irregular relationship between the term values and the corresponding quantum defects for a spectral series generally is an indication of the presence of a perturbing series, of which

usually only one or two terms appreciably affect the series in question. The extra-configurational series members have the same Laporte parity and (in the  $LS$  coupling case, which is all that need be considered in Edlén's spectra) the same multiplicity and  $L$  value as the series under consideration. Irregularity arises when the two series overlap or nearly overlap, in which case the members of the one series share their properties with neighboring members of the other with a consequent ambiguity as to configuration. Thus the members of a series may show an energy trend leading toward a false series limit, even though the term or terms mainly responsible for the complication may remain undiscovered. Although perturbing terms can be pointed out for almost all of Edlén's spectral series, we shall list here only those cases in which an analysis appears to lead to definite improvements in term values,

<sup>1</sup> B. Edlén, *Nova Acta Reg. Soc. Scient. Upsaliensis*, Ser. IV IX, No. 6 (1933).

<sup>2</sup> A. G. Shenstone and H. N. Russell, *Phys. Rev.* **39**, 415 (1932).

<sup>3</sup> N. G. Whitelaw, *Phys. Rev.* **44**, 544 (1933).