# ELECTRONIC STATES AND BAND SPECTRUM STRUCTURE IN DIATOMIC MOLECULES. VIII. SOME EMPIRICAL RELATIONS IN σ-TYPE DOUBLING

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### Abstract

Some of the empirical relations which exist in  $\sigma$ -type doubling are summarized. In particular, the magnitudes of the doublet intervals as a function of j, and in relation to  $\Delta E/B$ , are considered. The observed relations, although very varied, are consistently in agreement with theoretical work of Van Vleck (cf. preceding paper). Van Vleck's work shows definitely that the <sup>3</sup>P levels involved in the second positive nitrogen bands are both normal (not inverted).

*Empirical Relations.* In previous papers of this series,<sup>1</sup> data have been accumulated on the sign<sup>2</sup> and magnitude of the difference  $F_A(j) - F_B(j)$  in  $\sigma$ -type doubling. It seems appropriate now to summarize the empirical results, so that they may be more readily available for comparison with theory. This is done in Table I below.—When reference is made to previous papers of this series, they are cited by number (I, II, etc.).

The differences found empirically between corresponding  $F_A(j)$  and  $F_B(j)$  terms for singlet states can be expressed in the following way,<sup>3</sup> where  $\alpha = A$  or B:

$$F_{\alpha}(j) = C_{\alpha} + B_{\alpha}^{*} [j(j+1) - \sigma^{2}] + c_{\alpha}j + \cdots$$

$$\tag{1}$$

Except in the He<sub>2</sub> bands, where a partial uncoupling of  $\sigma$  from the molecular axis occurs,<sup>4</sup>  $C_{\alpha} = C_{\beta} = C$  and  $c_{\alpha} = 0 = c_{\beta}$ .

For doublet and triplet states, the following expressions are empirically adequate provided  $|\Delta E/B|$  is not too small; corresponding expressions hold (cf. Table I of VII)<sup>1</sup> for small values of  $|\Delta E/B|$ :

$$F_{i\alpha}(j) = C_{i\alpha} + B_{i\alpha}^* [j(j+1) - \sigma_i^2] + c_{i\alpha}(j+\frac{1}{2}) + \cdots$$
(2)

In Eq. (2), i=1 or 2 for doublet states, 1, 2, or 3 for triplet states. We have already considered how  $F_{i\alpha}(j)$  depends on *i* for doublet states (cf. VII, Tables I, II, and Fig. 1).

We are now interested in the dependence of  $F_{\alpha}(j)$  or  $F_{i\alpha}(j)$  on  $\alpha$ . In many cases the observed differences between  $F_{i\alpha}(j)$  and  $F_{i\beta}(j)$  states can be expressed by assuming a difference in the  $B^*$ 's only, or in the c's only, of

<sup>1</sup> R. S. Mulliken, Phys. Rev. 1926-8: I-VII of this series.

<sup>2</sup> Probably no definite significance can be attached at present to the *sign* of  $F_A - F_B$ , since the subscripts A and B have been assigned by a method which is probably arbitrary (cf. VI, pp. 789–92). They are at any rate not to be identified with the two types of Kronig symmetry.<sup>21</sup>

<sup>3</sup> Cf. II, Eq. (3): Phys. Rev. 28, 1207 (1926).

<sup>4</sup> W. Weizel, Zeits. f. Physik 52, 175 (1928).

# TABLE I. Summary of empirical energy relations in $\sigma$ -type doubling. (Note: where a specific reference is not given, the data are from VII of this series.)

a. <sup>1</sup>P states.

 $H_2$  (initial levels, Werner bands<sup>5</sup>):  $F_A(j) - F_B(j)$  moderately large, negative, increasing with j, varying with vibrational quantum number.

 $He_2$  (cf. section e, below)

CO (final state of Angström and Thalén bands):<sup>6</sup>  $F_A(j) - F_B(j) \sim 0$ 

AlH:  $F_A(j) - F_B(j)$  negative:  $B^*_A \backsim 5.935$ ,  $B^*_B \backsim 6.00$ ,  $c_{\alpha} \backsim 0$ , for  $n = 0.^{6, 7}$  $F_2: F_A(j) - F_B(j)$  obeying Eq. (1), with  $c_{\alpha} \backsim 0.^{4a}$ 

b. <sup>2</sup>P states (cf. Table II of VII, for  $\Delta E$  values). Note:  $F_{i\alpha}$  states are <sup>2</sup>P<sub>1/2</sub> states for normal <sup>2</sup>P levels (HgH, etc.) and <sup>2</sup>P<sub>2/2</sub> for inverted <sup>2</sup>P levels (OH, BO).

Molecule	$F_{1\alpha}$ states	$F_{2\alpha}$ states
HgH	$F_{1A}(j) - F_{1B}(j)$ increases linearly with $j + \frac{1}{2}$ for low $j$ values, with $c_{1A} = +1.70$ , $c_{1B} = -1.70$ for $n = 0$ according to calculations of Birge, <sup>8</sup> and $c_{1A} = +1.42$ , $c_{1B} = -1.42$ for n = 1, according to Hulthén. <sup>9</sup> For large $jvalues, F_{1A} - F_{1B} is no longer linear in j,but increases more and more slowly with j(cf. Table 7 of Hulthén's 1925 paper10).$	$F_{2A}$ $(j) - F_{2B}$ $(j)$ ~0 except in perturbations. <sup>9</sup>
CdH	Similar to HgH; $c_{1A} \sim +0.3$ , $c_{1B} \sim -0.3$	$F_{2A}(j) - F_{2B}(j)$
ZnH	Similar to HgH; $c_{1A} \sim +0.15$ , $c_{1B} \sim -0.15$	$ \begin{array}{c} \sim 0 \\ F_{2A}(j) & -F_{2B}(j) \end{array} $
NO (lower ${}^{2}P$ )	$F_{1A}(j) - F_{1B}(j) - 0.01j$	$ \begin{array}{c} \sim 0 \\ F_{2A}(j) & -F_{2B}(j) \end{array} $
NO (upper $^{2}P$ )	$ F_{1A}(j) - F_{1B}(j)  \sim 0.025j$ or $0.005j$	$\widetilde{F}_{2A}(j) - F_{2B}(j)$
CaH	Doublet spacings apparently irregular	$\int_{\text{Irregular}}^{\infty 0}$
MgH	$F_{1A}(j) - F_{1B}(j) \backsim 0$ or slightly positive for small <i>j</i> until <i>j</i> $\backsim 10$ , then becoming increas- ingly negative, approaching a value of about $-0.4$ for $j \ge 18$ .	$F_{2A}(j) - F_{2B}(j)$ small, negative, slightly more so than $F_{1A}(j) - F_{1B}(j)$
СН	$B_{1A}^* = 14.207; B_{1B}^* = 14.170$ (cf. VI, p. 799), hence $F_{1A}(j) > F_{1B}(j)$ .	$B_{2A}^* = 14.207;$ $B_{2B}^* = 14.170$ (cf. VI, p. 799)

<sup>4a</sup> H. G. Gale and G. S. Monk, Astrophys. I. (in press).

<sup>5</sup> T. Hori, Zeits. f. Physik 44, 845-6 (1927).

<sup>6</sup> Cf. II: Phys. Rev. 28, 1202 (1926).

<sup>7</sup> E. Bengtsson and E. Hulthén, Zeits. f. Physik 52, 275 (1928).

<sup>8</sup> According to Birge (Nat. Res. Council Report on Molecular Spectra, pp. 179-181, Eqs. (162), (163), and  $\alpha'$  value on p. 181), the term values for the  $n = 0^2 P_{1/2}$  state of HgH (initial state of  $\lambda 4017$  band) can be represented by  $F^{\pm} = B(j \pm \alpha)^2$ , with  $\alpha = 0.130 \pm 0.005$ . (Birge's  $F^+$  with  $B(j+\alpha)^2$ , corresponds to  $F_A$  here, and his  $F^-$ , with  $B(j-\alpha)^2$ , to  $F_B$  here.) Putting j+1/2 in place of Birge's j, since the latter corresponds to the numbering of the old quantum theory, inserting  $\alpha = 0.130$ , and B = 6.55 from Birge's Eq. (162), and multiplying out, one gets

$$F_A(j) = C + B[j(j+1)] + 1.70(j+1/2)$$
  

$$F_B(j) = C + B[j(j+1)] - 1.70(j+1/2)$$

<sup>9</sup> E. Hulthén, Zeits. f. Physik 50, 319 (1928).

<sup>10</sup> E. Hulthén, Zeits. f. Physik **32**, 32 (1925).

TABLE I. (continued.)

 $F_{1A}(j) - F_{1B}(j) \sim +0.04j^2$  (cf. Table VII and Fig. 3 of VII)

 $F_{2A}(j) - F_{2B}(j)$ negative to j = 4, then positive,  $\sim 0.03j^2$  (cf. Table VII and Fig. 3 of VII; but cf. ref. 11 for correction)

 $F_{2A}(j) - F_{2B}(j) \sim -0.026j$  $F_{1A}(j) = F_{1B}(j)$ c. <sup>3</sup>P states.

 $He_2$  (cf. e, below);  $H_2$  (cf. ref. 15a)

 $C_2$  (Swan) and  $N_2$  (second positive) bands<sup>12</sup>; in these  ${}^{3}P \rightarrow {}^{3}P$  transitions, the observed  $\sigma$ -type doublets represent differences (or possibly sums) of separations for the initial and final

<sup>3</sup>*P* terms, and so do not give direct information in regard to the individual <sup>3</sup>*P* levels. In the C<sub>2</sub> bands,  $\Delta E/B$  is probably fairly small so that the bands correspond closely for large *j* values to Hund's case  $b_i^{12, 13}$  the observed doublet separations are about equal in all the branches for large values of *j*; they are given<sup>14</sup> by  $\Delta \nu \sim 3.934 \times 10^{-4} j_k^2$ . For small values of *j*,  $\Delta \nu$  approaches zero for the  $R^c$  and  $R^v$  branches (and presumably also for the  $P^c$  and  $P^v$  branches, but they are not resolved), but for the R<sup>r</sup> branches (presumably also for the P<sup>r</sup> branches),  $\Delta \nu$ approaches a constant value  $(\Delta\nu \sim 0.40)^{14}$  as j approaches 0. In the second positive nitrogen bands, <sup>12, 15</sup> where the  $\Delta E/B$  values are larger, the doublet

<sup>11</sup> R. S. Mulliken, Phys. Rev. 32, 997 (1928).

<sup>12</sup> Cf. R. S. Mulliken, Phys. Rev. 29, 645-646 (1927).

<sup>13</sup> That Hund's case b is approached for large j values in the Swan bands is indicated by the fact that the triplets draw together and finally become unresolvable, as j increases, in both P and R branches. In the N<sub>2</sub> bands, the triplet separations slowly diminish with increasing j, but the triplets remain resolved to the end.

<sup>14</sup> Cf. J. D. Shea, Phys. Rev. **30**, 824 (1927). Shea's j is really  $j_k''+1$ . Shea's "stagger" is half the width  $\Delta \nu$  of the  $\sigma$ -type doubling.—A re-examination of the data indicates that we have here a transition between two *inverted* P levels, with the  $R^r$  branch corresponding to  $P_0 \rightarrow P_0$ .

<sup>15</sup> A re-examination of the data (cf. ref. 12) on the second positive nitrogen bands shows that they are emitted in a transition between two normal  ${}^{3}P$  states of fairly large  $\Delta E$ , and that the  $P_3$ ,  $R_3$ ;  $P_2$ ,  $R_2$ ;  $P_1$ ,  $R_1$ , branches respectively correspond to  ${}^{3}P_2 \rightarrow {}^{3}P_2, {}^{3}P_1 \rightarrow {}^{3}P_1$ , and  ${}^{3}P_0 \rightarrow {}^{3}P_0$ transitions (as supposed, but not proved, in ref. 12). The evidence is as follows: For small j, the  $\Delta F$  values correspond to  ${}^{3}P_{ab}$  initial and final states, i.e.  ${}^{3}P$  states near case a, but with a tendency toward case b (cf. VII for corresponding discussion of doublet states). Thus it is possible to determine  $B^*$  values and j values. It is found that  $B_3^* > B_2^* > B_1^*$ , for both upper and lower <sup>3</sup>P states, also that  $j = j_k - 1$  for the  $P_3$  and  $R_3$  branches,  $j = j_k$  for  $P_2$  and  $R_2$ ,  $j = j_k + 1$ for  $P_1$  and  $R_1$  (assuming that  $j_k$  (i.e.  $j_k'$  and  $j_k''$ ) is the same for all three members of the natural triplets which exist for large j values, and that j is then equal to  $j_k$  for the middle component). Both these relations correspond to the identification of  $F_3 \rightarrow F_3$  with  $P_3$  and  $R_3$ , and so on. (The relation  $B^*(F_3) > B^*(F_2) > B^*(F_1)$  agrees with the theoretical work of Hill and Van Vleck (Phys. Rev. 32, 261, 1928)). The evidence just given does not alone suffice to determine whether the triplets are normal or inverted. But according to Van Vleck's recent work (cf. preceding paper), we can identify the  $P_1$  and  $R_1$  branches with  ${}^{3}P_0 \rightarrow {}^{3}P_0$ , and so on, on the basis of  $\sigma$ -type doubling data (cf. Table I, c). Hence  ${}^{3}P_{0}$  corresponds to  $F_{1}$ , and so on, which means normal triplets.

It should be remarked that the missing lines give no support to this interpretation. The writer's Table I of ref. 12 is incorrect in respect to the missing lines predicted by the theory: the *predicted* values of j'' for the first lines of the  $P_1$  and  $P_3$  branches should be interchanged, and similarly for the  $R_1$  and  $R_3$  branches. (The *j* values given in Table I for the *observed* first lines are, however, correct.) The disagreements may probably be attributed to the expected weakness of the early lines of the  $P_1$  and  $R_1$  branches (j values very small) and to difficulties in interpretation caused by the large total number of lines present.

<sup>15a</sup> Cf. O. W. Richardson and K. Das, Proc. Roy. Soc. 122A, 688 (1929).

BO

OH

#### TABLE I. (continued.)

separations are vanishingly small for the  $P_3$  and  $R_4$  branches, just detectable for  $P_2$  and  $R_2$ , and somewhat larger and independent of  $j(\Delta\nu \sim 0.24)$  for  $P_1$  and  $R_1$ .

# d. Case b <sup>2</sup>D state.

CH  $\lambda 4300: F_{1A}(j) = F_{1B}(j); F_{2A}(j) = F_{2B}(j)$ 

## e. $He_2$ bands.

Most of the He<sub>2</sub> levels (*P* and *D* states) show very wide  $\sigma$ -type doubling. The doublet widths increase rapidly with increase in the principal quantum number, and show a very varied behavior in different states.<sup>16</sup> As Weizel has shown,<sup>17</sup> these pecularities can be explained by a gradual uncoupling of  $\sigma$  from the molecular axis.

a gradual uncoupling of  $\sigma$  from the molecular axis. The He<sub>2</sub> bands fall into two groups, the "orthohelium" group of bands ("main series" and related bands) and the "parhelium" group ("second series" and related bands). The writer has hitherto assumed (ref. 16 and elsewhere<sup>18</sup>) that both groups represent singlet states of He<sub>2</sub>, but others have fallen into the habit of assuming that the orthohelium levels are triplet states (with triplets so narrow as to be unresolved) and that the parhelium levels are singlet states. In view of Weizel's recent work.<sup>17</sup> it seems probable that these assumptions are correct

In view of Weizel's recent work,<sup>17</sup> it seems probable that these assumptions are correct. For the relatively stable  $2^{3}P$  state of He<sub>2</sub>, according to Curtis, the  $\sigma$ -type doubling can be represented by a quadratic formula, with  $F_A(j) > F_B(j)$ :  $B_A = 7.334$ ,  $B_B = 7.310$ ,  $c_A = c_B = 0$ . For other P and D states, the relations are more complicated,<sup>16, 17</sup> probably corresponding to various degrees of uncoupling of  $\sigma$ .

Eqs. (1)-(2), these two cases corresponding respectively to a  $\sigma$ -type doubling varying as j(j+1) or as j. In some cases (especially He<sub>2</sub>) both  $B^*$ 's and c's must be assumed to differ for the A and B substates.

Theory and conclusions: Hulthén has pointed out<sup>19</sup> that the selection rules of  $\sigma$ -type doubling can be expressed by a division of all the rotational states of a molecule into two practically non-combining systems of terms; combinations between such term-systems occur only in weak satellite branches<sup>20</sup> such as  $Q_{1A1B}$  and  $Q_{2A2B}$  of OH (cf. VII). Kronig<sup>21</sup> has made great progress in the theory of  $\sigma$ -type doubling, and has accounted for the observed selection rules for both homopolar and heteropolar molecules; he has also shown that the width of the  $\sigma$ -type doublets should vary as j(j+1) in <sup>1</sup>P states. This is in agreement with the experimental data on AlH.<sup>7</sup> Van Vleck, in recent theoretical work (cf. preceding paper), has reached valuable conclusions in regard to the magnitude of the separations  $F_A - F_B$  to be expected in  $\sigma$ -type doubling, in the general case of molecules possessing a spin (cf. summary in section 8 of his paper).

One of the most striking relations in Table I is the contrast in certain case  $a {}^{2}P$  states between the large separations  $F_{A} - F_{B}$  for the  ${}^{2}P_{1/2}$  levels and the negligible separations for the  ${}^{2}P_{3/2}$  levels. Examples are HgH, with

<sup>16</sup> Cf. R. S. Mulliken, Phys. Rev. 28, 1215 (1926); W. E. Curtis, Proc. Roy. Soc. 118A, 164–167 (1928); W. Weizel, ref. 17.

<sup>17</sup> W. Weizel, Zeits. f. Physik **52**, 175 (1928).

<sup>18</sup> Especially, Proc. Nat. Acad. Sci. 12, 158 (1926).

<sup>19</sup> E. Hulthén, Zeits. f. Physik **46**, 349 (1928).

<sup>20</sup> Hulthén (ref. 19, bottom p. 351) mentions the occurrence of weak satellites of similar type in CH and MgH; apparently no published data exist in regard to these. According to Kronig (ref. 21, p. 353) such satellites must be attributed to the effect of external influences, such as electric fields, on the molecules.

<sup>21</sup> R. de L. Kronig, Zeits. f. Physik 46, 814 (1928); 50, 347 (1928).

a normal  ${}^{2}P$  state, where the large separation is for  $F_{1A} - F_{1B}({}^{2}P_{1/2} \text{ levels})$ ; and BO, with an inverted  ${}^{2}P$ , where the large separation is for  $F_{2A} - F_{2B}$ (also  ${}^{2}P_{1/2}$  levels). Evidently the case *a* designations  ${}^{2}P_{1/2}$  and  ${}^{2}P_{3/2}$  are more fundamental here than the essentially case *b* designations  $F_{1}$  and  $F_{2}$ . In contrast to these results for case *a*  ${}^{2}P$  states is the fact that near case *b* (OH, MgH, CH) the separations  $F_{1A} - F_{1B}$  and  $F_{2A} - F_{2B}$  are small and nearly equal. Analogous relations exist in the  ${}^{3}P$  states of C<sub>2</sub> (case *b*) and N<sub>2</sub> (case *a*). All these conclusions are in excellent agreement with Van Vleck's theoretical work. Other relations shown in Table I, such as the linear variation of the doublet separations with *j* in case *a*  ${}^{2}P_{1/2}$  states, and the tendency toward variation with j(j+1) in  ${}^{1}P$  states, are also in good agreement with Van Vleck's results. In the case of the second positive N<sub>2</sub> bands, Van Vleck's work makes it possible, as it was not previously, to conclude definitely that the  ${}^{3}P$  levels involved are both normal.<sup>15</sup>

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