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CALCULATION OF FORCE CONSTANTS WITH THE MAXIMUM OVERLAP METHOD, II

MOLECULES WITH LONE PAIR ELECTRONS OR EMPTY ORBITALS (SHORT COMMUNICATION)

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Introduction

In a previous paper [5] the force constants of tetrahedral molecules were computed on the assumption that the energy of the molecules was proportional to the sum of overlap integrals between the bonding orbitals. The sum of overlap integrals was computed with the *maximum overlap method* [6]. In that case the number of bonding orbitals of the central atom was identical with the number of ligands.

The *maximum overlap method* can also be used in cases, where there are fewer ligands than bonding orbitals on the central atom, but the result does not depend on the non-bonding orbital being empty or occupied by a lone pair. The two cases clearly differ from each other physically. so we must must first decide, which of the two possible cases is represented by the hybrid orbitals, obtained by the *maximum overlap method.*

. 1

If the geometry of the above-mentioned two types of molecules is taken into account, it can be seen that the difference is not only quantitative but also qualitative, *i.e.* the symmetry of the molecules is different. (For example,

BF_2 belongs to the D_3 group, while NH_3 to the C_{3v}, group.) On the basis of this qualitative difference it will be shown that the hybrids obtained with the *maximum overlap method* correspond to the case of empty orbitals.

XY_2 and XY_3 type molecules were examined in a general form. We used only *s* and *p* orbitals, and consequently the XY_i distances and the Y_i-X-Y_j angles were equal in the same molecule. In the following we will vary only the bond angle.

If the overlap integrals between the atomic orbitals are known, the overlap matrix can be computed ($\mathbf{S}$), and the maximal sum of overlaps between the bonding orbitals (MAX) can be obtained in the following way [1, 6]:

$$\mathrm{MAX} = \mathrm{tr}(\mathbf{S}\mathbf{S}^{\mathrm{T}})^{1/2} \tag{1}$$

where $\mathbf{S}^{\mathrm{T}}$ is the transposed of $\mathbf{S}$. The elements of $\mathbf{S}$ depend only on the geometrical data of the molecule, namely in our case the Y_i-X-Y_j angle, denoted in the following by α, and the atomic overlap integrals between the ligand orbitals and the *s* and *p* orbitals of the central atom, denoted by S and P, respectively. Using Eq. (1), the maximal sum of overlaps, MAX, can be obtained as a function of these three parameters. We succeeded in expressing the maximal overlap with a relatively simple formula in both cases:

$$XY_2 : MAX = \sqrt{2S^2 + P^2(1+\cos\alpha)} + \sqrt{p^2(1-\cos\alpha)a} \tag{2}$$

$$XY_3 : MAX = 2\sqrt{2}P\sin\alpha + \sqrt{3}\sqrt{S^2 + P^2\sqrt{1 - 1.33\sin^2\alpha}} \tag{3}$$

Having obtained Eqs. (2) and (3), the maximal value of MAX was searched with respect to the angle α. It is clear that the maximum overlap method predicts this configuration to be the most stable. In this way we derived an equation from which the equilibrium bond angle could be expressed explicitly. We obtained the same formula for both cases:

$$\cos\alpha_o = S^2/P^2 \tag{4}$$

We found, moreover, that if $S/P > 1$ for XY_2 molecules and if $S/P > 2^{-1/2}$ for XY_3 molecules, the equilibrium bond angle would be 180^o and 120^o, respectively. In the case of common molecules S/P is always greater than 1. It follows that the hybrid orbitals obtained by the maximum overlap method correspond to the case of empty non-bonding orbitals.

2

Papers in the literature dealing with the problem of lone pair electrons conclude that the experimental equilibrium data in the case of molecules with lone pair electrons cannot be reproduced with the maximum overlap method, unless an empirical parameter is introduced.

DEL RE *et al.* [2] reproduced the experimental bond angle of water by introducing a parameter which represented the interaction of the lone pair electrons with the others. This parameter was chosen in such a way as to fit the experimental data.

The works of VOLKOV [8] have shown that no serious mistake is made if the lone pair electrons are considered to be on the s orbital, and treated as an inert pair.

According to our calculation, we ought to decrease the value of S to obtain results, in accordance with the former procedures. But if there is no theoretical reason for doing so, it must be considered an arbitrary action.

It appears that for the consideration of the lone pair, further effects must be taken into account. We refer primarily to the electrostatic interaction of the electrons. If the central atom does not possess a lone pair, the electrostatic repulsions of the electrons are almost compensated, because the bonding electrons are equivalent or nearly equivalent. If the central atom does possess a lone pair, the electrostatic repulsions no longer be considered to be compensated. This problem requires further detailed investigation.

. 2

Before speaking about the numerical calculations, a theoretical problem will be discussed with the aid of Eq. (4). We know from experimental results that if a bond distance increases, there is a decrease in the s content of the bonding orbital [7]. This phenomenon can be interpreted in the case of XY_2 and XY_3 type molecules with the *maximum overlap method.*

The connection between the equilibrium bond and the s content of the hybrid orbital has to be investigated first. On the basis of the geometry of the s and p orbitals, it is clear that the angle between the hybrid orbitals decreases when there is a decrease in the s content of the hybrid. Moreover, it can be seen that the hybrid orbital always points to the direction of the ligand, because we are dealing with the maximum overlap configuration. In this way the angle between the hybrids is the same as the angle between the bonds.

Next, we investigate the connection between the ratio S/P and the bond length. On the basis of the geometry of the s and p orbitals it can be seen that S/P is a monotonically decreasing function of the bond length. Thus it can be seen using Eq. (4) that the experimental facts are in accordance with the results of the *maximum overlap method.*

. 2

In order to show that the maximum overlap method can be used if the nonbonding orbital is empty, the force constants of BF_3 were calculated. In our calculations the same method was used as in the case of tetrahedral molecule [5]. The bonding orbital of fluorine was taken to be *sp* hybrid. Only the bending and the stretching – bending force constants were computed, because the model is unstable to stretching.

The symmetry coordinates are shown in Table I. r_i is the distance between the i-th F atom and the B atom, α_{ij} is the F_i - B - F_j angle and β_i is the angle between the threefold symmetry axis and the i-th bond. The effective nuclear charges are shown in Table II.

Table I

Symmetry coordinates and force constants of planar XY_3 molecules

Symmetry class	Symmetry coordinate	Force constant	
A_1'	$S_1 = 3^{-1/2}(\delta r_1 + \delta r_2 + \delta r_3)$	F_{11}	
A_2''	$S_2 = 3^{-1/2} r_o(\delta\beta_1 + \delta\beta_2 + \delta\beta_3)$	F_{22}	
E'	$S_1 = 2^{-1/2}(\delta r_2 - \delta r_3)$	F_{33}	F_{34}
	$S_1 = 2^{-1/2} r_0(\delta\alpha_{13} - \delta\alpha_{12})$	F_{44}	

r_o is the equilibrium bond length.

Table II

The effective nuclear charge of the Slater orbitals

	$2s$	$2p$
B	1.608	1.569
F	2.564	2.550

Table III

The calculated and the experimental force constants of BF_3

	Reference [4]	Reference [3]	Calculated
F_{22}	—	0.865	0.865
F_{34}	-0.268	-0.313	-0.311
F_{44}	0.525	0.515	0.323

Table III contains the calculated and the experimental values of the force constants. The constant factor was chosen so that the calculated F_{22} should agree with the experimental one. The results are qualitatively in agreement with the experimental values, as in the case of the tetrahedral molecules. The sign of the non-diagonal force constant is correct, but its numerical agreement must be considered accidental.

SUMMARY

We have shown that the *maximum overlap method* can be used, provided the central atom does not possess any lone pair electrons.

The stretching and stretching-bending force constants of BF_3 were computed up to a constant factor with our previously applied method. The sign of the non-diagonal force constant was obtained correctly in this case, too.

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