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# CALCULATION OF FORCE CONSTANTS WITH THE MAXIMUM OVERLAP METHOD, I

TETRAHEDRAL MOLECULES  
(SHORT COMMUNICATION)

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## 1

It is well known that the molecular force field cannot be determined unambiguously from the vibrational spectrum. Other, experimental data depending on the force field are rarely available. A simplified model is assumed then for the force field, which contains less parameters and thus is unambiguously determined by the available data (mostly only the vibrational frequencies). One of the most widely used models is the valence force field, in which it is assumed that the off-diagonal force constants in internal valence coordinate representation are zero. Thus in this model the interaction force constants are neglected.

From the force constants of small molecules determined exactly by means of additional data [3, 9, 10, 14 to 17] we can see that, in general, the interaction force constants cannot be neglected, and that the non-vanishing interaction force constants in molecules of the type  $XY_k$  are mainly due to the change in the hybridization of the central atom [6].

On the basis of hybridization force fields have been elaborated by LINNETT and MILLS [7, 8].

In our study we present a more general quantumchemical model with

the maximum overlap approximation. In this approximation we assume the bond energy to be proportional with the overlap integral of the bonding orbitals of the two atoms in the bond [4]. Having determined the best hybridization and the corresponding sum of overlap integrals as a function of the internal coordinates (if the molecule is symmetrical, that of the symmetry coordinates), the force constants multiplied with an unknown constant factor are obtained.

Our main goal was to find the signs of the interaction force constants because of the approximative character of the maximum overlap method. Regarding the nature of our approximation, we expect to get meaningful results only for the stretch-bend and bend-bend interaction force constants. The model is not stable for the stretching force constants if we do not take into account the repulsive forces acting between two atoms in a bond. But, in general, the main problem is represented by the interactions containing bending.

The method described in the present paper may be applied for molecules or fragments of a molecule with a central atom that is surrounded by ligands and has no lone pair electrons. If the central atom does possess a lone pair, one cannot expect the maximum of the sum of overlaps to be near the equilibrium of the molecule, because the maximum overlap method does not take the lone pair into account. Detailed investigation of this problem will be made in another publication.

## 2

Let the state function of the molecule be the linear combination of the atomic orbitals of the atoms in the molecule. Our task is now to obtain the linear combination of the atomic orbitals (hybridization) for which the sum of overlap integrals between the bonding orbitals is maximum.

The problem can generally be solved with the variational method, or with the method of DEL RE [2]. MURREL has described a procedure [11] for the computation of the hybridization in a molecule containing a central atom surrounded by ligands with known bonding orbitals. GOLEBIEWSKI has simplified this procedure [5].

Let the vector of the orbitals of the central atom be  $\phi = (\phi_1, \phi_2, \dots, \phi_n)$  the vector of the best hybrid orbitals  $\psi = (\psi_1, \psi_2, \dots, \psi_n)$  and that of the ligand orbitals  $\Theta = (\Theta_1, \Theta_2, \dots, \Theta_n)$ ,  $k \leq n$ .

The matrix  $\mathbf{S}$  is defined by the following equation:

$$\mathbf{S}_{ij} = \langle \Theta_i | \phi_j \rangle \quad (1)$$

MUREL and GOLEBIEWSKI have shown that the maximal value of the sum of the overlap integrals is:

$$s = \text{tr}(\mathbf{S}\mathbf{S}^T)^{1/2}, \quad (2)$$

and the best hybrid orbitals are determined by the following equation:

$$\psi = (\mathbf{S}\mathbf{S}^T)^{1/2}\mathbf{S}\phi. \quad (3)$$

For the determination of  $(\mathbf{S}\mathbf{S}^T)^{1/2}$  we refer to [12].

It can be shown easily using Eq. (3) that the best hybrid orbitals will possess the same spatial symmetry as the ligand orbitals.

### 3

The notation of the internal coordinates of a tetrahedral  $T_d$  molecule can be seen in Fig. 1:  $r_1, \alpha_{12}, \dots$  denote deviations from the equilibrium values. The symmetry coordinates are presented in Table I.

*Fig. 1.* Internal coordinates of the tetrahedral  $XY_4$  molecule

**Table I**

*The symmetry coordinates of a tetrahedral  $T_d$  molecule*

Symmetry class	Coordinate	Force constant
$A_1$	$S_1 = 2^{-1}(r_1 + r_2 + r_3 + r_4)$	$F_{11}$
E	$S_2 = 12^{-1}r_o(2\alpha_{12} - \alpha_{13} - \alpha_{14} - \alpha_{23} - \alpha_{24} + 2\alpha_{34})$	$F_{22}$
$F_2$	$S_3 = 2^{-1}(r_1 + r_2 - r_3 - r_4)$	$F_{33}$
	$S_4 = 2^{-1}r_o(\alpha_{12}a - \alpha_{34})$	$F_{44}$

$r_o$  is the equilibrium bond length

Using the symmetry representation, we will have interaction force constants only in the  $F_2$  species. The interaction of the internal bending coordinates can be calculated from the difference between  $F_{22}$  and  $F_{44}$ . But the symmetry force constants cannot be converted into internal force constants because the six angle coordinates are redundant.

We have calculated the maximum overlap with the MURREL – GOLEBIEWSKI method at nine values of  $S_2$  and  $S_4$  about the equilibrium state. In both cases  $\alpha_2$  was given the values  $-8^\circ, -6^\circ, -4^\circ, -2^\circ, 0^\circ, 2^\circ, 4^\circ, 6^\circ, 8^\circ$ . The calculation of  $S_4$  was performed at five different values of  $S_3$  :  $-0.106 \text{ \AA}; -0.053 \text{ \AA}; 0; 0.053 \text{ \AA}$  and  $0.106 \text{ \AA}$ . On the basis of the relation  $E = -ks$  ( $E$  is the energy of the molecule,  $s$  is the sum of overlaps and  $k$  is a constant) the force constants are given by the equation:

$$F_{ij} = -k \left( \frac{\delta^2 s}{\delta S_i \delta S_j} \right)_o \quad ij = 22, 34, 44 \quad (4)$$

*Fig. 2.* The change of maximum overlap with the bending vibration of the species  $E$  and  $F_2$ , of methane at  $S_3 = 0$

The functions  $s(S_2)$  and  $s(S_3, S_4)$  were approximated by polynomials of second degree in  $S_2$  and  $S_4$ , respectively. The result hardly changed using polynomials of higher degree. We have got  $F_{22}$  and  $F_{44}$  as the second derivatives of the polynomials.

$F_{34}$  was determined from the equation

$$F_{34} = F_{44} \left( \frac{\delta S_4}{\delta S_3} \right)_{s=\max} \quad (5)$$

which follows from the definition of the force constants. Some typical diagrams are shown in Figs 2 and 3.

*Fig. 3.* The change of maximum overlap with the bending vibration of the species  $F_2$  of silane at various values of  $S_3$

#### 4

Our calculations were carried out for the molecules  $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{CF}_4$  and  $\text{CCl}_4$ . The effective nuclear charges used in the Slater type orbitals and the

equilibrium geometrical data of the molecules are given in Table II [1, 13]. Fluorine and chlorine atoms were supposed to be  $sp$ -hybridized, because it produced greater overlap with the atomic orbitals of the central atom than the assumption of pure  $s$  or  $p$  orbitals.

**Table II**

*Atomic function and equilibrium bond lengths of the molecules*

Atom	Principal quantum number	Effective $Z_{ns}$	nuclear charge $Z_{np}$	charge $Z_{nd}$
C	2	1.6083	1.5679	
Si	3	1.6344	1.4284	0.3333
H	1	1.0000		
F	2	2.5639	2.5498	
Cl	3	2.3561	2.0387	
	CH <sub>4</sub>	SiH <sub>4</sub>	CF <sub>4</sub>	CCl <sub>4</sub>
$r_o(\text{\AA})$	1.093	1.483	1.302	1.778

**Table III**

*The force constants of CH<sub>4</sub>, SiH<sub>4</sub>, CF<sub>4</sub>, and CCl<sub>4</sub>; in mdyn/\AA*

Force constant	CH <sub>4</sub>		SiH <sub>4</sub>	
	calculated	lit.[9]	calculated	lit. [9]
	0.49	0.49	0.188	0.188
	-0.262	-0.206	-0.103	-0.023
	0.579	0.450	0.196	0.213
Force constant	CF <sub>4</sub>		CCl <sub>4</sub>	
	calculated	lit.[3]	calculated	lit. [10]
	0.71	0.71	0.311	0.311
	-0.322	-0.84	-0.210	-0.52
	0.733	0.02	0.320	0.38

The calculated force constants are presented in Table III. This table also contains the most reliable data available in the literature [3, 9, 10]. The values of  $k$  describing the connection between the energy and the overlap were chosen in such a way that the calculated  $F_{22}$  should agree with the experimental value.

It can be seen that the force fields of the molecules investigated are reflected quite well in our results. It is important that the sign of the inter-

action force constant  $F_{34}$  is in agreement with that of the experimental one.

But on the other hand, the results show that our model does not reflect the special characteristics of the force fields of the molecules investigated. So we can conclude from our results calculated so far that our model is fundamentally good, but requires further improvement. We suppose that the most important improvement would be the consideration of the mutual repulsion of the electron pairs on the central atom.

We tried to explain the difference between the force field of methane and silane by allowing the  $d$  orbitals of silicon to participate in the hybridization. The results, however, were practically the same as those obtained without the use of the  $d$  orbitals (Table III).

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#### SUMMARY

Bending and stretching-bending interaction force constants of methane, silane, carbon tetrafluoride and carbon tetrachloride have been determined by the maximum overlap approximation. The results are approaching the experimental data. Using the  $d$  orbitals of silicon left the results practically unchanged.

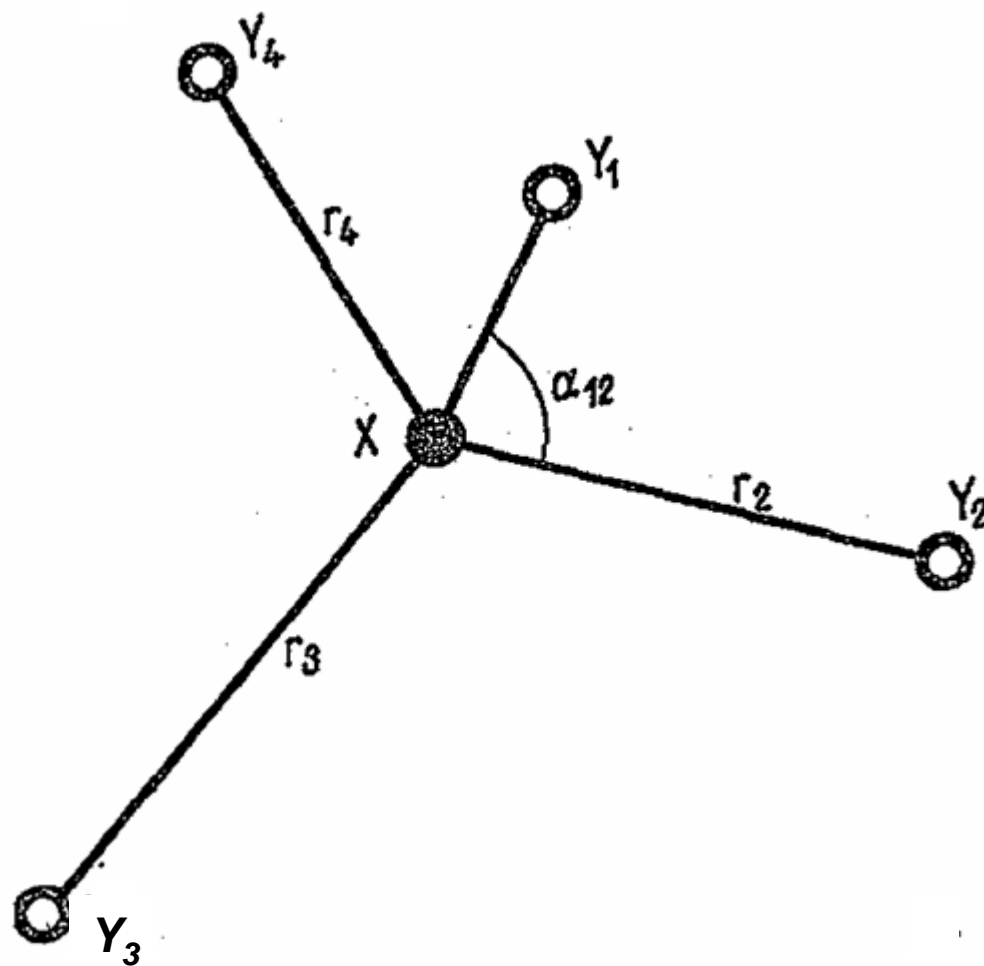
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*Fig. 1.* Internal coordinates of the tetrahedral XY<sub>4</sub> molecule



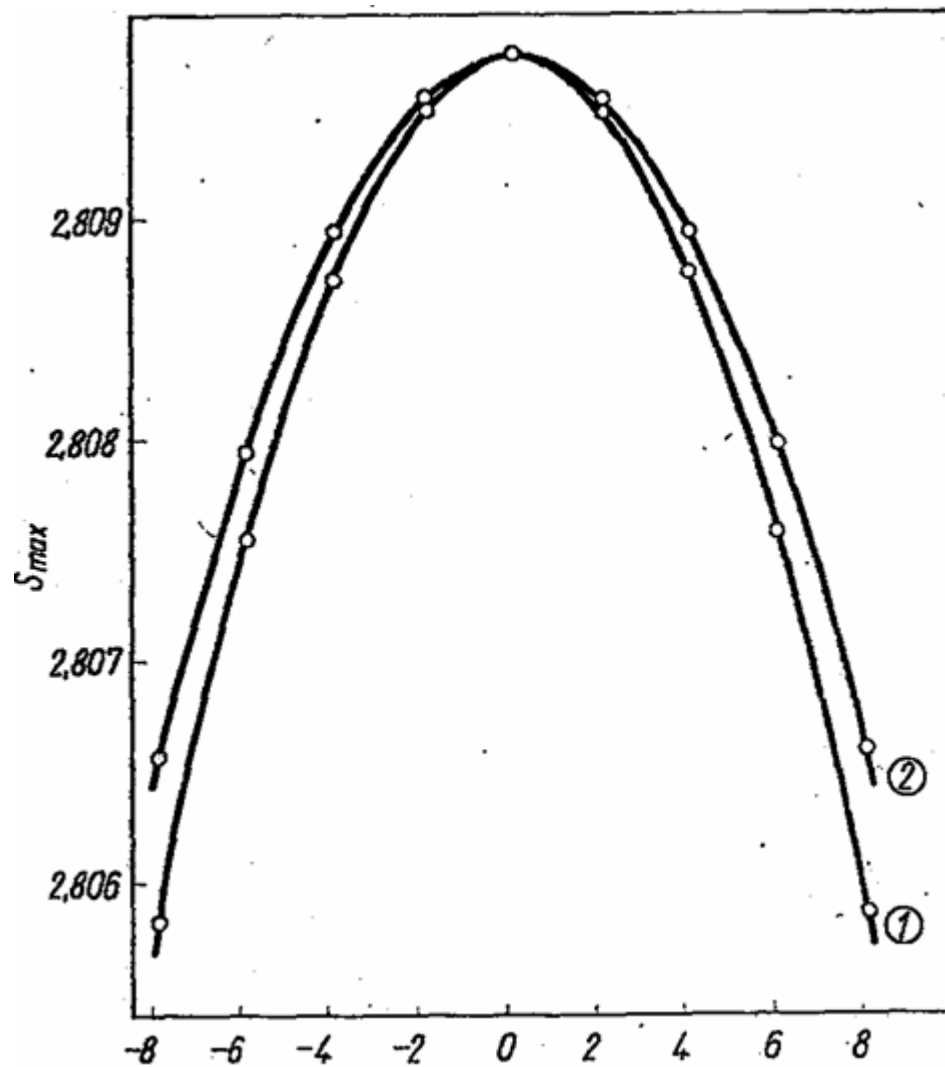


Fig. 2. The change of maximum overlap with the bending vibration of the species  $E$  and  $F_2$ , of methane at  $S_3 = 0$

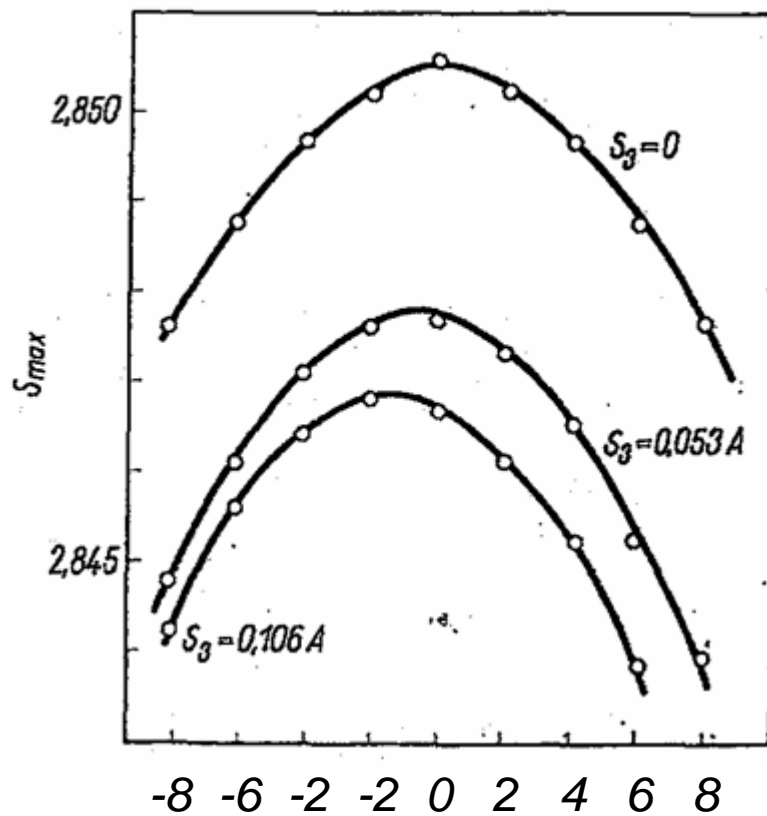


Fig. 3. The change of maximum overlap with the bending vibration of the species  $F_2$  of silane at various values of  $S_3$