GENERALIZED THEORY OF MAXIMUM OVERLAP*

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A method is presented for determination of best hybrid orbitals of a molecule of the type $MX_1X_2 \ldots X_K$ both on the central atom M and on the ligands X_1 through X_k with the aid of the criterion of maximum overlap introduced by Pauling.

The construction of hybrid orbitals for molecules of the type MX_K (homogeneous ligand sphere) and interpretation of the properties of a given molecule on their basis has been dealt with by Pauling.[1] Murrell[2] elaborated a method for the determination of hybrid orbitals of the central atom in the case of molecules of the type MX_K with a small or no symmetry using the condition of maximum overlap between the central atom and ligand orbitals and calculated in this way the best hybrid orbitals of the compound ClF_3. This method was modified and simplified[3-5]. (The relation between the method of maximum overlap and the Hückel MO method was pointed out by Lykos and Schmeising[6].) The method of maximum overlap was further used in calculating the hybridization of cyclopropane and similar molecules[7], in explaining the differences among measured bond lengths[4] in PCl_5, $SbCl_5$, SF_4 and ClF_3, in calculating various conformations[8] of ClF_5 and the bond angles[9-12] in H_2O and NH_3 and in studying complexes containing both σ and π bonds[13]. The authors[13], however, did not take into account the hybridization on ligands even when two atomic orbitals were localized on them, namely one for a σ bond and the other for a π bond. To determine the conformation of a molecule of the type MX_K on the basis of the method of maximum overlap, a "steepest descent" method was proposed[14].

The method of maximum overlap was originally formulated for molecules with a homogeneous ligand sphere while the hybridization of ligand orbitals was disregarded. In the present work the generalization for molecules with a heterogeneous ligand sphere is carried out. We take into account the hybridization on the central atom as well as on the ligands. The criterion of maximum overlap is generalized so that a weighed sum of overlap integrals is considered rather than a simple sum as proposed originally[2,3]. The weights influence the heterogeneity of the ligand sphere.

THEORETICAL

We shall consider a molecule of the type $MX_1X_2 \ldots X_K$, where M denotes central atom and X_1 through X_K ligands, which are generally different. On the central atom, a set of orthonormal real atomic orbitals is localized forming a column vector

$$\Phi = \{\varphi_i; i \in \langle 1, P \rangle\} ; \tag{1}$$

we assume that $P \geqq K$. Also on the i-th ligand X_i, a set of orthonormal real atomic orbitals is localized forming a column vector

$$\mathbf{X}_i = \{\chi_j^{(i)}; j \in \langle 1, Q_i \rangle\}, \tag{2}$$

where $Q_i \geqq 1$, $i \in \langle 1, K \rangle$. From the orthonormality of atomic orbitals it follows that

$$\Phi\Phi^T = \mathbf{I}_{(P)}, \qquad \mathbf{X}_i\mathbf{X}_i^T = \mathbf{I}_{(Q_i)}, \tag{3a,b}$$

where $\mathbf{I}_{(X)}$ denotes diagonal matrix, Φ^T transposed vector of Φ, similarly to $\mathbf{X}_i^T$ and $i \in \langle 1, K \rangle$.

In the space of atomic orbitals defined by Eq. (1), we select orthonormal hybrid atomic orbitals forming a column vector

$$\Psi = \{\psi_i; i \in \langle 1, K \rangle\} . \tag{4}$$

Analogously to Eqs (3) we have

$$\Psi\Psi^T = \mathbf{I}_{(K)} . \tag{5}$$

The relation between vectors Φ and Ψ is

$$\Psi = \mathbf{A}\Phi , \tag{6}$$

or in the component formalism $\psi_i = \sum_{j=1}^{P} a_{ij}\varphi_j$ for $i \in \langle 1, K \rangle$, *i.e.* $\mathbf{A}$ denotes transformation matrix of the type $K \times P$ with elements a_{ij}. On introducing Eq. (6) into (5) and using (3) we obtain a condition for the matrix $\mathbf{A}$:

$$\Psi\Psi^T = \mathbf{A}\Phi\Phi^T\mathbf{A}^T = \mathbf{A}\mathbf{I}_{(P)}\mathbf{A}^T = \mathbf{A}\mathbf{A}^T = \mathbf{I}_{(K)} . \tag{7}$$

In the i-th space defined by Eq. (2) we select a normalized hybrid atomic orbital and denote it as ϑ_i. It can be expressed as a linear combination of atomic orbitals localized on the given ligand:

$$\vartheta_i = \mathbf{c}_i^T\mathbf{X}_i = \sum_{j=1}^{Q_i} c_j^{(i)}\chi_j^{(i)}, \quad i \in \langle 1, K \rangle, \tag{8}$$

where $\mathbf{c}_i^T$ denotes row vector of coefficients $c_j^{(i)}$. From the condition that ϑ_i is normalized to one we obtain a condition for vector of coefficients $\mathbf{c}_i$

$$\mathbf{c}_i^T \mathbf{c}_i = \sum_{j=1}^{Q_i} c_j^{(i)} c_j^{(i)} = 1 , \quad i \in \langle 1, K \rangle ; \tag{9}$$

taking into account that the set of atomic orbitals localized on the i-th ligand, Eq. (2), is orthonormal. Now, the method of maximum overlap consists in determining such hybrid atomic orbitals (Eqs (4) and (8)) or such transformation matrix $\mathbf{A}$ in Eq. (6) and column vectors $\mathbf{c}_i$ in (8) that the weighed sum of overlap integrals $\langle \psi_i \mid \vartheta_i \rangle$ is maximum. We construct the functional

$$I = \sum_{i=1}^{K} k_i \langle \psi_i \mid \vartheta_i \rangle - \sum_{i,j=1}^{K} \frac{\lambda_{ij}}{2} \langle \psi_i \mid \psi_j \rangle - \sum_{i=1}^{K} \frac{\varepsilon_i}{2} \langle \vartheta_i \mid \vartheta_i \rangle , \tag{10}$$

in which the first summation expresses the weighed sum of overlap integrals between the i-th hybrid atomic orbital on the central atom and that on the ligand $\mathbf{X}_i$. The weight coefficients k_i characterize the inhomogeneity of the ligand sphere. They should be understood as semiempirical parameters which can be, for example, determined from energetic relations between the given ligand and the central atom. The second summation with Lagrange multipliers λ_{ij} expresses the restrictive condition (5) of orthonormality of the hybrid atomic orbitals on the central atom. Similarly, the third summation with Lagrange multipliers ε_i expresses the restrictive condition (9) for the hybrid atomic orbital on the i-th ligand. Introducing Eqs (6) and (8) into (10) we obtain

$$I = \sum_{i=1}^{K} \sum_{j=1}^{P} \sum_{l=1}^{Q_i} a_{ij} c_l^{(i)} k_i \langle \varphi_j \mid \chi_l^{(i)} \rangle - \sum_{i,j=1}^{K} \sum_{l=1}^{P} \frac{\lambda_{ij}}{2} a_{il} a_{jl} - \sum_{i=1}^{K} \sum_{j=1}^{Q_i} \frac{\varepsilon_i}{2} (c_j^{(i)})^2 , \tag{11}$$

where $\langle \varphi_j \mid \chi_l^{(i)} \rangle$ denotes overlap integral between the j-th atomic orbital of the central atom and l-th atomic orbital of the ligand X_i. The conditions for the functional (11) to be stationary (i.e. the mathematic expression of the maximum overlap) are

$$\partial I / \partial a_{ij} = 0 \quad \text{for} \quad i \in \langle 1, K \rangle ; \quad j \in \langle 1, P \rangle , \tag{12a}$$

$$\partial I / \partial c_j^{(i)} = 0 \quad \text{for} \quad i \in \langle 1, K \rangle ; \quad j \in \langle 1, Q_i \rangle . \tag{12b}$$

The condition (12a) applied to Eq. (11) gives

$$\sum_{l=1}^{Q_i} k_i c_l^{(i)} \langle \varphi_j \mid \chi_l^{(i)} \rangle = \sum_{l=1}^{K} \tfrac{1}{2} (\lambda_{il} + \lambda_{li}) \, a_{lj} , \tag{13}$$

for $i \in \langle 1, K \rangle$ and $j \in \langle 1, P \rangle$. If we introduce the matrices $\boldsymbol{B}$ and Λ with the elements

$$B_{ij} = \sum_{l=1}^{Q_i} k_i c_l^{(i)} \langle \varphi_j \mid \chi_l^{(i)} \rangle \,, \quad \Lambda_{il} = \tfrac{1}{2}(\lambda_{il} + \lambda_{li}) \,, \qquad (14a, b)$$

then Eq. (13) can be rewritten in the matrix form as

$$\boldsymbol{B} = \Lambda \boldsymbol{A} \,. \qquad (15)$$

Assuming that the matrix Λ is not singular we can express from Eq. (15) the transformation matrix

$$\boldsymbol{A} = \Lambda^{-1} \boldsymbol{B} \,. \qquad (16)$$

According to the definition ($14b$), Λ is a symmetrical matrix: $\Lambda^{\mathrm{T}} = \Lambda$. Introducing Eq. ($16$) into ($7$) we obtain

$$\Lambda^{-1} \boldsymbol{B} \boldsymbol{B}^{\mathrm{T}} \Lambda^{-1} = \boldsymbol{I}_{(K)} \,. \qquad (17)$$

which is fulfilled if

$$\Lambda = (\boldsymbol{B} \boldsymbol{B}^{\mathrm{T}})^{1/2} \,. \qquad (18)$$

Combining this equation with (16) we obtain the final expression for the transformation matrix:

$$\boldsymbol{A} = (\boldsymbol{B} \boldsymbol{B}^{\mathrm{T}})^{-1/2} \, \boldsymbol{B} \,. \qquad (19)$$

It is clear from the derivation of this equation that it is equivalent to the condition for the functional ($12a$) to be stationary. If the coefficients $c_l^{(i)}$ of the expansion ($14a$) are fixed then the elements of the matrix $\boldsymbol{A}$ defined by Eq. (19) lead to the maximum of the functional (11).

The condition ($12b$) applied to Eq. (11) gives

$$\sum_{l=1}^{P} a_{il} k_i \langle \varphi_l \mid \chi_j^{(i)} \rangle = \varepsilon_i c_j^{(i)} \,, \qquad (20)$$

for $i \in \langle 1, K \rangle$ and $j \in \langle 1, Q_i \rangle$. We introduce a column vector $\boldsymbol{b}_i$ with the elements

$$b_j^{(i)} = \sum_{l=1}^{P} a_{il} k_i \langle \varphi_l \mid \chi_j^{(i)} \rangle \,. \qquad (21)$$

Eq. (20) can be then be rewritten in the matrix form as

$$\boldsymbol{b}_i = \varepsilon_i \boldsymbol{c}_i \,. \qquad (22)$$

This result combined with Eq. (9) gives the actual value of the Lagrange multiplier ε_i, from which it follows that

$$\mathbf{c}_i = (\mathbf{b}_i^T \mathbf{b}_i)^{-1/2}\, \mathbf{b}_i , \tag{23}$$

for $i \in \langle 1, K \rangle$. Eqs (19) and (23) express the necessary condition for the functional (10) or (11) to be stationary. These equations are coupled since it follows from Eq. $(14a)$ that the matrix $\mathbf{B}$ depends on the vectors $\mathbf{c}_i$; similarly it follows from Eqs (21) and (23) that the vectors $\mathbf{c}_i$ depend on the matrix $\mathbf{A}$. This means that their calculation must be performed by the iteration method, namely the following one: we choose a zero-th approximation $c_i^{(0)}$ of the vectors $\mathbf{c}_i$. From Eqs $(14a)$ and (19) we calculate the matrix $\mathbf{A}^{(0)}$, from which we calculate with the use of Eqs (21) and (23) the vectors $\mathbf{c}_i^{(1)}$. We repeat this procedure until the vectors and the matrix are self-consistent. If $Q_i = 1$ and $k_i = 1$ for $i \in \langle 1, K \rangle$, the solution of Eq. (23) is not necessary, Eq. (19) being reduced to one known from the simple theory of maximum overlap in which no hybridization on ligands is considered[3]. The first summation in Eq. (11), which represents the total bond strength, can be with the aid of Eqs $(14a)$ and (19) rewritten in the form

$$E = \mathrm{Sp}(\mathbf{AB}^T) = \mathrm{Sp}\{(\mathbf{BB}^T)^{1/2}\} . \tag{24}$$

If the eigenvalues of the symmetrical matrix $\mathbf{BB}^T$ are denoted as μ_1 through μ_K, Eq. (24) can be rewritten in the common form[3]

$$E = \sum_{i=1}^{K} \mu_i^{1/2} . \tag{25}$$

From a more detailed analysis of the proposed method it follows that the functional (11) has a maximum if the roots in $(\mathbf{BB}_i^T)^{-1/2}$ and $(\mathbf{b}_i^T \mathbf{b})^{-1/2}$ are taken with the positive sign.

BEST HYBRID ORBITALS FOR ClF$_3$

The described method was applied to a molecule of chlorine trifluoride. According to experimental data[10], ClF$_3$ is a planar molecule with bond angles $\sphericalangle F^1—Cl—F^2 = \sphericalangle F^1—Cl—F^3 = 87.5°$, bond lengths $R(Cl—F^1) = 1.598$ Å, $R(Cl—F^2) = R(Cl—F^3) = 1.698$ Å. For a unique definition of the overlap integrals, we assume that the molecule is situated in the $x-z$ plane, the Cl atom being placed in the origin of coordinates. On this atom, six Slater atomic orbitals are localized: $3s$, $3p_z$, $3p_x$, $3d_{z^2}$, $3d_{x^2-y^2}$ and $3d_{xz}$. The local coordinate system on each F atom is oriented so that the z axis is directed towards the Cl atom. Two Slater atomic orbitals are localized on the F atoms: $2s$ and $3p_z$ (the latter is oriented in the local coordinate system). The exponents of the Slater atomic orbitals were calculated according to the Slater rules. The values of the overlap integrals, $\langle \varphi_j \mid \chi_i^{(i)} \rangle$, calculated according to Mulliken and coworkers[11] from Eqs $(14a)$ and (21), are in Table I. The weight coefficients k_i were set equal to one (homogeneous ligand sphere). The

iteration in solving Eqs (19) and (23) begins with $c_i^{(0)}$ ($i = 1, 2, 3$) chosen so that $c_i^{(j)} = Q_i^{-1/2}$ for $j \in \langle 1, Q_i \rangle$. We obtained after five iterations the total bond strength E defined by Eqs (24) and (25) with a precision to 10^{-8}. The calculations were performed on a computer of the type IBM 7040 with a program written in Fortran IV. The transformation matrix $\mathbf{A}$ is given in Table II and the vectors $\mathbf{c}_i$ ($i = 1-3$) are listed in Table III. The total bond strength E for the ClF_3

TABLE I

Overlap Integrals

| Central Atom | Ligands | | | | | |
| | F^1 | | F^2 | | F^3 | |
	$2s$	$2p_z$	$2s$	$2p_z$	$2s$	$2p_z$
$3s$	0·185527	0·165862	0·153519	0·142892	0·153519	0·142892
$3p_z$	0·272603	0·230325	0·009986	0·008886	0·009986	0·008886
Cl $3p_x$	0·	0·	0·228730	0·203515	−0·228730	−0·203515
$3d_{z^2}$	0·327181	−0·034238	−0·165877	0·009493	−0·165877	0·009493
$3d_{x^2-y^2}$	0·	0·	−0·288407	0·016504	0·288407	−0·016504
$3d_{xz}$	0·	0·	0·025184	−0·001441	−0·025184	0·001441

TABLE II

Transformation Matrix $\mathbf{A}$

| HAO's | Atomic orbitals | | | | | |
	$3s$	$3p_z$	$3p_x$	$3d_{z^2}$	$3d_{x^2-y^2}$	$3d_{xz}$
Cl - F^1	0·456883	0·681930	0·	0·570811	−0·020090	0·
Cl - F^2	0·384610	0·011812	0·705032	−0·304028	0·509414	0·054134
Cl - F^3	0·384610	0·011812	−0·705032	−0·304028	0·509414	−0·054134

TABLE III

Vectors $\mathbf{c}_i$ (for $i = 1,2,3$) for F^1, F^2, F^3

AO's	F^1	F^2	F^3
$2s$	0·906305	0·913089	0·913089
$2p_z$	0·422624	0·407761	0·407761

molecule is equal to $1·42277$; the contributions from different bonds are: $E(Cl-F^1) = 0·504708$, $E(Cl-F^2) = E(Cl-F^3) = 0·459033$ in accord with the fact that the $Cl-F^1$ bond is shorter than the others. Furthermore, calculations were performed with the assumption that only one atomic orbital is localized on the F atoms, namely either $2s$ or $2p_z$. For the total bond strength we then obtained $E_s = 1·30607$ or $E_p = 0·75202$. In these two calculations, the hybridization on ligands was not taken into account, so it was sufficient to solve only Eq. (19), a procedure equivalent to the Golebiewski formalism[3] of maximum overlap.

CONCLUSIONS

The problem of computing the hybrid atomic orbital both on the central atom and on the ligand can be formulated for special cases in different ways[12]. The advantage of our method consists in its generality and clear formulation. Moreover, the weight parameters k_i for distinguishing the heterogeneity of the ligand sphere can be simply introduced, the form of the final equations being preserved. The proposed iteration method of solving the coupled equations (19) and (23) was tested on a model calculation of the molecule of ClF_3. After five iterations, self-consistent values for transformation matrix A and vectors c_i were obtained.

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