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CONSTRUCTION OF THE BEST HYBRID ORBITALS FOR A MOLECULE MX_5

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The construction of the best hybrid orbitals of the central atom is an important problem of Pauling's theory [1] with respect to the quantum-mechanical characterization of the directed character of covalent bond. These orbitals determine the symmetry of the molecule and the strength of the covalent bond. According to M. Klessinger and R. McWeeny [2] the significance of determining the best hybrid orbitals of a central atom is the possibility to construct different group functions for molecules. The construction of hybrid orbitals is relatively a simple problem in the case of molecules with a high degree of symmetry.

J. N. Murrell [3] elaborated the semiempirical method of the construction of the best hybrid orbitals for molecules of the type M-(X_1, ..., X_k) based on the principle of a maximum overlap of hybrid orbitals of the central atom with all ligand orbitals which take part in creation σ-bonds. Murrell's method of maximum overlap represents a higher degree of the development of Pauling's theory of directed bonds because the overlap integrals are a better criterium for the strength of bonds than the strength of orbitals since in their calculations we have to take into consideration not only the angular part but also the radial part of the wave function and the internuclear distance. The stronger the bond the lower the energy of the molecule. Analogically we get in connection with assumption that the bond energy is proportional to the overlap, under the condition of the maximum overlap of the central atom orbital with the ligand orbitals, the best hybrid orbitals for our molecule. These ideas are the basis of Murrell's method which enables us to find the best hybrid orbitals for nonsymmetrical molecules too.

J. N. Murrell considers molecules of a type MX_k in which all ligands are directly bonded to the central atom. According to J. N. Murrell the best hybrid orbitals Ψ_i of the central atom M can be expressed by the form

$$\begin{bmatrix} \Psi_1 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \Psi_k \end{bmatrix} = \mathbf{A} \begin{bmatrix} \varphi_1 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \varphi_n \end{bmatrix} = \begin{bmatrix} a_{11} & \ldots\ldots & a_{1n} \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ a_{k1} & \ldots\ldots & a_{km} \end{bmatrix} \begin{bmatrix} \varphi_1 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \varphi_n \end{bmatrix} \tag{1}$$

where $n \geq k$ and φ_j ($j = 1, 2, \ldots, n$) are linear independent real and orthogonal atomic orbitals of the central atom. Single ligands are directly bonded to the central atom M with the help of orbitals $\Theta_1, \ldots, \Theta_k$ with the assumption that each ligand X_i has only one orbital Θ_i by which it takes part in the σ-bond. With respect to the fact that the $n + k$ of the orbitals $\Theta_1, \ldots, \Theta_k, \varphi_1, \ldots, \varphi_n$ satisfie the condition

$$\langle \Theta_i | \Theta_j \rangle = \delta_{ij}, \tag{2}$$

$$\langle \varphi_r | \varphi_s \rangle = \delta_{rs},$$

we can consider them as a semiorthogonal set of orbitals [4]. The coefficients a_{ij} of the matrix $\mathbf{A}$ are determined from the condition of the maximum sum of overlap integrals of the best hybrid orbitals of the central atom with the ligand orbitals forming σ-bonds with the central atom:

$$\sum_{i=1}^{k} \langle \Psi_i | \Theta_i \rangle = \sum_{i=1}^{k} \sum_{j=1}^{n} a_{ij} \langle \varphi_j | \Theta_i \rangle. \tag{3}$$

When we denote by $\mathbf{R}$ the overlap matrix between the orbitals Θ_i and φ_j and the overlap matrix between Θ_i and the best hybrid orbitals of the central atom Ψ_i by $\mathbf{S}$ we can find such a matrix $\mathbf{A}$ that

$$\mathbf{S} = \mathbf{AR} \tag{4}$$

in which the trace of the submatrix $\mathbf{S}$ constructed from the first k rows of matrix $\mathbf{S}$ is maximal. We take into consideration that the hybrid orbitals expressed in the form

$$\{\Psi\} = \mathbf{A}\,\{\varphi\} \tag{5}$$

are orthonormal. $\{\Psi\}$ and $\{\varphi\}$ are column matrices.

From the above it follows that the maximum overlap method is based on the assumption according to which the resonance integral between the pair of atoms i and j β_{ij} in case of σ- and π-interaction is directly proportional to the overlap integral [5]

$$\beta_{ij}(R) = k\, S_{ij}(R), \tag{6}$$

where k is a constant of proportionality, S_{ij} is the overlap integral and R is an internuclear distance. At the same time it is assumed that the bond order between the central atom M and ligands $X_1, \ldots, X_k$ is the same for all bonds.

The first step in the application of the maximum overlap method is the construction of the orthonormal set of atomic orbitals χ_i ($i = 1, 2, \ldots, n$):

$$\begin{bmatrix} \chi_1 \\ \cdot \\ \cdot \\ \cdot \\ \chi_n \end{bmatrix} = \mathbf{B} \begin{bmatrix} \varphi_1 \\ \cdot \\ \cdot \\ \cdot \\ \varphi_n \end{bmatrix} \tag{7}$$

which has such properties that all nonbonding orbitals $\chi_{k+1}, \ldots, \chi_n$ are orthogonal to all bonding ligand orbitals $\Theta_1, \ldots, \Theta_n$. Hence

$$\langle \Theta_t | \chi_i \rangle = \sum_{j=1}^{n} \langle \Theta_t | \varphi_j \rangle b_{ij} = 0, \tag{8}$$

for $i = k + 1$ to n, and $t = 1$ to k, and also

$$\sum_{j=1}^{n} (b_{ij} b_{i'j} - \delta_{ii'}) = 0. \tag{9}$$

The bonding orbitals $\chi_1, \ldots, \chi_k$ are orthogonal to all nonbonding orbitals $\chi_{k+1}, \ldots, \chi_n$ and mutually orthogonal. The bonding orbitals are constructed by the Schmidt process [6]. From k bonding orbitals we construct a square overlap matrix $\mathbf{P}$ of the order k. The process of maximalization of equation (3) is now equivalent to the process of maximalization of equation

$$\operatorname{tr} \mathbf{S} = \sum_{i,j=1}^{k} C_{ij} \langle \chi_j | \Theta_i \rangle \tag{10}$$

or, in matrix notation,

$$\operatorname{tr} \mathbf{S} = \operatorname{tr} (\mathbf{CP}), \tag{11}$$

where $(P)_{ij} = \langle \chi_i | \Theta_j \rangle$, $\mathbf{CC}^T = 1$.

According to Murrell the matrix $\mathbf{S}_1$ must be symmetric when the trace of the matrix $\mathbf{S}_1$ is maximal. We can determine the matrix $\mathbf{C}$ from the equation

$$\mathbf{C} = \mathbf{P}^{-1} (\mathbf{PP}^T)^{1/2}, \tag{11a}$$

where $\mathbf{P}\,\mathbf{P}^T$ is a symmetric and real matrix.

The best hybrid orbitals are given by

$$\{\Psi\} = \mathbf{C}\,\{\chi\} = \mathbf{C}\,\mathbf{B}_1\,\{\varphi\}, \tag{12}$$

where $\mathbf{B}_1$ is the submatrix formed by the first k rows of $\mathbf{B}$.

HYBRID ORBITALS FOR ClF_5

From the results of measurement of infrared and Raman spectra as well as from the NMR analysis in [7] it follows that the molecule ClF_5 has in a certain case a square pyramidal structure of the group C_{4v} (Fig. 1). The atom of chlorine has the electronic structure $1s^2 2s^2 2p^6 3s^2 3p^5$. Five electrons from the seven of an open shell take part in the σ-bond and the other two electrons are on one nonbonding orbital. We use at least six orbitals of the chlorine atom to describe the electronic structure of the molecule. The orbitals $3s$ and $3p$ are not enough and therefore we have to use the $3d$ orbitals of the chlorine atom too. We find the best hybrid orbitals of the chlorine atom on the basis of the principle of the maximum overlap method with the orbitals of the fluorine atom. We use the next set of atomic orbitals:

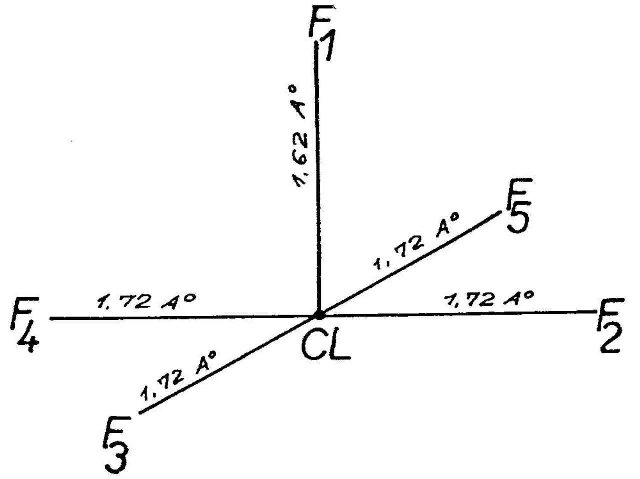

Fig. 1. Symmetry of the molecule ClF_5.

$3s = R_s$

$3p_z = \sqrt{3} \cos \Theta\, R_p$

$3p_x = \sqrt{3} \sin \Theta \cos \varphi\, R_p$

$3d_{z^2} = \sqrt{(5/4)}\,(3 \cos^2 \Theta - 1)\, R_d$

$3d_{xz} = \sqrt{15} \sin \Theta \cos \Theta \cos \varphi\, R_d$

$3d_{xz} = \sqrt{15} \sin \Theta \cos \Theta \sin \varphi\, R_d$

$$3p_y = \sqrt{3} \sin \Theta \sin \varphi \, R_p \qquad 3d_{x^2-y^2} = \sqrt{(15/4)} \sin^2\Theta \cos 2\varphi \, R_d$$

$$3d_{xy} = \sqrt{(15/4} \sin^2\Theta \sin 2\varphi \, R_d .$$

The R-s are normalized radial functions divided by $2(\pi)^{1/2}$.

To simplify the calculations we shall assume that the overlap integrals between different atomic orbitals and an unspecified ligand orbital are proportional to the projection of the angular part of the orbital on the central atom on the bond direction. In the calculation of the overlap integrals on this basis we shall not take into account that the $3s$, $3p$ and $3d$ atomic orbitals have different radial wave functions. With this assumption we construct the following overlap matrix:

$$\mathbf{R} = \begin{array}{c} \\ s \\ p_z \\ p_x \\ d_{z^2} \\ d_{x^2-y^2} \\ p_y \\ d_{xz} \\ d_{yz} \\ d_{xy} \end{array} \left(\begin{array}{ccccc} \Theta_1 & \Theta_2 & \Theta_3 & \Theta_4 & \Theta_5 \\ 1 & 1 & 1 & 1 & 1 \\ \sqrt{3} & 0 & 0 & 0 & 0 \\ 0 & \sqrt{3} & 0 & -\sqrt{3} & 0 \\ \sqrt{5} & -\frac{1}{2}\sqrt{5} & -\frac{1}{2}\sqrt{5} & -\frac{1}{2}\sqrt{5} & -\frac{1}{2}\sqrt{5} \\ 0 & \frac{1}{2}\sqrt{15} & -\frac{1}{2}\sqrt{15} & \frac{1}{2}\sqrt{15} & -\frac{1}{2}\sqrt{15} \\ 0 & 0 & \sqrt{3} & 0 & -\sqrt{3} \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{array} \right)$$

From the structure of the matrix $\mathbf{R}$ it follows that in the molecule ClF_5 and in similar molecules the orbitals s, p_z, d_{z^2}, p_x, $d_{x^2-y^2}$ and p_y of the chlorine atom and the corresponding p orbitals of the fluorine atom take part in the bonding. These six orbitals of the chlorine atom give five bonding orbitals, on which there is one electron from the chlorine atom and one from each fluorine atom. Besides we still have one nonbonding orbital which is occupied by two electrons of the chlorine atom. Other three orbitals of the chlorine atom. d_{xz}, d_{yz} and d_{xy} do not take part in the σ-bond and are orthogonal to each fluorine atomic orbital. These orbitals can take part in the π-bonds.

Let us construct one nonbonding orbital χ_6. There are $n(n-k) = 6$ coefficients to be determined, and $(n-k) \, . \, (n+k+1)/2$ equations of the type (8) and (12).

By solving the system of homogenous equations (12)

$$b_{61} + \sqrt{3}\, b_{62} + \sqrt{5}\, b_{64} = 0, \tag{12}$$

$$b_{61} + \sqrt{3}\, b_{63} - \tfrac{1}{2}\sqrt{5}\, b_{64} + \tfrac{1}{2}\sqrt{15}\, b_{65} = 0,$$

$$b_{61} - \tfrac{1}{2}\sqrt{5}\, b_{64} - \tfrac{1}{2}\sqrt{15}\, b_{65} + \sqrt{3}\, b_{66} = 0,$$

$$b_{61} - \sqrt{3}\, b_{63} - \tfrac{1}{2}\sqrt{5}\, b_{64} + \tfrac{1}{2}\sqrt{15}\, b_{65} = 0,$$

$$b_{61} - \tfrac{1}{2}\sqrt{5}\, b_{64} - \tfrac{1}{2}\sqrt{15}\, b_{65} - \sqrt{3}\, b_{66} = 0$$

and the equation (13)

$$b_{61}^2 + b_{62}^2 + b_{63}^2 + b_{64}^2 + b_{65}^2 + b_{66}^2 = 6$$

for the orbital χ_6 we get

$$\chi_6 = \frac{1}{2\sqrt{6}} (\sqrt{5}\, s - \sqrt{15}\, p_z + 2d_{z^2}). \tag{14}$$

Now we must construct the bonding orbitals χ_5, χ_4, χ_3, χ_2 and χ_1 by a linear combination of s, p_z, p_x, d_{z^2}, $d_{x^2-y^2}$ and p_y, which are orthogonal to χ_6. By the Schmidt process

$$\chi_k = N_k \{\varphi_k - \sum_{i=k+1}^{n} \langle \chi_i | \varphi_k \rangle \chi_i\}, \tag{15}$$

$$\chi_{k-1} = N_{k-1}\{\varphi_{k-1} - \sum_{i=k}^{n} \langle \chi_i | \varphi_{k-1} \rangle \chi_i\}, \tag{16}$$

we construct the following bonding orbitals:

$$\chi_5 = \frac{1}{2\sqrt{114}} \{19\, s + 5\sqrt{3}\, p_z - 2\sqrt{5}\, d_{z^2}\}, \tag{17}$$

$$\chi_4 = \frac{1}{\sqrt{19}} (2p_z + \sqrt{15}\, d_{z^2}),$$

$$\chi_3 = p_x ,$$

$$\chi_2 = d_{x^2-y^2} ,$$

$$\chi_1 = p_y .$$

It now remains to determine the linear combination of χ_1, …, χ_4 and χ_5 which has the maximum overlap with the ligand orbitals. The overlap between bonding orbitals χ_i and ligand orbitals is represented by the matrix $\mathbf{P}$:

$$\mathbf{P} = \begin{array}{c|ccccc} & \Theta_1 & \Theta_2 & \Theta_3 & \Theta_4 & \Theta_5 \\ \hline \chi_1 & 0 & 0 & \sqrt{3} & 0 & -\sqrt{3} \\ \chi_2 & 0 & \frac{1}{2}\sqrt{15} & -\frac{1}{2}\sqrt{15} & \frac{1}{2}\sqrt{15} & -\frac{1}{2}\sqrt{15} \\ \chi_3 & 0 & \sqrt{3} & 0 & -\sqrt{3} & 0 \\ \chi_4 & 7\sqrt{\frac{3}{19}} & -\frac{5}{2}\sqrt{\frac{3}{19}} & -\frac{5}{2}\sqrt{\frac{3}{19}} & -\frac{5}{2}\sqrt{\frac{3}{19}} & -\frac{5}{2}\sqrt{\frac{3}{19}} \\ \chi_5 & \frac{12}{\sqrt{114}} & \frac{12}{\sqrt{114}} & \frac{12}{\sqrt{114}} & \frac{12}{\sqrt{114}} & \frac{12}{\sqrt{114}} \end{array} . \tag{18}$$

The matrix **C** is

$$\mathbf{C} = \begin{bmatrix} .000 & .000 & .000 & .850 & .526 \\ .000 & .500 & .707 & -0.263 & .425 \\ .707 & -0.500 & .000 & -0.263 & .425 \\ .000 & .500 & -0.707 & -0.263 & .425 \\ -0.707 & -0.500 & .000 & -0.263 & .425 \end{bmatrix} . \tag{19}$$

The matrix of the overlap integrals between the best hybrid orbitals and the orbitals of fluorine atom is

$$\mathbf{S} = \mathbf{CP} = \begin{bmatrix} 2.957 & -0.254 & -0.254 & -0.254 & -0.254 \\ -0.254 & 2.932 & -0.229 & .483 & -0.229 \\ -0.254 & -0.229 & 2{,}932 & -0.229 & .483 \\ -0.254 & .483 & -0.229 & 2.932 & -0.229 \\ -0.254 & -0.229 & .483 & -0.229 & 2.932 \end{bmatrix} . \tag{20}$$

The trace of the matrix $\mathbf{S}_1$ is 14.686. The best hybrid orbitals are obtained from (17) and the expression for $\mathbf{P}^{-1}\ (\mathbf{PP}^T)^{1/2}$:

$$\begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \\ \Psi_5 \end{bmatrix} = \begin{bmatrix} .468 & .604 & .000 & .645 & .000 & .000 \\ .378 & .052 & .707 & -0.323 & .500 & .000 \\ .378 & .052 & .000 & -0.323 & -0.500 & .707 \\ .378 & .052 & -0.707 & -0.323 & .500 & .000 \\ .378 & .052 & .000 & -0.323 & -0.500 & -0.707 \end{bmatrix} \begin{bmatrix} s \\ p_z \\ p_x \\ d_{z^2} \\ d_{x^2-y^2} \\ p_y \end{bmatrix} \tag{21}$$

THE GOLOBIEWSKI METHOD

A simple method for constructing Ψ_i's was developed by P. G. Lykos and T. L. Gilbert [8], and independently and differently by A. Golobiewski [9]. In the Golobiewski method the matrix $\mathbf{R}^T$, which has k rows and n columns is denoted by **S**:

$$\mathbf{S} = \begin{bmatrix} \langle\Theta_1|\varphi_1\rangle \cdots\cdots\cdots \langle\Theta_1|\varphi_n\rangle \\ \cdot \qquad\qquad \cdot \\ \cdot \qquad\qquad \cdot \\ \cdot \qquad\qquad \cdot \\ \langle\Theta_k|\varphi_1\rangle \cdots\cdots\cdots \langle\Theta_k|\varphi_n\rangle \end{bmatrix} . \tag{22}$$

The matrix $\mathbf{SS}^T$ (of the order $k \leq n$) is symmetric and real and can be diagonalized by an orthogonal matrix **U**, thus

$$\mathbf{SS}^T = \mathbf{U}^T D(\alpha_1, \ldots, \alpha_k)\mathbf{U}, \tag{23}$$

where all α_i's are real and positive. For a given geometrical configuration and a given set of orbitals $\varphi_1, \ldots, \varphi_n$, the maximum possible value of the trace of $\mathbf{S}_1$ can be calculated from the formula

$$(\mathrm{tr}\ \mathbf{S}_1)_{\max} = \sum_{i=1}^{k} \alpha_i^{1/2}, \tag{24}$$

where all $\alpha_i^{1/2}$-s have to be taken as positive.

Provided that all α_i-s are different from zero, the matrix elements a_{ij} of the matrix **A** can be calculated with the use of the following explicit formula:

$$\begin{bmatrix} a_{11} \cdots\cdots\cdots a_{1n} \\ \cdot \\ \cdot \\ \cdot \\ a_{k1} \cdots\cdots\cdots a_{kn} \end{bmatrix} = \mathbf{U}^T D(\alpha_1^{-1/2}, \ldots, \alpha_k^{-1/2})\mathbf{US}, \tag{25}$$

where all square roots $\alpha_i^{1/2}$ have to be taken with a positive sign.

We find the best hybrid orbitals for the molecule ClF_5 by the Golobiewski simplified method.

The symmetric and real $\mathbf{SS}^T$ matrix is equal to

$$\mathbf{SS}^T = \begin{bmatrix} 9.000 & -1.500 & -1.500 & -1.500 & -1.500 \\ -1.500 & 9.000 & -1.500 & 3.000 & -1.500 \\ -1.500 & -1.500 & 9.000 & -1.500 & 3.000 \\ -1.500 & 3.000 & -1.500 & 9.000 & -1.500 \\ -1.500 & -1.500 & 3.000 & -1.500 & 9.000 \end{bmatrix} \tag{26}$$

and

$$(\mathbf{SS}^T)^{-1/2} = \begin{bmatrix} .348 & .030 & .030 & .030 & .030 \\ .030 & .356 & .023 & -0.052 & .023 \\ .030 & .023 & .356 & .023 & -0.052 \\ .030 & -0.053 & .023 & .356 & .023 \\ .030 & .023 & -0.052 & .023 & .356 \end{bmatrix} . \tag{27}$$

The matrix of the best linear transformation coefficients

$$\mathbf{A} = \begin{bmatrix} .468 & .603 & .000 & .645 & .000 & .000 \\ .378 & .052 & .707 & -0.323 & .500 & .000 \\ .378 & .052 & .000 & -0.323 & -0.500 & .707 \\ .378 & .052 & -0.707 & -0.323 & .500 & .000 \\ .378 & .052 & .000 & -0.323 & -0.500 & -0.707 \end{bmatrix} . \tag{28}$$

The matrix of the best coefficients of linear transformation determined by the Golebiewski method is identical with the matrix $\mathbf{A}$ determined by the Murrell method. According to Golebiewski the „total bond strenght“ is determined through eigenvalues e_{ii} of the matrix $(\mathbf{SS}^T)^{1/2}$ in the form of [10]

$$E = \operatorname{tr}(\mathbf{S}_1)_{\max} = \operatorname{tr}(\mathbf{SS}^T)^{1/2} = \operatorname{tr} \mathbf{e}, \tag{29}$$

where $\mathbf{e}$ is a diagonal matrix whose diagonal elements are real and positive. For the molecule ClF_5 $e_{11} = 2.957$ and $e_{22} = e_{33} = e_{44} = e_{55} = 2.932$. The diagonal elements of E (29) have been chosen positive to ensure the maximum value of the trace tr $\mathbf{e}$. With a negative value for one (or more) of these elements we would get other extrem values of E. It follows that the e_{ii} values should be related to the orbital energies, and that choosing a negative sign for one or more e_{ii}-values in eq. $\mathbf{A} = \mathbf{U}^T \mathbf{e}^{-1} \mathbf{US}$ we would obtain the best linear combination Ψ_i, $i = 1, 2, \ldots, k$, for the excited states [10]. It can be seen from the result that the four values e_{ii} ($i = 2, 3, 4$, and 5) belonging to the overlap of the orbitals of the fluorine atoms (lying in the corners of a square pyramid) with the orbitals of the central atom are equal, while e_{11} belonging to the bond which is perpendicular to the four bonds lying in one plane is stronger as regards energy. The fact that the e_{11} Cl-F bond is shorter than the other four [7] suggests that the overlap between Ψ_1 and Θ_1 is to be preferred. Similar results were found by J. N. Murrell in the case of the molecule ClF_3 [3].

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