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Hybridization and Localization in the Tight-Binding Approximation

By

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In this paper we derive a procedure for determining the number of centers involved in the various σ bonds of a molecule and the corresponding hybrid atomic orbitals. The procedure is rigorous within the frame of the tight-binding approximation under the assumptions that: a) the binding atomic orbitals of a given atom are all described by the same Coulomb integrals, possibly with the exception of π orbitals; b) the bond integrals between any two atomic orbitals are proportional to the corresponding overlap integrals, through a constant which may depend upon the particular pair of atoms under consideration.

It is claimed in this paper that the use of the procedure described in it makes it possible to decide, knowing the appropriate overlap integrals, to what extent the σ-system of a molecule can be described in terms of two or three-center bonds, and what the best hybrid atomic orbitals for such a description shall be. The calculations are simple because they only involve the diagonalization of a number of $n \times n$ matrices, n being the number of atomic orbitals with which *one* atom is included in the calculation.

Es wird ein Verfahren angegeben, um die Zahl der an den verschiedenen σ-Bindungen eines Moleküls beteiligten Zentren und die entsprechenden atomaren Hybridfunktionen zu bestimmen. Das Verfahren ist im Rahmen der Näherung der lokalisierten Bindungen unter der Annahme exakt, daß a) die bindenden Einelektronenfunktionen eines gegebenen Atoms alle das gleiche Coulomb-Integral haben (eventuell mit Ausnahme von π-Funktionen) und b) die Bindungsintegrale zwischen je zwei Atomfunktionen den entsprechenden Überlappungsintegralen proportional sind; die Proportionalitätskonstante kann vom speziellen Atompaar abhängig sein.

Das hier angegebene Verfahren erlaubt, bei Kenntnis der entsprechenden Überlappungsintegrale zu entscheiden, inwieweit das σ-System eines Moleküls durch Zwei- oder Dreizentrenbindungen beschrieben werden kann und welches die für eine solche Beschreibung besten Atomhybridfunktionen sind. Die Rechnungen sind einfach, da sie nur die Diagonalisierung einer Reihe von $n \times n$-Matrizen verlangen, wobei n die Zahl der Einelektronenatomfunktionen ist, mit der *ein* Atom in die Rechnung eingeht.

Dans cet article, on établit un procédé pour déterminer le nombre de centres compris dans les différentes liaisons σ d'une molécule et les orbitales atomiques hybrides correspondantes. Le procédé est rigoureux dans le cadre de l'approximation des orbitales moléculaires sous les hypothèses suivantes: a) les orbitales atomiques de liaison d'un atome donné sont toutes décrites par les mêmes intégrales coulombiennes b) les intégrales de liaison entre deux orbitales atomiques sont proportionnelles aux intégrales de recouvrement correspondantes, avec une constante qui peut dépendre de la paire d'atomes considérée.

L'emploi du procédé décrit dans cet article devrait permettre de décider, étant données les intégrales de recouvrement appropriées, dans quelle mesure le système-σ d'une molécule peut être décrit comme formé de liaisons à 2 ou 3 centres, quelles devraient être les orbitales atomiques hybrides les meilleures pour une telle description. Les calculs sont simples, du fait qu'ils comprennent seulement la diagonalisation d'un certain nombre de matrices $n \times n$, n étant le nombre d'orbitales atomiques avec lequel *chaque* atome intervient *individuellement* dans le calcul.

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Introduction

Semi-empirical tight-binding calculations are usually carried out only on the π electrons of unsaturated molecules. The reason for this limitation is to be sought, at least in part, in the various complications that arise if one tries to extend the method to the σ bonds, especially if one wants to derive explicitly from this type of calculation information on such features of the σ electron systems like hybridization and bond localization.

These complications, however, are not as serious as it may seem at first sight. In fact, the procedure described in this paper makes it possible to determine in a unique way a hybridized basis for any system of atoms, in full agreement with the principle of maximum overlap. As a consequence of this, the separation of molecular orbitals into different classes becomes possible as a well-defined approximation, so that, in addition to permitting an easy treatment of all the binding electrons, the new procedure gives a precise criterion for discussing on the basis of calculations such questions as orbital following, number of centers participating in a bond, etc.

Notation and Statement of the Problem

In a complete tight-binding approximation, the customary atomic orbital basis usually consists of many orbitals per atom: therefore the basis χ can be assumed to consist of subsets χ_a, where a denotes a single atom of the molecular or crystal network: i.e. the elements of χ_a are atomic orbitals $\chi_{\mu a}$ all belonging to a.

We shall assume that all the elements of χ are pure orbitals, all referred to a single system of coordinate axes, but centred on the corresponding nuclei (e.g. all the $2pz$ orbitals will be parallel to a given z-axis). The overlap matrix of a given subset χ_a with itself will be assumed to be the identity; that with another subset χ_b will be obtained from the usual tables via appropriate unitary transformations, T_{ab}, so that

$$\begin{aligned} S_{aa} &= (\chi_a^+, \chi_a) = I \\ S_{ab} &= (\chi_a^+, \chi_b) = T_{ab}^+ \, S_{ab}^0 \, T_{ab} \end{aligned} \tag{1}$$

where S_{ab}^0 is the overlap matrix obtained when the subsets χ_a, χ_b are referred to a system whose z-axis passes through the centers a and b. S_{ab}^0, and hence S_{ab}, is usually not zero, because the elements of χ are supposed to be strictly one-centre functions.

In general, the basis χ can be replaced by any new basis abtained from it via a non-singular transformation U preserving the norm of the basis elements; this property is particularly interesting when the transformation U does not combine elements belonging to different subsets, and is unitary; for, in that case, those features of the subsequent calculation which depend on the idea that the elements of a χ_a are eigenfunctions belonging to degenerate eigenvalues of an atomic operator are not affected by the change of the basis. Such a transformation gives what is called a hybrid basis, and is a block diagonal transformation, each block of which, U_a, is unitary.

The new basis χ' will then be:

$$\chi' = (\chi_1 U_1, \chi_2 U_2, \cdots, \chi_N U_N), \tag{2}$$

and S_{ab} will change into:

$$S'_{ab} = U_a^+ \, S_{ab} \, U_b. \tag{3}$$

Since there are infinitely many possible U's, a special choice of a particular U must derive from particular requirements. For the purpose of introducing hybridization in the ordinary sense we shall require that the transformation U shall transform the matrix S' so that it comes as close as possible to the form of a block diagonal matrix with 2×2 blocks, each involving two different centers.

This condition has a physical meaning if the matrix H of the tight-binding equation

$$H\,C = S\,C\,E \tag{4}$$

(H being the matrix representation of the effective one electron Hamiltonian in the basis χ, E its diagonal form, and C the transformation which takes H into E, subject to the condition $C^{+} S\, C = I$) has the same structure as S: then the condition just introduced essentially means that we are looking for a new basis χ' which will allow us to treat our electron system as far as possible as a system of independent two-centre two-orbital systems. If this new χ' can be defined uniquely, it will automatically tell us whether the molecular orbitals obtained from (4) can indeed be treated as two-centre orbitals, and, if this is not so, how many centres are involved in the different sets of molecular orbitals obtained from (4).

Hybridization in a Diatomic Molecule

Many aspects of the problem stated above can be clarified by a discussion of a diatomic molecule.

Let the two atoms a and b enter the MO-LCAO calculation each with four orbitals, so that the basis of pure orbitals will be:

$$\chi \equiv (2s_a\ 2p\sigma_a\ 2p\pi_a\ 2p\pi'_a\ 2s_b\ 2p\sigma_b\ 2p\pi_b\ 2p\pi'_b) \tag{5}$$

where the notation has the customary meaning. Let us consider first the overlap matrix and the problem of its block diagonalization. First of all, we remark that the two π and the two π' orbitals naturally give separated blocks, so that we can reduce the basis in which we are interested to

$$\chi \equiv (2s_a\ 2p\sigma_a\ 2s_b\ 2p\sigma_b) \tag{6}$$

The corresponding overlap matrix will have the structure:

$$S = \left(\begin{array}{c|c} I & S_{ab} \\ \hline S^{+}_{ab} & I \end{array}\right), \tag{7}$$

with

$$S_{ab} \equiv \begin{pmatrix} S\,(2s_a,\, 2s_b) & S\,(2s_a,\, 2p\sigma_b) \\ S\,(2p\sigma_a,\, 2s_b) & S\,(2p\sigma_a,\, 2p\sigma_b) \end{pmatrix}. \tag{8}$$

Let us now apply the transformation U defined in (3) to χ. The new overlap matrix will be:

$$S' = \left(\begin{array}{c|c} I & U^{+}_{a}\, S_{ab}\, U_b \\ \hline U^{+}_{b}\, S^{+}_{ab}\, U_a & I \end{array}\right), \tag{9}$$

where, in agreement with our previous remarks, we have set

$$U = \left(\begin{array}{c|c} U_a & O \\ \hline O & U_b \end{array}\right). \tag{10}$$

U_a and U_b are, in our particular case, unitary transformations of the second order. Therefore, they will be defined by angles φ_a and φ_b. If U transforms χ into the basis

$$\chi' \equiv (h_{1a}\, h_{2a}\, h_{1b}\, h_{2b}) \tag{11}$$

we may impose that

$$S\,(h_{1a}, h_{2a}) = S\,(h_{2a}, h_{1b}) = 0 \tag{12}$$

and, under these circumstances, S' is evidently a block diagonal matrix. This transformation is always possible, because we have two variables φ_a and φ_b to be evaluated for the conditions (12). Now, the matrix

$$H' = (\chi'^{+}, \mathscr{H}\chi') = U^{+}HU \tag{13}$$

cannot be diagonalized in blocks similar to those obtained in S' by the choice of φ_a and φ_b satisfying (12), unless the off-diagonal elements of H are all proportional, through the same constant k, to the corresponding elements of S, and unless the diagonal elements of H corresponding to different orbitals of a given atom are all equal to one another.

This is the most important conclusion of the discussion of our problem for a diatomic molecule, because it can be generalized to the case of polyatomic systems. Therefore, anticipating the results of the following section, we can state that the concept of hybridization follows naturally from the quest for a basis affording the highest possible degree of localization in the tight-binding approximation, under the assumptions that: a), the orbitals of a given atom correspond to the same values of the integrals

$$\alpha_{\mu a} = \int \chi_{\mu a}^{*}\, \mathscr{H}_{\text{eff}} \chi_{\mu a}\, d\tau = \alpha_a \tag{14}$$

b) that all the integrals $\beta_{\mu a, \nu b} = \int \chi_{\mu a}^{*}\, \mathscr{H} \chi_{\nu b}\, d\tau$ between any pair of different orbitals are proportional to the corresponding overlap integrals:

$$\beta_{\mu a, \nu b} = k_{ab}\, S_{\mu a, \nu b} \tag{15}$$

where k_{ab} may depend upon the particular pair of atoms under consideration (Mulliken approximation [2]).

Hybridization in a Polyatomic Molecule

Let us now turn our attention to the problem of a polyatomic molecule. As before, let us divide our basis χ into subsets $\chi_a, \chi_b, \cdots$ relating to individual atoms. The matrices S and H will have the forms:

$$S = \left(\begin{array}{c:c:c:} I & S_{ab} & S_{ac} \\ \hdashline S_{ab}^{+} & I & S_{bc} \end{array}\right. \quad H = \left(\begin{array}{c:c:c:} \alpha_a\, I & k_{ab}\, S_{ab} & k_{ac}\, S_{ac} \\ \hdashline k_{ab}\, S_{ab}^{+} & \alpha_b\, I & k_{bc}\, S_{bc} \end{array}\right. . \tag{16}$$

In principle, our problem calls for a block-diagonal transformation U of the basis χ that will leave the diagonal blocks of S and H unchanged and transform the remaining part of the matrix so that each row and column contain only one element. In general, it is impossible to obtain this result in a rigorous way. It may happen to be realized, at least approximately, in certain specific cases. Our problem in this section is just that of elaborating a general procedure for defining the matrix U so that it will indeed give the result in question to the extent to which this is possible.

We have already concluded that assumption (15) is a necessary condition for this type of problem. Therefore, if our transformation changes a block S_{ab} of S in a certain way, the same result will hold for H, as is seen from (16), if, as it happens, the factors α_a, α_b and k_{ab} are numbers.

Let us now apply the transformation U to H. We obtain:

$$S' = U^{+} S\, U = \left(\begin{array}{c|c|c} I & U_a^{+} S_{ab}\, U_b & U_a^{+} S_{ac}\, U_c \\ \hline U_b^{+} S_{ab}^{+}\, U_a & I & U_b^{+} S_{bc}\, U_c \\ \hline U_c^{+} S_{ac}^{+}\, U_a & U_c^{+} S_{bc}^{+}\, U_b & I \end{array}\right). \tag{17}$$

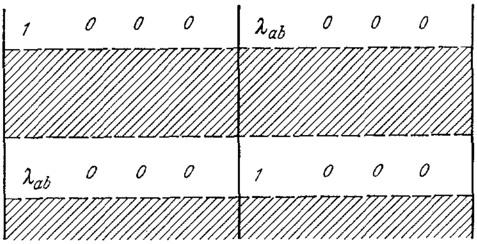
The blocks we have in S' are still 4×4 blocks*. We would reach an ideal situation (in the sense stated above) if we could make the rows of the matrix S' contain only one off-diagonal element each, these elements never being in the same columns. This requirement may be expressed (without any loss in generality) as simply that, e.g., the matrix $S'_{ab} = U_a^{+} S_{ab}\, U_b$ should have only its first diagonal element different from zero, the matrix S'_{ac} should have only its second diagonal element different from zero, etc. This requirement cannot be satisfied. Therefore, we must modify it by imposing only that in the submatrix

$$\tilde{S}_{ab} = \begin{pmatrix} I & S'_{ab} \\ S_{ab}^{\prime +} & I \end{pmatrix} \tag{18}$$

the first row and the fifth row should contain only one off-diagonal element. This would correspond to forming one "localized" bond between a and b, if the rest of S' were not there: as will be seen, even this modest requirement cannot be rigorously satisfied.

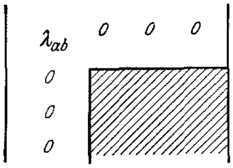
The structure we want for $\tilde{S}_{ab}$ is

$\tilde{S}_{ab} =$



and, since $\tilde{S}_{ab}$ is symmetric, this amounts to requiring that:

$S'_{ab} =$



This obviously corresponds to the requirement

$$\begin{aligned} (U_a^{+} S_{ab}\, U_b)_{1\nu} &= \lambda_{ab}\, \delta_{1\nu} \\ (U_b^{+} S_{ab}^{+}\, U_a)_{1\nu} &= \lambda_{ab}\, \delta_{1\nu} \end{aligned} \tag{19}$$

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* We confine our considerations to the case where χ_a contains only 4 orbitals

that is:

$$U_{a1}^{+} S_{ab} U_b = \lambda_{ab} (1000) \tag{20}$$

(where U_{a1}^{+} is the transpose of the first column of U_a), and

$$U_{b1}^{+} S_{ab}^{+} U_a = \lambda_{ab} (1000). \tag{21}$$

Multiplying (20) and (21) by U_b^{+} and U_a^{+} on the right, we finally have:

$$\begin{aligned} U_{a1}^{+} S_{ab} &= \lambda_{ab} U_{b1}^{+} \\ U_{b1}^{+} S_{ab}^{+} &= \lambda_{ab} U_{a1}^{+} \end{aligned} \tag{22}$$

and, consequently, substituting and transposing,

$$\begin{aligned} S_{ab} S_{ab}^{+} U_{a1} &= \lambda_{ab}^{2} U_{a1} \\ S_{ab}^{+} S_{ab} U_{b1} &= \lambda_{ab}^{2} U_{b1} \end{aligned} \tag{23}$$

Eqs. (23) imply that U_{a1} and U_{b1} must be eigenvectors $\bar{U}_{a1}$ and $\bar{U}_{b1}$ of $S_{ab} S_{ab}^{+}$ and $S_{ab}^{+} S_{ab}$. Eqs. (23) define $\bar{U}_{a1}$ and $\bar{U}_{b1}$ with the additional condition that λ_{ab}^{2} should be the highest eigenvalue of the matrices in question.

So far, we have considered the matrix $\tilde{S}_{ab}$ of Eq. (18). If we turn now to the total matrix (17), we may impose the same conditions (20) and (21) on the second rows of S'_{ac} and S'^{+}_{ac}, and this will give additional equations like (23) for U_{a2}, U_{c2}, etc., until we have exhausted four conditions per atom*. However, the result will be in general a set of equations not compatible with the condition that U_a, U_b, etc., should be unitary. In general, the matrices S_{ab}, S_{ac}, etc. do not commute, and hence $\bar{U}_{a1}$, $\bar{U}_{a2}$, $\bar{U}_{a3}$, $\bar{U}_{a4}$ cannot be the columns of a unitary $\bar{U}_a$. Therefore, we must find another transformation U_a which will differ as little as possible from $\bar{U}_a$ but will be unitary. This can be obtained by requiring that:

a) The angles between $\bar{U}_{a1}$ and U_{a1}, $\bar{U}_{a2}$ and U_{a2}, etc., shall be as small as possible;

b) U_{ai} shall be closer to $\bar{U}_{ai}$, the higher the eigenvalue corresponding to $\bar{U}_{ai}$.

This leads to the condition:

$$\delta \left\{\Sigma_i \left[\lambda_{ai}^{2} (\bar{U}_{ai}^{+} U_{ai} + U_{ai}^{+} \bar{U}_{ai}) - \Sigma_j M_{ij} U_{ai}^{+} U_{aj}\right] \right\} = 0$$

whence one gets

$$\bar{U}_a \Lambda_a^2 = M_a U_a \tag{24}$$

Λ_a^2 being the diagonal matrix whose non-zero elements are $\lambda_{a1}^2 = \lambda_{ab}^2$, $\lambda_{a2}^2 = \lambda_a^2$, etc. Eq. (24) can be solved by setting $U_a = V_a W_a^{+}$, where V_a and W_a are unitary matrices. Then, if m_a is the diagonal form of M_a (which we will assume to be symmetric), we write:

$$M_a = V_a m_a V_a^{+}. \tag{25}$$

Therefore, (24) reads

$$\bar{U}_a \Lambda_a^2 = V_a m_a W_a^{+}.$$

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* Although the non-vanishing overlap matrices of an atom with the other atoms of a given molecule are often more than 4, only four hybrids can be formed in our case, and therefore only four conditions can be imposed. In accordance with the idea that we wish to reproduce the chemical formula of a compound, it will be convenient to take into account only the matrices corresponding to atoms directly bound to each other in the ordinary chemical formula: therefore, if an atom is only linked to two or three other atoms, the remaining values of λ^2 will be assumed to be zero. The "*lone-pair*" hybrids will then follow directly from the orthogonality conditions imposed through the procedure given below.

This is equivalent to:

$$\begin{aligned} \bar{U}_a \Lambda_a^2 W_a &= V_a m_a, \\ \Lambda_a^2 \bar{U}_a^+ V_a &= W_a m_a. \end{aligned} \tag{26}$$

This in turn gives

$$\begin{aligned} \Lambda_a^2 \bar{U}_a^+ \bar{U}_a \Lambda_a^2 W_a &= W_a m_a^2, \\ \bar{U}_a \Lambda_a^4 \bar{U}_a^+ V_a &= V_a m_a^2, \end{aligned} \tag{27}$$

so that our problem is reduced to two eigenvalue problems.

Combining all the equations corresponding to (23) with (27) with the elements of Λ_a^2 equal to the highest eigenvalues of the corresponding equations of the type (23), we obtain finally the block diagonal unitary matrix U, which may be called the "*hybridization*" matrix.*

It will be seen that the conditions (23) happen to be similar to those given by LYKOS and SCHMEISING [*4*].

Details of Computations

The procedure outlined above is straightforward, and does not involve any particular computational problem. We will only give here the explicit form of the matrix T_{ab} of eq. (1).

As has been mentioned, if the atomic orbitals are taken parallel to a given reference system $\bar{z}\bar{x}\bar{y}$, the overlap matrix between two atoms S_{ab}^0 is transformed into S_{ab} by the unitary transformation**

$$T_{ab} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & l & m & n \\ 0 & -\dfrac{lm}{p} & p & -\dfrac{mn}{p} \\ 0 & -\dfrac{n}{p} & 0 & \dfrac{l}{p} \end{pmatrix} \tag{28}$$

where l, m, n, are the projections of the unit vector associated to the distance between a and b on the axes $\bar{z}$, $\bar{x}$, $\bar{y}$, and

$$p = \sqrt{l^2 + n^2}.$$

This transformation can be ignored in most manipulations required for finding the eigenvalues and eigenvectors of the matrices $S_{ab}^+ S_{ab}$ and $S_{ab} S_{ab}^+$. For instance, if C_{ab} is a unitary transformation,

$$C_{ab}^+ S_{ab}^+ S_{ab} C_{ab} = C_{ab}^+ T_{ab}^+ S_{ab}^{0+} S_{ab}^0 T_{ab} C_{ab}$$

Therefore, if C_{ab} is the transformation which diagonalizes $S_{ab}^+ S_{ab}$, $C_{ab}^0 = T_{ab} C_{ab}$ is the transformation which diagonalizes $S_{ab}^{0+} S_{ab}^0$ and

$$C_{ab} = T_{ab}^+ C_{ab}^0 . \tag{29}$$

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* It is easily proved that one must ensure that $m_a = V^+_a \bar{U}_a \Lambda^2_a W_a$ is a diagonal matrix with non-negative elements. This condition may require a change in the signs of the columns of W with respect to the signs they have after the diagonalization of Eq. 27.

** The parallel pz orbitals are supposed to point in the same direction, so that their overlap will be negative in S^0_{ab}.

Applications

To make possible a better evaluation of the scope of the procedure suggested in this paper we give here two simple examples. We show first of all that the possibility of three-center bonds follows automatically from the above procedure. This is immediate if we consider a system of three atoms, a, b, c, with the following basis orbitals:

$$\chi = (2s_a \; 2p\sigma_a \; 1s_b \; 2s_c \; 2p\sigma_c) \,.$$

The $2p\pi$ and $2p\pi'$ orbitals are excluded because the system is planar. The matrix S will then be

$$S = \begin{pmatrix} 1 & 0 & S_{ab} & 0 & 0 \\ 0 & 1 & S'_{ab} & 0 & 0 \\ S_{ab} & S'_{ab} & 1 & S_{bc} & -S'_{bc} \\ 0 & 0 & S_{bc} & 1 & 0 \\ 0 & 0 & -S'_{bc} & 0 & 1 \end{pmatrix}$$

where

$$S_{ab} = S\,(2s_a,\, 1s_b) \quad S'_{ab} = S\,(2p\sigma_a,\, 1s_b)$$
$$S_{bc} = S\,(1s_b,\, 2s_c) \quad S'_{bc} = |\,S\,(1s_b,\, 2p\sigma_c)|$$

The overlap integrals between a and c are neglected in S for the sake of simplicity. Now,

$$S_{ab}\,S^{+}_{ab} = \begin{pmatrix} S^2_{ab} & S_{ab}S'_{ab} \\ S_{ab}S'_{ab} & S'^2_{ab} \end{pmatrix} = \begin{pmatrix} \cos\varphi & \sin\varphi \\ \sin\varphi & \cos\varphi \end{pmatrix} \begin{pmatrix} S^2_{ab} + S'^2_{ab} & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi \end{pmatrix}$$

with $\operatorname{tg}\varphi = \dfrac{S'_{ab}}{S_{ab}}$

and

$$S^{+}_{bc}\,S_{bc} = \begin{pmatrix} S^2_{bc} & -S_{bc}S'_{bc} \\ -S_{bc}S'_{bc} & S^{2\prime}_{bc} \end{pmatrix} = \begin{pmatrix} \cos\vartheta & -\sin\vartheta \\ \sin\vartheta & \cos\vartheta \end{pmatrix} \begin{pmatrix} S^2_{bc} + S'^2_{be} & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \cos\vartheta & \sin\vartheta \\ -\sin\vartheta & \cos\vartheta \end{pmatrix}$$

with $\operatorname{tg}\vartheta = -\dfrac{S'_{bc}}{S_{bc}}$

The general procedure given above gives therefore:

$$U = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 & 0 & 0 \\ \sin\varphi & \cos\varphi & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & \cos\vartheta & \sin\vartheta \\ 0 & 0 & 0 & -\sin\vartheta & \cos\vartheta \end{pmatrix}$$

and hence

$$S' = \begin{pmatrix} 1 & 0 & \sqrt{S^2_{ab} + S'^2_{ab}} & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ \sqrt{S^2_{ab} + S'^2_{ab}} & 0 & 1 & \sqrt{S^2_{bc} + S'^2_{bc}} & 0 \\ 0 & 0 & \sqrt{S^2_{bc} + S'^2_{bc}} & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

Here it is evident that, if $\sqrt{S^2_{ab} + S'^2_{ab}}$ and $\sqrt{S^2_{bc} + S'^2_{bc}}$ are of the same order of magnitude, neither can be neglected, and we have thus derived from the matrix S a matrix S' corresponding to a three-centre bond.

This three-centre bond may not exist in reality if one of the two square roots is much smaller than the other, a situation which is possible if the distances ab, bc for which the energy is at a minimum are much different from each other.

The inclusion of a strong bond between a and c in S also changes the results, because of the dependence of U_a on both S_{ab} and S_{ac}: however, it is clear that this change does not affect the qualitative conclusion just reached, that many-center bonds are indeed predicted in certain cases by the procedure under discussion.

We give now a numerical example, in order to give an idea of the changes one obtains in S by passing to $U^{+}SU$. We consider here the molecule NF_3, with tetrahedral angles $\widehat{FNF}$ and a distance $R(NF) = 1.37$ Å. The matrices S_{FF} are negligible, (the highest eigenvalue of $S_{FF}^{+} S_{FF}$ is $0.7317 \cdot 10^{-3}$, to be compared with the highest eigenvalue of $S_{NF} S_{NF}^{+}$, which is 0.2386). Therefore the calculation of hybridization matrix U requires the full procedure only for the block U_N, whereas the blocks U_{Fi} are given directly by the eigenvectors of $S_{NF}^{+} S_{NF}$. After all the calculations are carried out, U_N takes the form

$$U_N = (2s_{(N)}\; 2p_{z(N)} 2p_{x(N)}\; 2p_{y(N)}) \begin{pmatrix} 0.52912 & 0.52912 & 0.52912 & 0.40008 \\ 0.23099 & 0.23099 & 0.23099 & -0.91648 \\ 0 & 0.70711 & -0.70711 & 0 \\ 0.81650 & -0.40825 & -0.40825 & 0 \end{pmatrix}$$

where the z axis is chosen as the axis of the molecule, and the zy plane contains one F atom. The fact that there are three equivalent hybrids is just a consequence of the symmetry of the molecule: on the other hand, the p characters of the various hybrids are a direct consequence of the values of the overlap integrals. The p character of the lone pair hybrid is 0.84, which indicates for the NF_3 molecule a rather high lone pair moment; the p character of the binding hybrids is 0.72, the p character of a tetrahedral hybrid being 0.75.

As to the overlap matrix, we give here the overlap matrix for one NF pair:

$$S'_{NF} = \begin{pmatrix} 0.48562 & 0.00097 & 0 & -0.00558 \\ 0.03732 & -0.00644 & +0.07256 & -0.03631 \\ 0.03732 & -0.00644 & -0.07256 & -0.03631 \\ 0.00130 & -0.00531 & 0 & -0.08867 \end{pmatrix}$$

This matrix has the form we had required in order to derive Eq. (19) within 1%, and can be considered as containing only one non-zero element within 20% of its highest element. This is not a great accuracy: however, it is not much less than the accuracy one would expect for the description of a molecule in terms of localized bonds. In other words, even within the atomic orbital picture, one must consider the localized bond picture as a first order approximation whenever it is possible to use it; and this is clearly what appears from an inspection of S'_{NF}.

Conclusion

We have shown in the present note that it is possible to obtain the hybrids and the degree of localization of bonds for any σ-system with the only knowledge of the overlap integrals between the orbitals of the various atoms, under the assumption that, for a given pair of atoms, the bond integrals between the various atomic orbitals are proportional to the corresponding overlap integrals. This leads naturally to the criterion of maximum overlap and the resulting hybrids are determined uniquely in every case by diagonalization of a number of matrices whose order is 4, or 9 if d-orbitals are included in the calculations. The procedure gives both the best hybrids and the new overlap matrix between them. Therefore it makes possible a decision as to the extent to which the system under study can be treated as a system of independent 2-, 3-, $\cdots$, n- centre bonds. Thus, for example, the 3-centre bonds postulated by EBERHARD, CRAWFORD and LIPSCOMB [*3*] to explain the properties of boron hybrids follow immediately from the above procedure.

In order to evaluate energies from the new overlap matrix the Coulomb integrals and the proportionality constants between bond and overlap integrals should be evaluated. If the system under study can be treated as a system of two centre bonds, the values suggested in a previous paper of ours [*1*] can be used, because, even if those values were given for calculations neglecting overlap, there is a complete equivalence between these and those including overlap, under the assumptions made here, as was shown by the author in a previous paper [*2*].

In any case, it is interesting that complete information on the hybrids can be obtained directly with the only knowledge of overlap integrals.

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