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On the Use of Strictly Localized Orbitals for the Description of σ Bonds

RUDOLF POLÁK

Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

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The paper presents an examination of the possibility of describing the σ-electronic system of a molecule by means of strictly localized orbitals (SLO's) expressed in a minimum basis set of hybrid orbitals. In the first part of the paper the relationship between the basis sets of pure AO's and convenient HO's is discussed. Further, a criterion is introduced enabling one to analyse the posibility of using the SLO-description for the electronic pairs in σ bonds, and a method for the construction of the optimum SLO's in a given basis of HO's is derived. The general conclusions are illustrated by examples.

Es wird untersucht, wie weit es möglich ist, das σ-Elektronensystem eines Moleküls mittels streng lokalisierter Orbitale zu beschreiben, wobei ein Minimalsatz von Hybrid-Orbitalen benützt wird. Im ersten Teil der Arbeit wird der Zusammenhang zwischen den Sätzen von Basisfunktionen der ursprünglichen Atom-Orbitale und der geeigneten Hybrid-Orbitale diskutiert. Es wird ein Kriterium eingeführt, das die Analyse einer Möglichkeit der Benützung von streng lokalisierten Orbitalen für die Beschreibung der Elektronenpaare in σ-Bindungen gestattet. Ferner wird eine Methode für die Herstellung der optimalen streng lokalisierten Orbitale in einer gegebenen Basis von Hybrid-Orbitalen abgeleitet. Die allgemeinen Schlüsse werden an Beispielen erläutert.

On examine la possibilité de la description du système σ-éléctronique d'une molécule par des orbitales strictement localisées en utilisant une base minimale des orbitales hybridées. Dans la première partie on discute la relation des bases des orbitales atomiques pures et des orbitales hybridées convenables. Ensuite on introduit un critère qui permet d'analyser la possibilité de l'usage des orbitales strictement localisées pour la description des pairs électroniques dans les liaisons σ. On develope aussi une méthode pour la construction des orbitales strictement localisées optimales dans une base donnée des orbitales hybridées. Les conclusions générales sont illustrées par des examples.

1. Introduction

As evident from the analysis of "ab initio" SCF calculations of some molecules, it is possible to perform the transformation of molecular orbitals describing "σ electrons" into well localized orbitals [1–11] in all cases studied. In addition it is evident that:

a) different localizing procedures lead to very similar results [7–9],

b) it is possible to transform even virtual orbitals into localized orbitals [10],

c) the molecular orbitals of some semiempirical calculations can be transformed to localized orbitals resembling the localized orbitals derived from the SCF calculations [9, 10].

From this point of view, those approximative approaches to the solution of complicated electronic systems are justified, for which the pairs of electrons in classical σ bonds are described by strictly localized functions [12, 13]. The justification of such approaches was discussed recently [14, 15].

This work will discuss in greater detail the possibility to describe the general σ-electronic system by means of strictly localized orbitals and will develop a method for the construction of these strictly localized orbitals. The results are illustrated in examples.

2. Formulation of the Problem

In the following discussion let us restrict ourselves to the customary MO LCAO scheme. In all considerations only finite sets of normalized one-electron space functions are treated, for which we use the notation introduced by Montet, Keller and Mayer [16]. According to this notation we shall express the set of functions $\phi \equiv (\phi_1(x), \phi_2(x) \dots \phi_i(x) \dots \phi_l(x))$ by a matrix ${}_l\boldsymbol{\phi}$ the elements of which are defined by

$$({}_l\boldsymbol{\phi})_{x,i} = \phi_i(x)\,, \tag{1}$$

where the index l, denoting the number of functions $\phi_i(x)$ in the set under consideration, gives the number of columms. Thus ${}_l\boldsymbol{\phi}$ is partly discrete and partly continuous matrix with properties analogous to the ordinary matrices with discrete indices.

Let us define the following matrices corresponding to various sets of one-electron functions:

${}_m\boldsymbol{\chi}$: pure atomic orbitals (AO's) e.g. Slater-type orbitals (STO's)

${}_n\boldsymbol{\varphi}$: hybrid orbitals (HO's)

${}_n\boldsymbol{\psi}$: molecular orbitals (MO's) diagonalizing the one-electron Hamiltonian of the molecular problem. The matrix is composed of two matrices ${}_{n'}\boldsymbol{\psi}$ and ${}_{n''}\boldsymbol{\psi}$, corresponding to the ground state orbitals and virtual orbitals respectively, $n = n' + n''$.

${}_n\boldsymbol{\lambda}$: localized orbitals (LO's), which, analogously to ${}_n\boldsymbol{\psi}$, form two matrices ${}_{n'}\boldsymbol{\lambda}$ and ${}_{n''}\boldsymbol{\lambda}$, for which it holds

$$ {}_{n'}\boldsymbol{\lambda} = {}_{n'}\boldsymbol{\psi}\,\boldsymbol{U}'\,, \qquad {}_{n''}\boldsymbol{\lambda} = {}_{n''}\boldsymbol{\psi}\,\boldsymbol{U}''\,, \tag{2}$$

where $\boldsymbol{U}'$ and $\boldsymbol{U}''$ denote the unitary matrices transforming the MO's into the localized orbitals.

${}_n\boldsymbol{\eta}$: strictly localized orbitals (SLO's), forming two matrices ${}_{n'}\boldsymbol{\eta}$ and ${}_{n''}\boldsymbol{\eta}$ which do not preserve precisely the separation of the ground state orbitals and the virtual orbitals.

Let us assume that the LO's can be expressed in the basis of the hybrid orbitals

$$ {}_n\boldsymbol{\lambda} = {}_n\boldsymbol{\varphi}\,{}^{\lambda}_{n}\boldsymbol{C} \tag{3}$$

and for the sake of simplicity we shall suppose in the following that a minimal basis set of HO's is used for the construction of the LO's.

Let us note that Eq. (3) need not be satisfied in the case that m (the number of AO's) is bigger than n (the number of HO's) and that the corresponding MO's are found by the variation process in the basis of AO's.

If the LO's in the matrix ${}_{n}\boldsymbol{\lambda}$ are so well localized that their substitution in the Slater determinant by SLO's forming the matrix ${}_{n}\boldsymbol{\eta}$ is a good approximation (how to judge the justification of goodness of such substitution will be pointed out later), then the transition to the basis of the SLO's brings about the essential simplification in expressing the first-order density matrix ϱ and consequently, in the calculation of any physical quantity.

Let ${}_{n'}\boldsymbol{\eta}$ be the matrix formed by $k=(\mathrm{n}-n')$ two-centre orbitals (for the description of the pairs of electrons in σ bonds) and by $l=(n'-k)$ one-centre orbitals (for the description of pairs of electrons in lone pairs) and expressed in the form

$$ {}_{n'}\boldsymbol{\eta}={}_{n}\boldsymbol{\varphi}\,{}_{n'}^{\eta}\boldsymbol{C}\,, \tag{4a}$$

where

$$ {}_{n'}^{\eta}\boldsymbol{C}=\begin{array}{cccccccc} 1 & 2 & \dots & k\dots & & & & n' \\ \hline C_1 & 0 & \dots & 0 & 0 & 0 & \dots & 0 \\ C_2 & 0 & \dots & 0 & & & & \\ 0 & C_3 & & 0 & & & & \\ 0 & C_4 & & 0 & & & & \\ \vdots & \vdots & & \vdots & & & & \\ 0 & 0 & & C_{2k-1} & & & & \\ 0 & 0 & & C_{2k} & 0 & 0 & \dots & 0 \\ 0 & 0 & & 0 & C_{2k+1} & & & \\ 0 & 0 & & 0 & 0 & C_{2k+2} & \cdots & \\ 0 & 0 & & 0 & 0 & 0 & & C_{n'+k} \end{array} \tag{4b}$$

Then the spinless first-order density matrix [16] related to the one-determinant closed shell function built up from these SLO's is given by the formula,

$$\varrho=2\cdot{}_{n'}\boldsymbol{\eta}({}_{n'}\boldsymbol{\eta}^{+}\,{}_{n'}\boldsymbol{\eta})^{-1}\,{}_{n'}\boldsymbol{\eta}^{+} \tag{5}$$

where the overlap matrix ${}_{n'}\boldsymbol{\eta}^{+}\,{}_{n'}\boldsymbol{\eta}$ between the SLO's is not negligible in general. Nevertheless, let us suppose that the off-diagonal elements of this overlap matrix are negligibly small. Then one finds for the spatial density matrix the following expression:

$$\begin{aligned}\varrho(1,1')=2\cdot&\sum_{i=1}^{n'+k}|C_i|^2\,\varphi_i(1)\,\varphi_i^*(1')\\ &+\sum_{i=1}^{2k-1}[C_i\cdot C_{i+1}^*\cdot\varphi_i(1)\,\varphi_{i+1}^*(1')\\ &+C_{i+1}\cdot C_i^*\cdot\varphi_{i+1}(1)\,\varphi_i^*(1')]\,[1-(-1)^i]\,.\end{aligned}\tag{6}$$

The simple form (6) for the approximate first-order density matrix of the electron system enables a perfect partitioning of molecular quantities into contributions corresponding to atoms and bonds within the molecule under consideration. The meaning of such partitioning of molecular quantities has been widely discussed by Ruedenberg [17]. In connection with the possibility of using the approximate form of the first-order density matrix (6) there are two problems arising, i.e.: 1. under what conditions it is possible to take the overlap matrix of the SLO's ${}_{n'}\boldsymbol{\eta}^{+}{}_{n'}\boldsymbol{\eta}$ as the unit matrix, and 2. how to construct the corresponding SLO's.

3. On the Possibilities of Constructing Orthonormal SLO's

a) The problem we are going to solve in this chapter may be stated as follows: what condition must be fulfilled by the original basis of pure AO's, in order to enable the construction of the orthonormal SLO's in terms of a minimal basis set of HO's?

It was shown by Del Re [14], that by extending the basis of pure AO's, one can take proper linear combinations of them to get a limited number of "promoted-hybridized" orbitals, fulfilling special conditions. Simultaneously it was stated that the relationship of these orbitals to individual observables is as yet an open question. However, it is evident that the optimalization of these orbitals in regard to a special quantity leads to a deterioration of the results for other quantities.

In order to discuss our problem let us suppose that the basis χ and φ consist of intrinsically orthonormal subsets

$$\chi^{A} \equiv (\chi_1^{A} \ldots \chi_{m_A}^{A}) \quad \text{and} \quad \varphi^{A} \equiv (\varphi_1^{A} \ldots \varphi_{n_A}^{A})$$

respectively, where χ_i^{A} and φ_i^{A} denote the i-th AO and i-th HO, respectively, centered on the atom A of the molecule.

Let us look for a transformation matrix $\boldsymbol{T}$ transforming the original basis χ into the hybrid basis φ

$${}_{n}\boldsymbol{\varphi} = {}_{n}\boldsymbol{\chi}\boldsymbol{T}, \tag{7}$$

where the matrix $\boldsymbol{T}$ we assume in a quasi-diagonal form having $n_B \cdot m_B$ blocks, $(B = A, \ldots, K)$. Further, in the matrix

$${}_{\varphi}\boldsymbol{S} = \boldsymbol{T}^{+}{}_{\chi}\boldsymbol{S}\boldsymbol{T}, \tag{8}$$

where ${}_{\varphi}\boldsymbol{S}$ and ${}_{\chi}\boldsymbol{S}$ are overlap matrices corresponding to the basis φ and χ, respectively, there must be as many nonzero elements above the main diagonal as bonds we wish to have described with two-centre orbitals. Namely we shall require that the element $(\varphi_i^{A})^{+}\varphi_j^{B}$ is allowed to be different from 0 if the orbitals φ_i^{A} and φ_j^{B} have to form a basis for the description of the electron pair in the σ bond between atoms A and B.

Therefore, we will consider a molecule, the symmetry of which corresponds to the point group G.

First of all, let us introduce the concept of equivalent quantities concerning the molecule under consideration: we consider those quantities to be equivalent, which are members of a set being identical with each other, except for orientation and position in space and therefore being transformably mutually into each other by the operations of the pertinent symmetry group G.

Let us consider a molecule composed of sets of equivalent atoms. Assume there are ${}_{\mathrm{A}}l$ atoms in the set A, ${}_{\mathrm{B}}l$ atoms in the set B *etc.* and ${}_{\mathrm{K}}l$ atoms finally, in the last set K. Let us suppose that n_{A} hybrid orbitals belong to a chosen atom of the set A and that ${}_{\alpha}n_{\mathrm{A}}$ is the number of equivalent HO's belonging to the type (αA). Therefore, it must hold that $\sum\limits_{\beta} {}_{\beta}n_{\mathrm{A}} = n_{\mathrm{A}}$ and that the total number of equivalent orbitals of the type (αA) is equal to ${}_{\mathrm{A}}l \cdot {}_{\alpha}n_{\mathrm{A}}$, which is also the dimension of the reducible representation of the group G spanned by the HO's of the type (αA). This reducible representation can be decomposed unambigously into corresponding irreducible representations ${}_{\mathrm{A}}\gamma(\alpha, i)$ spanned by symmetry orbitals, where i labels species of the irreducible representation. Let ${}_{\mathrm{A}}k(\alpha, i)$ be the number of irreducible representations ${}_{\mathrm{A}}\gamma(\alpha, i)$ occuring in the reducible one and ${}_{\mathrm{A}}\boldsymbol{U}^{\alpha}$ the matrix, transforming the corresponding HO's to symmetry orbitals of the type (αA).

If we introduce the quasi-diagonal matrix $\boldsymbol{U}$,

$$\boldsymbol{U} = \begin{bmatrix} {}_{\mathrm{A}}\boldsymbol{U}^{\alpha} & 0 \ldots & & 0 \\ 0 & \ddots & & \\ \vdots & & {}_{\mathrm{B}}\boldsymbol{U}^{\beta} & \\ & & & \ddots \\ 0 & & & {}_{\mathrm{K}}\boldsymbol{U}^{\varkappa} \end{bmatrix} \tag{9}$$

then, after some rearrangement of the columns in the matrix ${}_{n}\varphi$, all symmetry orbitals ${}_{n}'\varphi$ of the molecule can be expressed as follows:

$${}_{n}'\boldsymbol{\varphi} = {}_{n}\boldsymbol{\varphi}\,\boldsymbol{U} . \tag{10}$$

In the matrix ${}_{\varphi}'\boldsymbol{S}$,

$${}_{\varphi}'\boldsymbol{S} = \boldsymbol{U}^{+}\,{}_{\varphi}\boldsymbol{S}\,\boldsymbol{U} , \tag{11}$$

which can be quasi-diagonalized due to the orthogonality relations for integrals (e.g. [18]), the number of distinct non-zero matrix elements is given by the formula

$$k = \sum_{i} \frac{k(i)}{2}\,[k(i) + 1] , \tag{12a}$$

where

$$k(i) = \sum_{\mathrm{B},\beta} {}_{\mathrm{B}}k(\beta, i) . \tag{12b}$$

k means therefore the number of symmetry independent matrix elements.

Of course the expression (12) gives generally the number of different matrix elements of any totally symmetric operator in respect to the symmetry operations of the group G. It is necessary to mention that the accidental equality of integrals is not taken into account.

Let us now estimate the number of parameters p, which are needed for the construction of the matrix $\boldsymbol{T}$.

Since it is sufficient to know only one of the total number, ${}_{\mathrm{A}}l \cdot {}_{\alpha}n_{\mathrm{A}}$, of equivalent orbitals of the type (αA) — the others being determined by the symmetry transformations — the complete number p_A of parameters for fixing HO's of all atoms in the set A is given by the expression

$$p_A = m_A \sum_{\beta} \frac{{}_{\beta}n_A}{{}_{\beta}n_A} . \qquad (13a)$$

Thus, for the total number of parameters p in the matrix $\boldsymbol{T}$ that are to be determined we have

$$p = \sum_{B} p_B . \qquad (13b)$$

If b designates the number of non-equivalent bonds, then these parameters are submitted to r restrictions due to the matrix Eq. (8) and the Eq. (12), so that

$$r = k - b \qquad (14)$$

and the number v of free parameters, which may be chosen in accordance with additional criteria (e.g. that of maximum overlap [19–21]), is

$$v = p - r . \qquad (15a)$$

Therefore, the condition

$$v \geqq 0 \qquad (15b)$$

indicates whether the basis of orthonormal SLO's in terms of a minimal basis set of HO's can be constructed.

The actual calculation of hybrid functions and thus of the parameters in the matrix $\boldsymbol{T}$ requires the solution of the system of equations of a second order as follows from Eq. (8). The tediousness and ambiguity of the solution are the weak side of the problem. For the practical calculation of the hybrids adequate for the construction of SLO's it is naturally possible to limit the number of restrictions since some overlap integrals are negligibly small in the basis of pure AO's and it is, for example, possible to respect only the overlap between the neighbouring atoms.

b) Illustrations and discussion. For illustration let us apply the preceding conclusions on the models of molecules Li_2 and LiH.

1. Example: Li_2 – The six electrons of the molecule Li_2, consisting of two equivalent atoms of type A, will require two one-centre equivalent SLO's corresponding to the inner shells and one two-centre SLO corresponding to the bond pair for their description.

Let us denote the basis of HO's $\varphi \equiv (\varphi_{1a}, \varphi_{2a}, \varphi_{1b}, \varphi_{2b})$ where the letters a and b distinguish the individual atoms. Further, let the equivalent orbitals φ_{1a} and φ_{1b} describe the electrons in the inner shell of atoms a and b, respectively (thus they are directly SLO's) and let the HO's with index 2 form the basis for the two-centre SLO (the non-zero overlap is being allowed here only between orbitals with the index 2). This condition represents in view of Eq. (4) five symmetry independent restrictions ($r = 5$) for the HO's. The relation $p = p_A = m_A \cdot 2 = 6$

fulfils the condition (15), thus the basis of pure AO's with $m_A = 3$ represents the basis with the smallest number of functions.

Let us denote the basis of pure AO's $\chi \equiv (\chi_{1a}, \chi_{2a}, \chi_{3a}, \chi_{1b}, \chi_{2b}, \chi_{3b})$, e.g. $(\chi_1, \chi_2, \chi_3)_a \equiv ((1s), 2s), (2p_x))_a$ where the symbols mean the corresponding STO's and the x-axis is supposed to pass through the atoms [the orbitals (1s) and (2s) are orthogonal and were obtained from the original basis of STO's by the Löwdin's symmetric orthogonalization].

As $r = 5$ and $p = 6$ there remains one free parameter according to (15). This parameter may be chosen from the condition that the HO describing the inner shell is spherically symmetric.

Substituting the actual values of overlap integrals for the internuclear distance $R = 5.051$ a.u. [22] and solving the system of equations following from the matrix Eq. (8) we get four solutions for the parameters in the matrix $\boldsymbol{T}$ from which only two are physically different.

If

$$({}_i\varphi_1, {}_i\varphi_2)_a = ((1s), 2s), (2p_x))_a [\boldsymbol{T}_a]_i ,$$

then

$$[\boldsymbol{T}_a]_1 = \begin{bmatrix} 0.989 & -0.001 \\ -0.145 & -0.009 \\ 0 & 1.000 \end{bmatrix} \quad \text{with} \quad ({}_1\varphi_{2a})^+ \, {}_1\varphi_{2b} = 0.217 ,$$

$$[\boldsymbol{T}_a]_2 = \begin{bmatrix} 0.997 & 0.071 \\ 0.083 & -0.855 \\ 0 & 0.513 \end{bmatrix} \quad \text{with} \quad ({}_2\varphi_{2a})^+ \, {}_2\varphi_{2b} = 0.057 .$$

(In the quoted results we suppose local coordinate systems on atoms a and b to have the x axis pointing towards the center of gravity of the molecule.)

2. Example: LiH – We shall describe the four electrons of the LiH molecule by means of a one-centre SLO corresponding to the inner shell of the Li atom and a two-centre SLO corresponding to the bond pair.

For the construction of the basis of HO's $\varphi \equiv (\varphi^{\mathrm{H}}, \varphi_1^{\mathrm{Li}}, \varphi_2^{\mathrm{Li}})$ with the appropriate orthogonalization properties, where φ_1^{Li} describes the inner shell, the basis of pure AO's with dimension 3 is sufficient, $\chi \equiv (\chi^{\mathrm{H}}, \chi_1^{\mathrm{Li}}, \chi_2^{\mathrm{Li}})$. In this case there does not remain any free parameter in the transformation matrix $\boldsymbol{T}$. For STO's, $\chi \equiv ((1s)^{\mathrm{H}}, (1s)^{\mathrm{Li}}, (2s)^{\mathrm{Li}})$, where ($s$) orbitals situated on the Li atom represent again the symmetric orthogonalized orbitals, at the internuclear distance $R = 3.015$ a.u. [22] we obtain the solution:

$$\boldsymbol{T} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0.993 & 0.115 \\ 0 & -0.115 & 0.993 \end{bmatrix} \quad \text{with} \quad (\varphi^{\mathrm{H}})^+ \, \varphi_2^{\mathrm{Li}} = 0.476 .$$

The extension of the basis of pure AO's gives the possibility of constructing more flexible hybrids because we are able to estimate certain parameters according to additional criteria. For example, if we assume:

$$(\varphi^{\mathrm{H}}, \varphi_1^{\mathrm{Li}}, \varphi_2^{\mathrm{Li}}) = ((1s)^{\mathrm{H}}, (1s)^{\mathrm{Li}}, (2s)^{\mathrm{Li}}, (2p_x)^{\mathrm{Li}})\,\boldsymbol{T} \tag{16}$$

(where the pure AO's are again STO's as defined earlier and the x-axis passes through the atoms), the requirements of spherical symmetry of the inner shell and maximum value of the overlap integral $(\varphi^{\mathrm{H}})^+ \varphi_2^{\mathrm{Li}}$, we obtain a single physically different solution, $\boldsymbol{T}_{\mathrm{Li}}$:

$$\boldsymbol{T}_{\mathrm{Li}} = \begin{bmatrix} 0.993 & 0.094 \\ -0.115 & 0.814 \\ 0 & 0.574 \end{bmatrix} \quad \text{with} \quad (\varphi^{\mathrm{H}})^+ \varphi_2^{\mathrm{Li}} = 0.708\,.$$

4. The Construction of Optimum SLO's

a) In this chapter we shall first define a criterion enabling us to decide whether the SLO is well suited for the description of the electronic pair in the given σ bond of the molecule. Further, we shall derive a direct method for the construction of the optimum SLO's in a given basis of HO's.

The spinless first-order density matrix ϱ related to the one-determinant closed shell function [23] has the following important property:

$$\boldsymbol{\phi}^+ \varrho \boldsymbol{\phi} = n\,, \qquad 0 \leqq n \leqq 2 \tag{17}$$

for any normalized orbital ϕ. For any occupied orbital $n = 2$ and $n = 0$ for any orbital which is orthogonal to the manifold of occupied orbitals. The relation (17) gives us the possibility to construct the SLO corresponding to a given bond l from the condition that the expression

$$\boldsymbol{\eta}_l^+ \varrho \boldsymbol{\eta}_l = n_l \tag{18}$$

has a maximum.

Further on, we shall restrict ourselves to the following problem. Let us suppose that we have a basis set of HO's which we consider suitable for the construction of the SLO's in the molecule studied and that in this basis it is also possible to express the MO's, ${}_n\boldsymbol{\psi} = {}_n\boldsymbol{\varphi}\,{}^{\psi}_{n}\boldsymbol{C}$. With these limitations we then find the optimum two-centre SLO describing the electronic pair in the chosen bond l. We may write

$$\varrho = {}_n\boldsymbol{\varphi}\,\boldsymbol{P}\,{}_n\boldsymbol{\varphi}^+\,, \tag{19}$$

where $\boldsymbol{P} = 2\,{}^{\psi}_{n'}\boldsymbol{C}\,{}^{\psi}_{n'}\boldsymbol{C}^+$. Due to the Eq. (4) the normalized orbital describing the electrons in the chosen bond l between atoms A and B is given by

$$\boldsymbol{\eta}_l = {}_n\boldsymbol{\varphi}\,{}^{\eta}_{n'}\boldsymbol{C}_l = C_{2l-1}\,\varphi_{2l-1}^{\mathrm{A}} + C_{2l}\,\varphi_{2l}^{\mathrm{B}}\,. \tag{20a}$$

Using a more convenient notation

$$C_{2l-1} = q \quad \text{and} \quad C_{2l} = q \cdot b \tag{20b}$$

where

$$q = (1 + b^2 + 2bs)^{-1/2}\,, \qquad s = (\varphi_{2l-1}^{\mathrm{A}})^+ (\varphi_{2l}^{\mathrm{B}})$$

and b is a variable parameter, it is possible to write using Eqs. (18), (19) and (20)

$$n_l = {}_{n}^{\eta}\boldsymbol{C}_l^{+}\, {}_{\varphi}\boldsymbol{S}\boldsymbol{P}\, {}_{\varphi}\boldsymbol{S}\, {}_{n}^{\eta}\boldsymbol{C}_l = q^2 [g_{\mathrm{A}} + 2b\, g_{\mathrm{AB}} + b^2 g_{\mathrm{B}}]\,, \tag{21}$$

where

$$\begin{aligned} g_{\mathrm{A}} &= {}_{\varphi}\boldsymbol{S}_{2l-1}^{+}\boldsymbol{P}\, {}_{\varphi}\boldsymbol{S}_{2l-1}\,, \\ g_{\mathrm{B}} &= {}_{\varphi}\boldsymbol{S}_{2l}^{+}\boldsymbol{P}\, {}_{\varphi}\boldsymbol{S}_{2l}\,, \\ g_{\mathrm{AB}} &= {}_{\varphi}\boldsymbol{S}_{2l}^{+}\boldsymbol{P}\, {}_{\varphi}\boldsymbol{S}_{2l-1} \end{aligned}$$

and ${}_{\varphi}\boldsymbol{S}_i$ is the i-th column of the matrix ${}_{\varphi}\boldsymbol{S}$.

Extremizing (21) we get two values for b

$$b_{1,2} = \frac{-y \pm \sqrt{y^2 - 4xz}}{2x} \tag{22}$$

corresponding to the minimum and to the maximum value. The meaning of the symbols in (22) is as follows:

$$\begin{aligned} x &= g_{\mathrm{AB}} - s g_{\mathrm{B}}\,, \\ y &= g_{\mathrm{A}} - g_{\mathrm{B}}\,, \\ z &= s g_{\mathrm{A}} - g_{\mathrm{AB}}\,. \end{aligned}$$

It may be expected that one value of b will be positive, corresponding to the two-centre orbital occupied in the ground state. The second value of b will be negative and corresponds to the minimum of the projection into the space of the occupied functions and belongs to the virtual orbital.

b) Illustrations and discussion: We shall now show the construction of SLO's for σ-electronic bonds in the molecules of acetylene, ethylene and ethane. This group of molecules is of interest because the hybrid atomic orbitals of carbon in acetylene, ethylene and ethane are of the sp, sp^2, and sp^3 type, respectively, according to the classical point of view.

It has been shown [9] that the localizing procedure transforms the molecular orbitals into well localized orbitals in the case of the SCF calculations [24] employing precise molecular integrals as well as in the case of the "extended Hückel theory" with Hoffmann's parameterization scheme [25]. The resulting localized orbitals for both types of calculations are very similar. This similarity shows itself both in numerical values of the coefficients ${}_{n}^{\lambda}C$ and, above all, in the changes of their values when going from acetylene and ethylene to ethane, which also manifests itself in the values of dipole moments of the C–H bonds of these three molecules [26]. Let us, therefore, consider the ground state of the valence electrons of the three molecules in question as being described by means of the one-determinant closed shell function constructed from the "extended Hückel theory" MO's.

Let the HO's ${}_{n}\varphi$ be formed by (1s) STO's localized on the nuclei of the hydrogen atoms and by (sp^k) hybrid orbitals localized on the nuclei of the carbon atoms $k = 1, 2$ and 3 for acetylene, ethylene and ethane, respectively. Again these HO's are linear combinations of STO's.

Let us first observe the SLO's describing the three types of C–C bonds. From symmetry it follows that $b=1$. The value q and the corresponding "occupation" numbers, calculated according to (21), are given in the Table 1. It is evident that the classical hybrid functions are most appropriate for the description of the C–C bond of ethane.

Table 1. SLO's *(Direct Method) and their "occupation" numbers*

	C–C bond ($b=1$)		C–H bond		
	q	$n_{\mathrm{C-C}}$	b	q	$n_{\mathrm{C-H}}$
Acetylene	0.5170	1.974	0.7469	0.6112	1.9980
Ethylene	0.5320	1.982	0.8415	0.5853	1.9936
Ethane	0.5511	1.989	0.8766	0.5806	1.9921

In accordance with the notation introduced in (20) the normalized two-centre SLO, describing the C–H bond is denoted:

$$\eta_{\mathrm{C-H}}=q(\varphi_{\mathrm{C}}+b\cdot\varphi_{\mathrm{H}})\,.$$

The optimum values b and the corresponding "occupation" numbers for the three molecules are given in Table 1. It is worth noting that the chosen basis of HO's is more advantageous for the description of the C–H bonds and that the rate of compatibility for the three molecules runs in the opposite direction than in the case of the C–C bonds.

In [9] has been shown that it is possible to construct very well localized orbitals in terms of classical hybrid functions by means of a unitary transformation of the molecular orbitals. From these localized orbitals it is possible to get the parameter b as the ratio quotient of the coefficient at the hydrogen orbital and of the coefficient at the carbon orbital and to get, therefore, the corresponding SLO's in an alternative way. The results obtained in such a way are shown in Table 2 and it is evident that the differences between the "occupation" numbers in both cases are outside the limits of the indicated precision. For the sake of comparison we present in Table 2 the parameters "b" and "q", which have the same meaning as above but which result from the localized orbitals obtained by means of the transformation of SCF MO's [9]. The numerical values of these parameters confirm the former statement about the similarity of localized orbitals obtained from EHT MO and SCF MO.

Table 2. SLO's *for the* C–H *bonds derived from localized* MO's

	SCF		EHT		
	b	q	b	q	$n_{\mathrm{C-H}}$
Acetylene	0.7322	0.6257	0.7773	0.6010	1.9979
Ethylene	0.8165	0.5946	0.8618	0.5790	1.9936
Ethane	0.8510	0.5896	0.8799	0.5796	1.9921

The approximation of the first-order density matrix in the form of the Eq. (6) requires at least an approximate orthonormality of the SLO's. It is evident from Table 3, where the overlap integrals for the neighbouring SLO's are given, how far this requirement is fullfilled for the chosen basis of HO's.

It is possible to decide whether the substitution of molecular orbitals by strictly localized orbitals is a good approximation or not either by means of the comparison of calculations for several physical quantities considering the corresponding types of wave functions or by means of the analysis of the first-order density matrix. The comparison of the total gross orbital populations [27] indicated in Table 4 gives partial information. φ_H means the hydrogen atomic orbital, φ_{CH} and φ_{CC} denote the carbon hybrid orbitals pointing towards the hydrogen atom and the neighbouring carbon atom, respectively.

Table 3. *Overlap integrals between the neighbouring* SLO's (EHT)

	$S_{C-H, C-C}$	$S_{C-H, C-H}$
Acetylene	0.1010	—
Ethylene	0.1415	0.1474
Ethane	0.1325	0.1596

Table 4. *Comparison of total gross populations in terms of* HO's. *Upper row: for* SLO's *given in the second part of Table 2; lower row: for* EHT MO's

	$n(\varphi_H)$	$n(\varphi_{CH})$	$n(\varphi_{CC})$
Acetylene	0.857	1.143	1.000
	0.839	1.167	0.994
Ethylene	0.914	1.086	1.000
	0.879	1.119	1.004
Ethane	0.924	1.076	1.000
	0.882	1.116	1.007

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Dr. Rudolf Polák
Institute of Physical Chemistry
Czechoslovak Academy of Sciences
Máchova 7, Prague 2, Czechoslovakia