ON THE EQUIVALENCE OF PAULING'S DIRECTED BONDS THEORY, THE MAXIMUM OVERLAP PRINCIPLE AND THE MOLECULAR ORBITAL METHOD

By Alojzy Gołębiewski

Department of Theoretical Chemistry, Jagellonian University, Kraków*

The general properties of the maximum overlap method and its relation to the directed bonds theory and the molecular orbital method were discussed. The maximum overlap method was applied to explain the experimentally observed differences in bond lengths in PCl_5, $SbCl_5$, SF_4, ClF_3, and also to explain semi-quantitatively the bond length-shortening in $Cr(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$. Finally, a possibility of constructing best hybrid orbitals for excited states is shortly discussed.

1. Introduction

The Pauling directed bonds theory (d.b. theory, for brevity) is evidently one of the simplest methods used for the description of bonds in molecules of the type MX_k, where $k = 0, 1, 2, \ldots$ (Cartmell & Fowles 1961; Wells 1962; P. J. Durrant & B. Durrant 1962). The main assumptions of this theory are as follows: 1) The hybridized atomic orbitals of M, $\psi_1, \ldots, \psi_k$, should be directed towards the ligands $X_1, \ldots, X_k$ accordingly; 2) The "bond strengths" of physically equivalent bonds should be the same; 3) A possible freedom in the choice of hybrid orbitals should be fixed with the use of the maximum overlap criterium.

The d.b. theory can be generalized to include multicentered bonds and bent bonds. This generalization follows directly from what is called the "maximum overlap criterium" (Murrell 1960).

Let $\varphi_1, \ldots, \varphi_n$ be a set of atomic orbitals of M, and $\theta_1, \ldots, \theta_k$ a set of atomic orbitals of the ligands. Murrell suggested to look for k best hybrid orbitals of the central atom M,

$$
\begin{pmatrix} \psi_1 \\ \cdot \\ \cdot \\ \cdot \\ \psi_k \end{pmatrix} = a \begin{pmatrix} \varphi_1 \\ \cdot \\ \cdot \\ \cdot \\ \varphi_n \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdot & a_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ a_{k1} & a_{k2} & \cdots & a_{kn} \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \cdot \\ \cdot \\ \cdot \\ \varphi_n \end{pmatrix}
\tag{1}
$$

(where $n \geqslant k$) such that the sum of all "bond strengths"

$$
\sum_{i=1}^{k} \langle \theta_i | \psi_i \rangle \equiv \operatorname{tr} \boldsymbol{S}_1
\tag{2}
$$

* Address: Katedra Chemii Teoretycznej U J, Kraków, ul. Krupnicza 41, Poland

is a maximum; the matrix S_1 in Eq. (2) is given by the formula:

$$S_1 = \begin{pmatrix} \langle\theta_1|\psi_1\rangle \cdots \langle\theta_1|\psi_k\rangle \\ \vdots \quad \ddots \quad \vdots \\ \langle\theta_k|\psi_1\rangle \cdots \langle\theta_k|\psi_k\rangle \end{pmatrix} = \begin{pmatrix} \langle\theta_1|\varphi_1\rangle \cdots \langle\theta_1|\varphi_n\rangle \\ \vdots \quad \ddots \quad \vdots \\ \langle\theta_k|\varphi_1\rangle \cdots \langle\theta_k|\varphi_n\rangle \end{pmatrix} a^T \overset{\text{def.}}{=} S a^T \qquad (3)$$

A simple method of constructing $\psi_i s$ was developed by Lykos and Gilbert (1961), and independently and differently by the author (1961).

In next sections I discuss some general aspects of the maximum overlap method, and also its relation to the *d.b.* theory and the molecular orbital method. To illustrate the utility of the maximum overlap method it was applied to the discussion of bond lengths in PCl_5, $SbCl_5$, SF_4, ClF_3, $Cr(CO)_6$, $Fe(CO)_5$ and $Ni(CO_4)$. The method was generalized to cover π-bonding and electronic excited states.

2. General remarks on the maximum overlap method

If a set of $n+k$ orbitals, $\theta_1, \ldots, \theta_k, \varphi_1, \ldots, \varphi_n$ (where $n \geqslant k$) satisfies the condition (4),

$$\langle\theta_i|\theta_j\rangle = \delta_{ij},$$

$$\langle\varphi_r|\varphi_s\rangle = \delta_{rs}, \qquad (4)$$

we will call it a "semi-orthogonal" set. In particular it may be the set of atomic orbitals of the MX_k system (Murrell 1961), the set of $2p_\pi$ orbitals of alternant conjugated hydrocarbons (Coulson & Longuet-Higgins 1947) or the set of bond orbitals in the LCBO MO method of saturated hydrocarbons (Hall 1951).

Let us construct the overlap integral matrix S (3) and the matrix SS^T, where S^T means S transposed. The author has shown (1961) that the condition (2) leads to the following formula for best linear transformation coefficients (1),

$$a = (SS^T)^{-\frac{1}{2}} S \qquad (5)$$

and to the following formula for the maximum of the "total bonds strength",

$$E = (\text{tr } S_1)_{\max} = \text{tr } (SS^T)^{\frac{1}{2}} \qquad (6)$$

It follows that to find a and E we have to calculate the inverse square root matrix $(SS^T)^{-\frac{1}{2}}$ first. This calculation can be carried out in one of the following two ways.

The matrix (SS^T) (of the order not greater than $k \leqslant n$) can be diagonalized with the matrix u (say), such that

$$(SS^T) = u^T e^2 u \qquad (7)$$

where e is a diagonal matrix which diagonal elements are real and positive (Murrell 1961). From the equations (5)—(7) it follows immediately that

$$E = \text{tr } e \qquad (8)$$

$$a = u^T e^{-1} u S \qquad (9)$$

Alternatively we can calculate $(SS^T)^{-\frac{1}{2}}$, and hence E and a, following a way proposed by Hall (1955) on a different occasion. Let us write $(SS^T)^{-\frac{1}{2}} = Q$. The matrix Q can be conveniently found by iteration,

$$Q_{i+1} = \frac{1}{2}\left\{3I - Q_i^2(SS^T)\right\}Q_i \tag{10}$$

where $Q_0 = \frac{1}{2}I$. Having found Q we can proceed to the calculation of E and a:

$$E = \operatorname{tr} Q^{-1} \tag{11}$$

$$a = QS \tag{12}$$

Finally we note that according to Eq. (3) $S_1 = Sa^T$, and according to Eq. (3) and (5), $S_1 = (SS^T)^{\frac{1}{2}}$. It follows that also a particular bond strength, $\langle\theta_i|\psi_i\rangle$ say, can be easily expressed in terms of the S matrix elements:

$$\langle\theta_i|\psi_i\rangle = [(SS^T)^{\frac{1}{2}}]_{ii} = [u^T e u]_{ii} = [Q^{-1}]_{ii} \tag{13}$$

The use of the above method to concrete physical problems will be illustrated in next sections. At present I like to put attention to the following topics:

First of all we note that

$$E = \operatorname{tr}(SS^T)^{\frac{1}{2}} = \operatorname{tr}(SS^T)^{-\frac{1}{2}} S \cdot S^T = \operatorname{tr} aS^T \tag{14}$$

It follows from this equation that the best linear coefficients a_{ij} play exactly the same role as the bond orders in the LCAO MO method.

We note that the construction of best linear combinations $\psi_1, ..., \psi_k$ is possible, if $n \geqslant k$. Otherwise the matrix SS^T would be singular (what can be proved easily) and formula (9) would loose the validity. The condition $n \geqslant k$ does not restrict the generality of the method. It plays, however, some role in the interpretation of the results. For example, we will see in section 7 that Giacometti (1955) generalized the d.b. theory to include the π-bonds. In this case, however, the condition $n \geqslant k$ was not fulfilled. In consequence the d.b. theory of π-electrons was not consistent with the maximum overlap principle. According to the last one we should rather ask for best linear combinations of ligand orbitals and not for the best hybrid orbitals of the central atom.

We also note that if we linearly transform the θ_i and the φ_j orbitals,

$$\varphi' = b\varphi, \quad \theta' = c\theta \tag{15}$$

(where b and c are orthogonal matrices) then, in accordance with the definition of S (3),

$$SS^T = c^T S' bb^T S'^T c = c^T S' S'^T c = c^{-1}(S'S'^T)c \tag{16}$$

It follows from Eq. (16) that the matrices SS^T and $S'S'^T$ are similar. Hence the total bonds strength E is invariant to orthogonal transformations of $\theta_i s$ and $\varphi_j s$. In this way the directed bonds representation of the MX_k systems is completely equivalent (in this approximation) to any other representation of delocalized bonds.

Finally we note that the diagonal elements of e (7) have been chosen positive to ensure the maximum value of the trace tr e. With a negative value for one (or more) of these elements we would come to other extremal values of E. It follows that $e_{ii}s$ should be related to orbital energies, and that choosing a negative sign for one or more e_{ii}-values in Eq. (9) we should obtain the best linear combinations ψ_j, $j = 1, 2, ..., k$, for the excited states.

3. An approximate relation between the change of the structure and the maximum value of the total bonds strength

We may be interested in the change of the total bonds strength E induced by a change of the structure of the molecule. With this purpose let us remind that according to Eq. (10) the matrix $\boldsymbol{Q} = (\boldsymbol{SS}^T)^{-\frac{1}{2}}$ can be found by iteration, and that the convergence of the iteration is very good. Therefore, if we put $\boldsymbol{S}' = \boldsymbol{S} + d\boldsymbol{S}$ and $d(\boldsymbol{SS}^T) = \boldsymbol{S}(d\boldsymbol{S}^T) + (d\boldsymbol{S})\boldsymbol{S}^T$ we can write

$$(\boldsymbol{S}'\boldsymbol{S}'^T)^{-\frac{1}{2}} \approx \frac{1}{2}\{3\boldsymbol{I} - (\boldsymbol{SS}^T)^{-1}(\boldsymbol{S}'\boldsymbol{S}'^T)\}(\boldsymbol{SS}^T)^{-\frac{1}{2}} \tag{17}$$

Hence

$$dE = d(\text{tr}\,\boldsymbol{S_1})_{\max} = \frac{1}{2}\,A\,\text{tr}\{(\boldsymbol{SS}^T)^{-\frac{1}{2}}d(\boldsymbol{SS}^T)\} \tag{18}$$

where $0 < A \sim 1$.

4. Reduction formulae for atomic overlap integrals

In almost all practical applications of the maximum overlap principle we need the explicit formulae for overlap integrals between the s, p and d orbitals. Besides, usually at least one of the orbitals is situated relative to the bond axis as symmetrically as only possible. For these cases which seem to be sufficiently general we derived some reduction formulae. To be definite, we assumed that the θ_i orbitals are situated symmetrically, and the φ_j orbitals
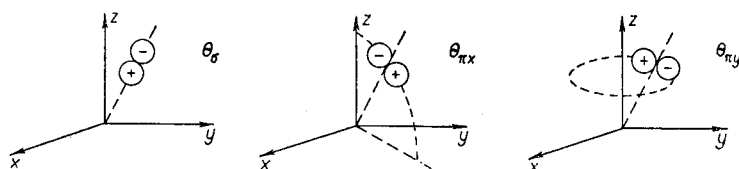

Fig. 1

deliberately. Finally we assumed three kinds of θ_i-orbitals in respect to the symmetry properties relative the bond axis. We reproduce these types in Fig. 1.

With the above assumptions all overlap integrals $\langle\theta_i|\varphi_j\rangle$ can be expressed in terms of the angular coordinates of the center of θ_i-orbital and in terms of one of the following

integrals (Fig. 2):

$$\langle \theta_{\sigma z} | \varphi_{d_{z^2}} \rangle = S_{\sigma d}(X)$$

$$\langle \theta_{\sigma z} | \varphi_{p_z} \rangle = S_{\sigma p}(X)$$

$$\langle \theta_{\sigma z} | \varphi_s \rangle = S_{\sigma s}(X) \tag{19}$$

$$\langle \theta_{\pi y} | \varphi_{d_{xy}} \rangle = S_{\pi d}(X)$$

$$\langle \theta_{\pi y} | \varphi_{p_y} \rangle = S_{\pi p}(X)$$

Fig. 2

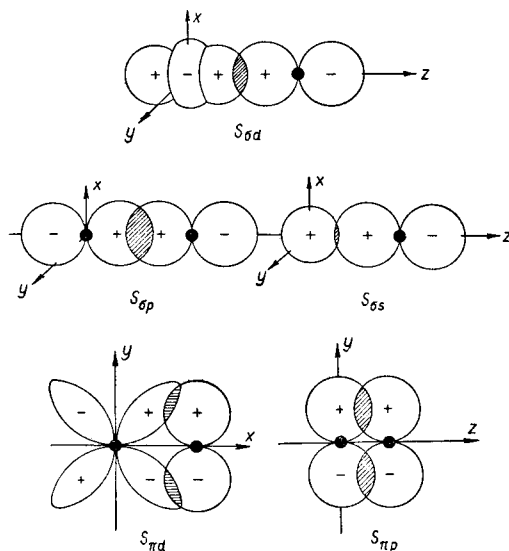In the case of θ_σ-orbitals the following reduction formulae are valid:

$$\langle \theta_\sigma | s \rangle \quad = S_{\sigma s}(X)$$

$$\langle \theta_\sigma | p_x \rangle \quad = \sin \vartheta_X \cdot \cos \varphi_X \cdot S_{\sigma p}(X)$$

$$\langle \theta_\sigma | p_y \rangle \quad = \sin \vartheta_X \cdot \sin \varphi_X \cdot S_{\sigma p}(X) \tag{20}$$

$$\langle \theta_\sigma | p_z \rangle \quad = \cos \vartheta_X \cdot S_{\sigma p}(X)$$

$$\langle \theta_\sigma | d_{xy} \rangle \quad = \frac{1}{2} \sqrt{3} \sin^2 \vartheta_X \cdot \sin 2\varphi_X \cdot S_{\sigma d}(X)$$

$$\langle \theta_\sigma | d_{xz} \rangle \quad = \frac{1}{2} \sqrt{3} \sin 2\vartheta_X \cdot \cos \varphi_X \cdot S_{\sigma d}(X)$$

$$\langle \theta_\sigma | d_{yz} \rangle \quad = \frac{1}{2} \sqrt{3} \sin 2\vartheta_X \cdot \sin \varphi_X \cdot S_{\sigma d}(X) \tag{21}$$

$$\langle \theta_\sigma | d_{x^2-y^2} \rangle \quad = \frac{1}{2} \sqrt{3} \sin^2 \vartheta_X \cdot \cos 2\varphi_X \cdot S_{\sigma d}(X)$$

$$\langle \theta_\sigma | d_{z^2} \rangle \quad = \frac{1}{2} (3 \cos^2 \vartheta_X - 1) \cdot S_{\sigma d}(X)$$

Analogously in the case of θ_π-orbitals one obtains the formulae:[1]

$$\langle \theta_{\pi x} | d_{xz} \rangle = \cos 2\vartheta_X \cdot \cos \varphi_X \cdot S_{nd}(X)$$

$$\langle \theta_{\pi x} | d_{yz} \rangle = \cos 2\vartheta_X \cdot \sin \varphi_X \cdot S_{nd}(X)$$

$$\langle \theta_{\pi x} | d_{xy} \rangle = \frac{1}{2} \sin 2\vartheta_X \cdot \sin 2\varphi_X \cdot S_{nd}(X) \qquad (22)$$

$$\langle \theta_{\pi x} | d_{x^2-y^2} \rangle = \frac{1}{2} \sin 2\vartheta_X \cdot \cos 2\varphi_X \cdot S_{nd}(X)$$

$$\langle \theta_{\pi x} | d_{z^2} \rangle = -\frac{1}{2} \sqrt{3} \sin 2\vartheta_X \cdot S_{nd}(X)$$

$$\langle \theta_{\pi y} | d_{xz} \rangle = -\cos \vartheta_X \cdot \sin \varphi_X \cdot S_{nd}(X)$$

$$\langle \theta_{\pi y} | d_{yz} \rangle = \cos \vartheta_X \cdot \cos \varphi_X \cdot S_{nd}(X)$$

$$\langle \theta_{\pi y} | d_{xy} \rangle = \sin \vartheta_X \cdot \cos 2\varphi_X \cdot S_{nd}(X) \qquad (23)$$

$$\langle \theta_{\pi y} | d_{x^2-y^2} \rangle = -\sin \vartheta_X \cdot \sin 2\varphi_X \cdot S_{nd}(X)$$

$$\langle \theta_{\pi y} | d_{z^2} \rangle = 0$$

$$\langle \theta_{\pi x} | p_x \rangle = \cos \vartheta_X \cdot \cos \varphi_X \cdot S_{np}(X)$$

$$\langle \theta_{\pi x} | p_y \rangle = \cos \vartheta_X \cdot \sin \varphi_X \cdot S_{np}(X) \qquad (24)$$

$$\langle \theta_{\pi x} | p_z \rangle = -\sin \vartheta_X \cdot S_{np}(X)$$

$$\langle \theta_{\pi y} | p_x \rangle = -\sin \varphi_X \cdot S_{np}(X)$$

$$\langle \theta_{\pi y} | p_y \rangle = \cos \varphi_X \cdot S_{np}(X) \qquad (25)$$

$$\langle \theta_{\pi y} | p_z \rangle = 0$$

In these formulae ϑ_X and φ_X mean the angular coordinates of the atom X, on which the θ-orbital is centered (Fig. 1). $S(X)$ means that the standard integral (19) depends still on bond length and the nature of both atoms.

The overlap integrals $S_{\sigma s}$, $S_{\sigma p}$, $S_{\sigma d}$, $S_{\pi p}$ and $S_{\pi d}$ (19) can be evaluated if one knows the radial parts of the orbitals. However, Pauling (regarding $S_{\sigma s}$, $S_{\sigma p}$ and $S_{\sigma d}$) and Giacometti (regarding $S_{\pi d}$ and $S_{\pi p}$) suggested a simple approximate relation between these integrals. Following their idea we assume that the overlap integrals (19) are approximately proportional to the product of the maximum values of projections of angular parts of both orbitals on the bond axis. In this approximation

$$S_{\sigma p} = \sqrt{3}\, S_{\sigma s}; \qquad S_{\sigma d} = \sqrt{5}\, S_{\sigma s} \qquad (26)$$

and (if θ_σ is assumed to be a sp hybrid orbital),

$$S_{\pi p} = \frac{0.75\sqrt{2}}{1+\sqrt{3}}\, S_{\sigma s}; \qquad S_{\pi d} = \frac{\sqrt{10}}{3+\sqrt{3}}\, S_{\sigma s} \qquad (27)$$

---

[1] If $\vartheta_X = 0$, then φ_X (Fig. 1) is not defined. With no loss of generality one can take then that $\varphi_X = 0$.

5. *Best hybrid orbitals in the case of the tetrahedral structure of* MX_4

Suppose, we are interested in the sp^3 hybrid orbitals in the case of a tetrahedral environment of ligands (Fig. 3).
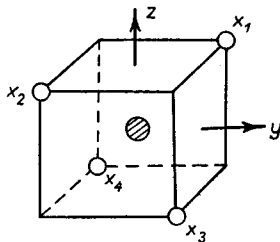
Fig. 3

Constructing the S matrix (taking formally $S_{\sigma s} = 1$) we find:

$$S = \begin{pmatrix} 1 & -1 & 1 & 1 \\ 1 & 1 & -1 & 1 \\ 1 & 1 & 1 & -1 \\ 1 & -1 & -1 & -1 \end{pmatrix}; \quad SS^T = 4I \qquad (28)$$

Hence $S_1 = (SS^T)^{\frac{1}{2}} = 2I$ and, according to equation (13), all four bonds are equivalent yielding the bond strength 2.000 pro bond. From Eq. (5) and (28) we immediately find the best hybrid orbitals:

$$\begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = (SS^T)^{-\frac{1}{2}} S \begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \varphi_3 \\ \varphi_4 \end{pmatrix} = \tfrac{1}{2} \begin{pmatrix} 1 & -1 & 1 & 1 \\ 1 & 1 & -1 & 1 \\ 1 & 1 & 1 & -1 \\ 1 & -1 & -1 & -1 \end{pmatrix} \begin{pmatrix} s \\ p_x \\ p_y \\ p_z \end{pmatrix} \qquad (29)$$

If we change now the angular coordinates of the ligand no 1 by $d\vartheta$ and $d\varphi$ we find that

$$dS = \begin{pmatrix} 0 & -2^{-\frac{1}{2}}d\vartheta - d\varphi & 2^{-\frac{1}{2}}d\vartheta - d\varphi & -2^{\frac{1}{2}}d\vartheta \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \qquad (30)$$

Substituting this equation to Eq. (18) and taking account of the fact that $(SS^T)^{-\frac{1}{2}} = \tfrac{1}{2} I$ in this example, we find that $dE = d(\mathrm{tr}\, S_1)_{\max} = 0$. Hence the tetrahedral environment of ligands in MX_4 corresponds to an extremum of E.

6. *The variation of bond lengths in* PCl_5, $SbCl_5$, SF_4 *and* ClF_3

It was found experimentally that not all bonds in PCl_5, $SbCl_5$, SF_4 and ClF_3 are equivalent. For example according to Rouault (1940) PCl_5 and $SbCl_5$ have the shape shown in Fig. 5, with two kinds of bonds, a and b. In the case of PCl_5 he found that $R_a = 2.04 \pm$

± 0.02 Å, $R_b = 2.19 \pm 0.02$ Å. Similarly in the case of $SbCl_5$ he found that $R_a = 2.31 \pm \pm 0.06$ Å and $R_b = 2.43 \pm 0.06$ Å.

The unequivalence of bonds was also established in the case of SF_4 (Tolles & Gwinn 1962). It was found that the molecule exhibits the symmetry properties of the C_{2v}-group, with two bonds distributed almost linearly ($186°56' \pm 30'$) and other two angularly ($101°33' \pm \pm 30'$). The appropriate bond lengths are equal to 1.646 Å and 1.545 Å. As sulphur has a lone pair in this compound, the structure of SF_4 can be closely related to that in Fig. 5.
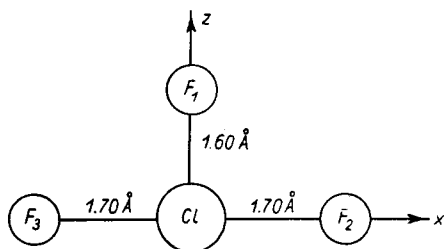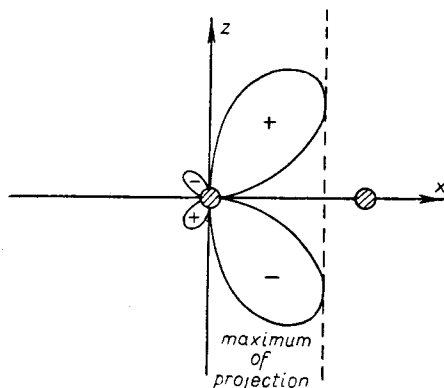

Fig. 4

Fig. 5

The same should be true for ClF_3 in which chlorine has two lone pairs and three ligands. Indeed, Smith (1953) found the T-shape for this molecule, where the almost linear bonds correspond to the b-type bonds of Fig. 5, the other bond to the a-type bond. The structure of ClF_3 is shown in Fig. 4.

It follows that all four molecules are related to the trigonal bipyramidal hybridization and that we would explain the observed variation of bond lengths if we show that b-bonds have a smaller value of the bond strength than the a-bonds.

Assuming the $sp^{3-n}d^{1+n}$ hybridization and following the procedure described in section 2 (in a way similar to that in the preceding section) we find that $(S_1)_{11} = (S_1)_{22} = 2.9289$, $(S_1)_{33} = (S_1)_{44} = (S_1)_{55} = 2.9623$. Hence, according to the maximum overlap principle, one should distinguish two groups of equivalent bonds, a and b, where the b-type bonds should be distinctly weaker than the a-type bonds. This is in a complete accord with experiment. We also note that the lone pairs in SF_4 and ClF_3 occupy those corners of Fig. 5 which correspond to the greatest values of the bond strengths.

The structure of the above molecules is usually discussed in terms of the sp^3d hybridization (Wells 1962; P. J. Durrant & B. Durrant 1962; Cartmell & Fowles 1961) and not, as in the present paper, of $sp^{3-n}d^{1+n}$. Then, however, the b-type bonds should be much stronger (2.948) than the a-type bonds (2.237). This is clearly in contradiction to experiment.

Dyatkina and Shirmazan (1959) discussed the a-type and b-type bond strengths for the following hybridizations of the central atom: sdp^3, spd^3, $sdpf^2$, sdp^2f and sd^3f. In all

these cases the b-type bonds appear to be stronger than the a-type bonds what disagrees with the experimental data.

It appears therefore that the hybridization of the central atom is rather close to $sp^{3-n}d^{1+n}$, where $n = 1\frac{1}{9}$.

7. The π-bonding effect in some metal carbonyls

The π-bonding effect in $Cr(CO)_6$, $Fe(CO)_5$ and $Ni(CO)_4$ was discussed by Giacometti (1955) in terms of the $d.b.$ theory. In the case of these carbonyls a distinct bond shortening is observed (in comparison with the sum of bond radii):

$$Cr(CO)_6 \ldots \ldots \text{ by } 0.10 \pm 0.04 \text{ A},$$

$$Fe(CO)_5 \ldots \ldots \text{ by } 0.16 \pm 0.03 \text{ Å},$$

$$Ni(CO)_4 \ldots \ldots \text{ by } 0.18 \pm 0.03 \text{ A}.$$

To explain this shortening directed π-orbitals of the shape shown in Fig. 6 were constructed. It was shown in the case of $Ni(CO)_4$, for example, that not more than three such
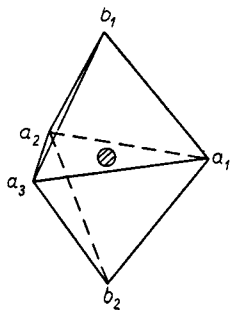

Fig. 6

orbitals could be constructed. Assuming resonance he averaged the π-bond strengths over all four bonds. His results for all three carbonyls are given in Table I.

However, as already noticed in section 2, the $d.b.$ theory is not equivalent in this case to the maximum overlap theory since it does not exploit all possibilities of maximizing the overlap. We will discuss therefore the π-bonding effect in terms of the maximum overlap principle, asking for the best linear combinations of ligands' σ- and π-type orbitals. To do so we assume what follows: 1) The CO group is bonded as $:C = \overset{..}{O}$, where the hybridization of C is sp and of $O - sp^2$; additionally we assume that the π-bond of CO does not conjugate with the metal; 2) The metal-carbon σ-bonds have the origin in the lone pairs of carbon atoms and the free central atom orbitals; 3) The metal-carbon π-bonds have their origin in the electronic pairs of the central atom and the free $2p_\pi$ orbitals of the carbon atoms; 4) The overlap integrals (19) can be approximated with the relations (26)—(27).

TABLE I.

Bond strengths in metal carbonyls according to the *d.b.* theory

Type of the bond	Averaged bond strengths		
	$Cr(CO)_6$	$Fe(CO)_5$	$Ni(CO_4$
σ, in absence of π-bonds	2.924	2.949	2.949
σ, in presence of π-bonds	2.923	2.930	2.930
π	1.50	1.57	1.77*

Using the method developed in sections 2 and 4 we obtained the results given in Table II.

TABLE II.

Bond strengths in metal carbonyls according to the maximum overlap principle

Molecule	Average bond strengths			
	σ	$\sigma+\pi$	π-bonding effect (maximum overlap principle)	π-bonding effect (*d.b.* theory)
$Cr(CO)_6$	2.924	3.652	0.728	0.672*
$Fe(CO)_5$	2.949	3.876	0.927	0.704
$Ni(CO_4$	2.949	3.940	0.991	0.793

One can see from Table II what follows:

1) The *d.b.* theory developed by Giacometti gives a smaller π-bonding effect than the maximum overlap principle. Indeed, this is what we have expected.

2) Our results agree with the experiment better than those obtained by Giacometti. From the column 4 of Table II we recognize that our results explain both, the order of increase of the bond-shortening (31) and the large jump of the bond-shortening between $Cr(CO)_6$ and $Fe(CO)_5$ in comparison with the pair $Fe(CO)_5$, $Ni(CO)_4$.

8. On the equivalence of Pauling's d.b. theory, the maximum overlap principle and the molecular orbital method

Basing on the LCAO MO method a simple method of bond orders calculation for alternant conjugated hydrocarbons has been developed by Hall (1955). He assumed for this purpose (after Hückel) that all Coulomb integrals are equal and that all atomic overlap can be neglected. The method was rediscussed by the author (Gołębiewski 1963) and extended to what was called the "semi-diagonalized" systems.

---

*) Giacometti used a different reference value for π-type overlap integrals; to make the results comparable one has to multiply his results by $1.5 \dfrac{\sqrt{2}}{3+\sqrt{3}}$. In table II this factor is already taken into account.

It seems interesting to note that there is a striking formal analogy between the mentioned Hall approach and the maximum overlap approach discussed in this paper:

The LCAO MO method

a) The ground state energy is given by the formula

$$E = \text{tr } (\boldsymbol{HH}^+)^{\frac{1}{2}}$$

where $\boldsymbol{H}$ is a resonance integrals matrix;

b) The ground state energy is equal to the sum of orbital energies e_i', which are the eigenvalues of $(\boldsymbol{HH}^+)^{\frac{1}{2}}$,

$$E = \text{tr } \boldsymbol{e'}$$

c) The not vanishing bond orders form a matrix $\boldsymbol{P}$ which can be found from the formula

$$\boldsymbol{P} = (\boldsymbol{HH}^+)^{-\frac{1}{2}} \boldsymbol{H}$$

d) The ground state energy can be easily expressed in terms of $\boldsymbol{P}$ and $\boldsymbol{H}$.

$$E = \text{tr } (\boldsymbol{PH}^+)$$

The maximum overlap method

a) The total bonds strength is given by the formula

$$E = \text{tr } (\boldsymbol{SS}^T)^{\frac{1}{2}}$$

where $\boldsymbol{S}$ is an atomic overlap integrals matrix;

b) The total bonds strength can be expressed in terms of the eigenvalues of $(\boldsymbol{SS}^T)^{\frac{1}{2}}$, e_i,

$$E = \text{tr } \boldsymbol{e}$$

c) The transformation coefficients for best linear combinations (best hybrid orbitals) follow from the formula

$$\boldsymbol{a} = (\boldsymbol{SS}^T)^{-\frac{1}{2}} \boldsymbol{S}$$

d) The matrix $\boldsymbol{a}$ can be interpreted as the bond order matrix, so as

$$E = \text{tr } (\boldsymbol{aS}^T)$$

This analogy is still more complete if we take the approximation introduced by Mulliken, that $\boldsymbol{H} \approx \boldsymbol{S}$.

The maximum overlap method (with the d.b. theory in particular) and the LCAO MO method follow apparently from different principles. And yet both methods yield much of the information the same. This coincidence gives a sounder basis to the maximum overlap principle and the d.b. method. However, it shows also for limitations; it seems that both methods are molecular orbitally grounded for "semi-diagonalized" systems only (Gołębiewski 1963), and only if $\langle \theta_i | \hat{H} \theta_i \rangle = \langle \varphi_j | \hat{H} \varphi_j \rangle$ for any i and j.

Pauling's directed bonds theory is a special case of the maximum overlap theory, developed for MX_k systems. This theory can be molecular orbitally based only then, when the number of central atom orbitals exceeds the number of ligand orbitals. We have seen on examples (sections 7) that it might not be so. In this case the maximum overlap criterium seems to give a better agreement with experiment than the directed bonds theory.

It follows reciprocally that the π-electronic MO's of conjugated alternant hydrocarbons satisfy the maximum overlap condition, but that it may not be true for unalternant hydrocarbons.

Finally we note that the e_i-values of the maximum overlap approach, (7), are numerically equal to the orbital energies of the LCAO MO method. It follows that indeed it should be possible to construct best linear combinations (best hybrid orbitals) for the excited states and to correlate them with the spectra. We will return to this question later.

REFERENCES

Cartmell, E. and Fowles, G. W. A., *Valency and Molecular Structure*, London, 1961.

Coulson, C. A. and Longuet-Higgins, H. C., *Proc. Roy. Soc.* (GB), **A192**, 16 (1947).

Durrant, P. J. and Durrant, B., *Introduction to Advanced Inorganic Chemistry*, London 1962.

Dyatkina, M. E., Shirmazan, M. G., *Izv. Akad. Nauk SSSR, Otd. khim. Nauk*, **1959**, 1751.

Giacometti, G., *J. chem. Phys.*, **23**, 2068 (1955).

Gilbert, T. L. and Lykos, P. G., *J. chem. Phys.*, **34**, 2199 (1961).

Gołębiewski, A., *Trans. Faraday Soc.* (GB), **57**, 1849 (1961).

Gołębiewski, A., *Acta phys. Polon.*, **23**, 235 (1963).

Gwinn, W. D., Tolles, W. M., *J. chem. Phys.*, **36**, 1119 (1962).

Hall, G. G., *Proc. Roy. Soc.* (GB), **A205**, 541 (1951).

Hall, G. G., *Proc. Roy. Soc.* (GB), **A229**, 251 (1955).

Murrell, J. N., *J. chem. Phys.*, **32**, 767 (1960).

Rouault, M., *Ann. Phys. (France)*, **14**, 78 (1940).

Smith, D. F., *J. chem. Phys.*, **21**, 609 (1953).

Wells, A. F., *Structural Inorganic Chemistry*, Oxford, 1962.