Maximum Overlap Hybridization in PF₅ and SF₄

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The method of Murrell as modified by Golebiewski has been applied to determine the maximum overlap hybrid orbitals for PF₅ and SF₄. For the former system, three cases have been considered: (i) overlap integrals of the central atom valence and F 2p orbitals are taken as angular parts of P atomic orbitals projected in the bond directions, (ii) evaluated using SCF atomic wave functions with equidistant F ligands, and (iii) calculated using experimental bond lengths. The resultant overall hybridizations are compared and discussed. For SF₄, only case (iii) has been carried out. In addition, the wave function of the lone pair orbital is obtained with symmetry consideration and orthonormality relationships among all the hybrids. This appears to be an inexpensive way to determine the form of the lone pair and to estimate its size.

INTRODUCTION

The concept of hybridization has played an important role in the understanding of bonding in molecules. Hybrid orbitals for molecules containing equivalent bonds can be deduced by standard applications of group theory. On the other hand, for molecules possessing little or no symmetry, or for systems with non-equivalent bonds, the principle of maximum overlap is generally invoked in the construction of hybrid orbitals. An elegant method applicable to all MXₖ systems was first developed by Murrell and later simplified by Golebiewski. The version by Golebiewski, which is briefly described below, will be applied to PF₅ and SF₄, each of which has two non-equivalent sets of hybrid orbitals.

In a previous paper, the form and size of the lone pair orbitals in carbene-, ammonia-, and water-like systems were determined by a simple version of hybridization theory. In this note, the same is achieved for the SF₄, instead of only the s and p orbitals as in the previous cases, the approach to the determination of the lone pair is entirely different.

METHOD OF CALCULATION

For a molecule MXₖ, the bonded hybrid orbitals hᵢ on M are linear combinations of orthonormal atomic orbitals φᵢ:

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where \( n \geq k \). In addition, the ligands \( X_1, \ldots, X_k \) are assumed to be \( \sigma \)-bonded to \( M \) by means of orbitals \( \Theta_1, \ldots, \Theta_k \) respectively. To determine the coefficient matrix \( A \), the overlap matrix

\[
S = \begin{pmatrix}
\langle \Theta_1 | \varphi_1 \rangle & \cdots & \langle \Theta_1 | \varphi_n \rangle \\
\vdots & \ddots & \vdots \\
\langle \Theta_k | \varphi_1 \rangle & \cdots & \langle \Theta_k | \varphi_n \rangle
\end{pmatrix}
\]

is first constructed and then the real symmetric matrix \( SS^T \) (\( S^T \) being the transpose of \( S \)) diagonalized by an orthogonal matrix \( u \):

\[
SS^T = u^T d (a_1, \ldots, a_k) u
\]

where \( d \) is a diagonal matrix with real positive elements (the eigenvalues) \( a_1, \ldots, a_k \). The matrix \( A \) in equation (1) can then be calculated explicitly by the formula

\[
A = u^T d (a_1^{-1/2}, \ldots, a_k^{-1/2}) u S
\]

where all square roots \( a_i^{-1/2} \) are taken as positive. The hybrids \( h_i \) obtained in this way are the maximum overlap bonded hybrid orbitals on the central atom \( M \).

When the bonded hybrids are obtained, the lone pair hybrid may be determined with symmetry consideration and orthonormality relationships among all the hybrid orbitals.

RESULTS AND DISCUSSION

A. The PF\(_5\) System

With reference to the coordinate system for PF\(_5\) shown in Figure 1, the following P atomic orbitals (\( \varphi_i \)) have the proper symmetry to contribute to the formation of the five hybrids: 3s, 3p, 3dz\(^2\), (3px, 3py), and (3d\(_{x^2-y^2}\), 3d\(_{xy}\)). Of these seven orbitals, the first three are fully utilized, i.e., each with a weight of 1, while the last two pairs compete with each other to give a total weight of 2.

To construct \( S \), the following three situations are considered:

Case (i): In the simplest type of approximation\(^2\), the \( \sigma \)-type overlap integrals may be taken as projections of the angular parts of P atomic orbitals along the P—F bonds, giving the relative value 1, (3)\(^{1/3}\), and (5)\(^{1/5}\) for \( <3s(P)|2p(F)>\), \( <3p(P)|2p(F)>\), and \( <3d(P)|2p(F)>\), respectively. Thus the overlap matrix has the form:
MAXIMUM OVERLAP HYBRIDIZATION

Case (ii): The five P—F bonds are assigned the same length of 1.555Å the average of two experimental P—F bond distances. The overlap integrals are calculated using the SCF P and F wave functions of Berry et al. Numerical values \(< 3s (P) | 2p (F) > = 0.246590, < 3p (P) | 2p (F) > = 0.233804, and < 3d (P) | 2p (F) > = -0.055623 are then used in constructing the overlap matrix.

Case (iii): Using the experimental values of 1.577 Å and 1.534 Å for the axial and equatorial P—F bonds, respectively, and again employing the wave functions of Berry et al., a total of six overlap integrals are calculated. The numerical values are:

\(< 3s (P) | 2p (F) > | (axial) = 0.242270, < 3s (P) | 2p (F) > | (equatorial) = -0.250824;\n\(< 3p (P) | 2p (F) > | (axial) = 0.234372, < 3p (P) | 2p (F) > | (equatorial) = 0.232903;\n\(< 3d (P) | 2p (F) > | (axial) = -0.053345, < 3d (P) | 2p (F) > | (equatorial) = -0.057935.

Once the overlap matrix is constructed, the calculation of the hybrid orbitals is straightforward; the results for all three cases are given in Table I.

In case (i), since the elements of the overlap matrix involve only integers and their square roots, the coefficients of the resultant hybrids are expressible...
in closed algebraic forms. The overall hybridization $sp^{17/9}d^{19/9}$ agrees with the result obtained by Duffey\(^9\) in a less general way. In addition, Golebiewski also suggested that this is the hybridization involved in $PCS_5$, $SbCl_5$, $SF_5$, and $ClF_5$.\(^{18}\) This scheme indicates that the $3p_x$ and $3p_y$ orbitals contribute $4/9$ each to the hybridization, while the $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals contribute $5/9$ each. This over-emphasis of d-orbital participation results from the assumption that the $P$ $3d$ orbitals overlap more effectively than the $3p$ and $3s$ orbitals with the $F$ $2p$ orbitals. Inspection of the numerical values of the overlap integrals given above shows that this simplifying assumption is unrealistic.

As expected, the results of cases (ii) and (iii) are very similar since the bond lengths used in the evaluation of overlap integrals are nearly equal. In both instances, the $(3p_x, 3p_y)$ orbitals contribute more than $90\%$ to the overall hybridization, while the $(3d_{x^2-y^2}, 3d_{xy})$ pair contributes less than $10\%$. The relatively insignificant part played by the latter is a consequence of the ineffective $\sigma$-overlap of the $F$ $2p$ and the rather diffuse $P$ $3d$ orbitals.

If it were known beforehand that the overlap integrals between $P$ $3d$ and $F$ $2p$ orbitals were of such a small magnitude, the $(3d_{x^2-y^2}, 3d_{xy})$ pair might then be safely ignored, leaving only $3s$, $3p_x$, $3p_y$, $3p_z$, and $3d_{z^2}$ orbitals as a basis. Indeed, this then becomes a rather standard exercise in quantum chemistry.\(^{11}\) However, it must be emphasized that the overlap integrals must be calculated before making such an assumption; there may be some $PF_5$-like systems where the $(d_{x^2-y^2}, d_{xy})$ pair makes a significant contribution.

**B. The $SF_4$ System**

With reference to the coordinate system for $SF_4$ shown in Figure 2, it is evident that all the sulphur atomic orbitals in the M shell except the $3d_{xy}$ orbital have the proper symmetry to contribute to the formation of the four bonded hybrids. On the other hand, only $3s$, $3p_x$, and $3d_{z^2}$ orbitals do so for the lone pair hybrid.

To construct $S$, among the three situations considered for $PF_5$, only case (iii) is carried out for $SF_4$. In the calculation of the two-center overlap integrals, the structural parameters used are those given in Figure 2;\(^{12}\) the sulphur atomic wave functions employed are those reported by Craig and Thirunamachandran\(^{13}\) (hereafter referred to as CT); the fluorine functions are the ones used in the $PF_5$ study. The numerical values of the six basic overlap integrals are:

\[
\begin{align*}
<3s(S)|2p(F)> & = (1.646 \text{ Å}) = 0.22781, \\
<3s(S)|2p(F)> & = (1.545 \text{ Å}) = 0.25864; \\
<3p(S)|2p(F)> & = (1.646 \text{ Å}) = 0.26551, \\
<3p(S)|2p(F)> & = (1.545 \text{ Å}) = 0.27807; \\
<3d(S)|2p(F)> & = (1.646 \text{ Å}) = 0.03482, \\
<3d(S)|2p(F)> & = (1.545 \text{ Å}) = 0.01571.
\end{align*}
\]

The forms of the bonded hybrids ($h_i; i = 1, \ldots, 4$) are given in Table II. As mentioned earlier, there are only three coefficients to be determined for the lone
### TABLE I

*The Maximum Overlap Hybrid Orbitals in PF$_5$*

<table>
<thead>
<tr>
<th>Case</th>
<th>Hybrid</th>
<th>3s</th>
<th>3p$_x$</th>
<th>3p$_y$</th>
<th>3p$_z$</th>
<th>d$_x^2$</th>
<th>d$_{x^2-y^2}$</th>
<th>d$_{xy}$</th>
<th>Overall Hybridization</th>
</tr>
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<tbody>
<tr>
<td>(i)</td>
<td>$h_1$</td>
<td>a</td>
<td>0</td>
<td>0</td>
<td>(2)$^{1/2}$/2</td>
<td>$-c$</td>
<td>0</td>
<td>0</td>
<td>sp$^{3}$d$^{3}$/9</td>
</tr>
<tr>
<td></td>
<td>$h_2$</td>
<td>a</td>
<td>0</td>
<td>0</td>
<td>$-(2)^{1/2}$/2</td>
<td>$-c$</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h_3$</td>
<td>b</td>
<td>(2)$^{1/2}$/3</td>
<td>(6)$^{1/2}$/9</td>
<td>0</td>
<td>d</td>
<td>(30)$^{1/2}$/18</td>
<td>(10)$^{1/2}$/6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h_4$</td>
<td>b</td>
<td>$-(2)^{1/2}$/3</td>
<td>(6)$^{1/2}$/9</td>
<td>0</td>
<td>d</td>
<td>(30)$^{1/2}$/18</td>
<td>$-(10)^{1/2}$/6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h_5$</td>
<td>b</td>
<td>0</td>
<td>$-2(6)^{1/2}$/9</td>
<td>0</td>
<td>d</td>
<td>$-(30)^{1/2}$/9</td>
<td>0</td>
<td>sp$^{3}$d$^{3}$/9</td>
</tr>
<tr>
<td>(ii)</td>
<td>$h_1$</td>
<td>0.4365</td>
<td>0</td>
<td>0</td>
<td>0.7071</td>
<td>$-0.5563$</td>
<td>0</td>
<td>0</td>
<td>sp$^{3}$d$^{1.088}$</td>
</tr>
<tr>
<td></td>
<td>$h_2$</td>
<td>0.4365</td>
<td>0</td>
<td>0</td>
<td>$-0.7071$</td>
<td>$-0.5563$</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h_3$</td>
<td>0.4542</td>
<td>0.6926</td>
<td>0.3998</td>
<td>0</td>
<td>0.3564</td>
<td>$-0.0824$</td>
<td>$-0.1427$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h_4$</td>
<td>0.4542</td>
<td>$-0.6926$</td>
<td>0.3998</td>
<td>0</td>
<td>0.3564</td>
<td>$-0.0824$</td>
<td>0.1427</td>
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<tr>
<td></td>
<td>$h_5$</td>
<td>0.4542</td>
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<td>$-0.7997$</td>
<td>0</td>
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<td>0.1648</td>
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<tr>
<td>(iii)</td>
<td>$h_1$</td>
<td>0.4315</td>
<td>0</td>
<td>0</td>
<td>0.7071</td>
<td>$-0.5602$</td>
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<td>0</td>
<td>sp$^{3}$d$^{1.087}$</td>
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<tr>
<td></td>
<td>$h_2$</td>
<td>0.4315</td>
<td>0</td>
<td>0</td>
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<td>$-0.5602$</td>
<td>0</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>$h_3$</td>
<td>0.4574</td>
<td>0.6912</td>
<td>0.3991</td>
<td>0</td>
<td>0.3523</td>
<td>$-0.0860$</td>
<td>$-0.1489$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h_4$</td>
<td>0.4574</td>
<td>$-0.6912$</td>
<td>0.3991</td>
<td>0</td>
<td>0.3523</td>
<td>$-0.0860$</td>
<td>0.1489</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h_5$</td>
<td>0.4574</td>
<td>0</td>
<td>$-0.7982$</td>
<td>0</td>
<td>0.3523</td>
<td>0.1720</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

\[ a = \frac{[25 - (145)^{1/2}/720]^{1/2} [1 - (5/29)^{1/2}]}{720} + \frac{[25 + (145)^{1/2}/720]^{1/2} [1 + (5/29)^{1/2}]}{720} = 0.399451. \]
\[ b = \frac{[(1/3) - (2a^{1/3})]^{1/2}}{2} = 0.479643. \]
\[ c = \frac{[(1/2) - a^{1/2}]}{2} = 0.583472. \]
\[ d = \frac{[(1/3) - b^{1/3}]}{2} = -0.326150. \]
pair hybrid \((h_1)\) and they can be obtained uniquely with the orthonormality relationships among all the hybrid orbitals. The form of \(h_1\) is also given in Table II.

### TABLE II

**The Maximum Overlap Bonded Hybrids \((h_i, i=1, \ldots, 4)\) and the Lone Pair Hybrid \((h_1)\) of \(SF_4\)**

<table>
<thead>
<tr>
<th>Hybrid</th>
<th>Coefficients of Atomic Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(s)</td>
</tr>
<tr>
<td>(h_1)</td>
<td>0.5871</td>
</tr>
<tr>
<td>(h_2)</td>
<td>0.5871</td>
</tr>
<tr>
<td>(h_3)</td>
<td>0.3771</td>
</tr>
<tr>
<td>(h_4)</td>
<td>0.3771</td>
</tr>
<tr>
<td>(h_1)</td>
<td>0.0841</td>
</tr>
</tbody>
</table>

The profile of the lone pair orbital may be illustrated by plotting its probability density \(|h_1|^2\) against distance in the direction of its maximum. Figure 3 shows the \(|h_1|^2\) curve of \(SF_4\), the most interesting feature being a maximum at \(r_{max} = 0.635 \text{ Å}\). As suggested previously, this provides a plausible estimate of the size of the \(SF_4\) lone pair. Since other estimates for this value are not readily available in the literature, it is noted that the \(r_{max}\) values for the carbene, ammonia, and water lone pairs have been reported as 0.380, 0.289, and 0.244 Å, respectively. Therefore, the present estimate for \(SF_4\) appears to fall in a reasonable range.

Attention is now turned to the forms of hybrid orbitals. Since the sulphur 3s and 3p orbitals overlap much more effectively than the 3rd orbitals do with the fluorine 2p orbitals, it is not surprising that the maximum overlap model
yields that all bonded hybrids compose almost entirely of 3s and 3p orbitals, while the lone pair hybrid has an exceptionally high d-content. An obvious point to make at this juncture is that the quality of the lone pair orbital obtained by this method depends heavily on the quality of the atomic wave functions used. [When Clementi's sulphur 3s and 3p functions and the 3d orbitals of CT are used in the calculation, the resulting hybrids are quite similar to those listed in Table II. Therefore, it may be said that the Clementi and CT wave functions are comparable with each other.] Among the four bonded hybrids, those for the longer bonds ($h_1$ and $h_2$) have a d-content that is three times as large as that for $h_3$ and $h_4$. Again, this is a reflection on the difference between the two basic overlap integrals $\langle 3d(S) \mid 2p(F) \rangle$ (1.646 Å) and $\langle 3d(S) \mid 2p(F) \rangle$ (1.545 Å).

Finally, it is mentioned that applying the method described here to systems such as ClF_3 and BrF_3, which have two lone pairs and where d-orbital participation is expected, would not yield a unique solution for the lone pair hybrids. This is because there are not enough orthonormality relationships to determine all the coefficients. Rather, some additional assumptions have to be made in order to resolve this difficulty.

To conclude, the present method is an attempt to obtain inexpensively a quantitative picture of the lone pair orbital in SF_4-like systems. In view of the vital role the lone pairs play in models of directed valence such as the VSEPR theory, it appears worthwhile to pursue this method further, so that the lone pair orbitals of various molecular systems may be studied and compared.

Acknowledgement. The authors wish to thank Professor Z. B. Maksic and the referee for valuable comments.

REFERENCES

2. For a recent review in this field, see M. Randić and Z. B. Maksic, Chem. Rev. 72 (1972) 43.
Hibridizacija maksimalnog prekrivanja u molekulama PF₅ i SF₄

K. M. Sun, T. C. W. Mak i W. K. Li

Izračunani su hibridi maksimalnog prekrivanja za molekule PF₅ i SF₄ primjenom matrične metode Murrell-Golebiewski. Lokalizirana orbitala koja opisuje osamljeni par elektrona u molekuli SF₄ dobivena je s pomoću zahtjeva simetrije i ortonormiranja hibrida. Pokazano je da hibridizacija u molekuli PF₅ u prvoj aproksimaciji ima oblik sp³d. Odstupanje od toga kanonskog oblika vrlo je malo. Osamljeni par elektrona u molekuli SF₄ sadržava izrazito visok udjel d-orbitala.