Maximum Overlap Hybridization in PF5 and SF4

King-Mo Sun, Thomas C. W. Mak, and Wai-Kee Li**

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T. Hong Kong

The method of Murrell as modified by Golebiewski has been applied to determine the maximum overlap hybrid orbitals for PF_5 and SF_4. For the former system, three cases have been considered: σ overlap integrals of the central atom valence and F 2p orbitals are (*i*) 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 SF_4, 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.[1] 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.[2,3] An elegant method applicable to all MX_k systems was first developed by Murrell[4] and later simplified by Golebiewski.[5] The version by Golebiewski, which is briefly described below, will be applied to PF_5 and SF_4, each of which has two non-equivalent sets of hybrid orbitals.

In a previous paper,[6] 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 SF_4, 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 MX_k, the bonded hybrid orbitals h_i on M are linear combinations of orthonormal atomic orbitals Φ_j:

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* Address correspondence to these authors.

$$\begin{pmatrix} h_i \\ \vdots \\ h_k \end{pmatrix} = A \begin{pmatrix} \varnothing_1 \\ \vdots \\ \varnothing_n \end{pmatrix} = \begin{pmatrix} a_{11} & \cdots & a_{1n} \\ \vdots & & \vdots \\ a_{k1} & \cdots & a_{kn} \end{pmatrix} \begin{pmatrix} \varnothing_1 \\ \vdots \\ \varnothing_n \end{pmatrix}$$

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

$$S = \begin{pmatrix} \langle \theta_1 | \varnothing_1 \rangle & \cdots & \langle \theta_1 | \varnothing_n \rangle \\ \vdots & & \vdots \\ \langle \theta_k | \varnothing_1 \rangle & \cdots & \langle \theta_k | \varnothing_n \rangle \end{pmatrix}$$

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

$$SS^T = \mathbf{u}^T \mathbf{d} (\alpha_1, \ldots, \alpha_k) \mathbf{u} \tag{3}$$

where $\mathbf{d}$ is a diagonal matrix with real positive elements (the eigenvalues) $\alpha_1, \ldots, \alpha_k$. The matrix A in equation (1) can then be calculated explicitly by the formula

$$A = \mathbf{u}^T \mathbf{d} (\alpha_1^{-1/2}, \ldots, \alpha_k^{-1/2}) \mathbf{u} S \tag{4}$$

where all square roots $\alpha_i^{-1/2}$ are taken as positive. The hybrids h_i obtained in this way are the maximum overlap bonded hybrid orbitals on the central atom M.[5]

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

<div align="center">RESULTS AND DISCUSSION</div>

A. The PF$_5$ System

With reference to the coordinate system for PF$_5$ shown in Figure 1, the following P atomic orbitals (Φ_j) have the proper symmetry to contribute to the formation of the five hybrids: 3s, 3p$_z$, 3d$_{z^2}$, (3p$_x$, 3p$_y$), 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 σ-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, $(3)^{1/2}$, and $(5)^{1/2}$ for $< 3s\,(P) |$ $| 2p\,(F) >$,$< 3p\,(P) | 2p\,(F) >$, and $< 3d\,(P) | 2p\,(F) >$, respectively. Thus the overlap matrix has the form:

$$S = \begin{array}{c} \\ \theta_1 \\ \theta_2 \\ \theta_3 \\ \theta_4 \\ \theta_5 \end{array} \begin{array}{ccccccc} 3s & 3p_x & 3p_y & 3p_z & 3d_{z^2} & 3d_{x^2-y^2} & 3d_{xy} \\ \begin{pmatrix} 1 & 0 & 0 & (3)^{1/2} & (5)^{1/2} & 0 & 0 \\ 1 & 0 & 0 & -(3)^{1/2} & (5)^{1/2} & 0 & 0 \\ 1 & 3/2 & (3)^{1/2}/2 & 0 & -(5)^{1/2}/2 & (15)^{1/2}/4 & 3(5)^{1/2}/4 \\ 1 & -3/2 & (3)^{1/2}/2 & 0 & -(5)^{1/2}/2 & (15)^{1/2}/4 & -3(5)^{1/2}/4 \\ 1 & 0 & -(3)^{1/2} & 0 & -(5)^{1/2}/2 & -(15)^{1/2}/2 & 0 \end{pmatrix} \end{array}$$
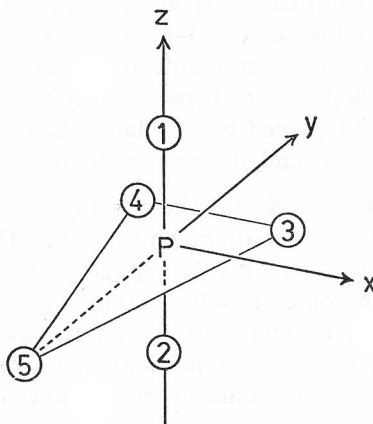
Figure 1. Coordinate system for PF₅

Case (ii): The five P—F bonds are assigned the same length of 1.555Å the average of two experimental P—F bond distances.[7] The overlap integrals are calculated using the SCF P and F wave functions of Berry et al.[8] 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[7] 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) $= 0.250824$;
$< 3p\,(P)\,|\,2p\,(F)>$ (axial) $= 0.234372$, $< 3p\,(P)\,|\,2p\,(F)>$ (equatorial) $= 0.232903$;
$< 3d\,(P)\,|\,2p\,(F)>$ (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 PCl_5, $SbCl_5$, SF_4, and ClF_3.[10] 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 then 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 σ-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, $3p_z$, 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:

$<$3s (S) | 2p (F)$>$ (1.646 Å) = 0.22781, $<$3s (S) | 2p (F)$>$ (1.545 Å) = 0.25864;

$<$3p (S) | 2p (F)$>$ (1.646 Å) = 0.26551, $<$3p (S) | 2p (F)$>$ (1.545 Å) = 0.27807;

$<$3d (S) | 2p (F)$>$ (1.646 Å) = 0.03482, $<$3d (S) | 2p (F)$>$ (1.545 Å) = 0.01571.

The forms of the bonded hybrids (h_i; i = 1, ..., 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 PF₅
Atomic Orbital Coefficients

Case	Hybrid	3s	$3p_x$	$3p_y$	$3p_z$	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	Overall Hybridization
(i)	h_1	a	0	0	$(2)^{1/2}/2$	$-c$	0	0	$sp^{17/9}\,d^{19/9}$
	h_2	a	0	0	$-(2)^{1/2}/2$	$-c$	0	0	
	h_3	b	$(2)^{1/2}/3$	$(6)^{1/2}/9$	0	d	$(30)^{1/2}/18$	$(10)^{1/2}/6$	
	h_4	b	$-(2)^{1/2}/3$	$(6)^{1/2}/9$	0	d	$(30)^{1/2}/18$	$-(10)^{1/2}/6$	
	h_5	b	0	$-2(6)^{1/2}/9$	0	d	$-(30)^{1/2}/9$	0	
(ii)	h_1	0.4365	0	0	0.7071	−0.5563	0	0	$sp^{2.9186}\,d^{1.0814}$
	h_2	0.4365	0	0	−0.7071	−0.5563	0	0	
	h_3	0.4542	0.6926	0.3998	0	0.3564	−0.0824	−0.1427	
	h_4	0.4542	−0.6926	0.3998	0	0.3564	−0.0824	0.1427	
	h_5	0.4542	0	−0.7997	0	0.3564	0.1648	0	
(iii)	h_1	0.4315	0	0	0.7071	−0.5602	0	0	$sp^{2.9113}\,d^{1.0887}$
	h_2	0.4315	0	0	−0.7071	−0.5602	0	0	
	h_3	0.4574	0.6912	0.3991	0	0.3523	−0.0860	−0.1489	
	h_4	0.4574	−0.6912	0.3991	0	0.3523	−0.0860	0.1489	
	h_5	0.4574	0	−0.7982	0	0.3523	0.1720	0	

$a = \{[25 - (145)^{1/2}/720]^{1/2} [1 - (5/29)^{1/2}] + [25 + (145)^{1/2}/720]^{1/2} [1 + (5/29)^{1/2}] = 0.399451.$

$b = [(1/3) - (2a^2/3)]^{1/2} = 0.476403.$

$c = [(1/2) - a^2]^{1/2} = 0.583472.$

$d = - [(1/3) - b^2]^{1/2} = - 0.326150.$

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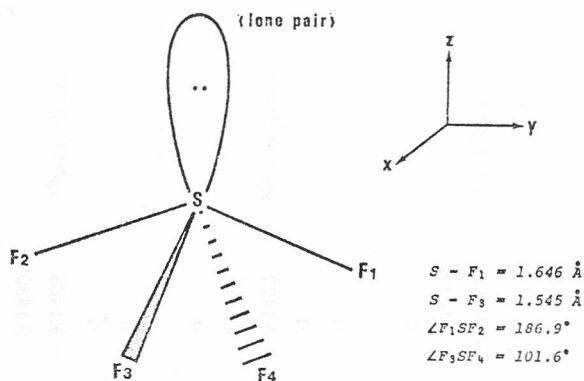Figure 2. Coordinate system and the relevant structural parameters of SF_4.

pair hybrid (h_l) and they can be obtained uniquely with the orthonormality relationships among all the hybrid orbitals. The form of h_l 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_l) *of* SF_4

Hybrid	Coefficients of Atomic Orbitals							
	s	p_z	p_x	p_y	d_{z^2}	$d_{x^2-y^2}$	d_{xz}	d_{yz}
h_1	0.5871	0.3390	0.0	0.7071	—0.0944	—0.1774	0.0	—0.0088
h_2	0.5871	0.3390	0.0	—0.7071	—0.0944	—0.1774	0.0	0.0088
h_3	0.3771	—0.5879	0.7058	0.0	0.0463	0.0999	—0.0437	0.0
h_4	0.3771	—0.5879	—0.7058	0.0	0.0463	0.0999	0.0437	0.0
h_l	0.0841	0.1317	0.0	0.0	0.9877	0.0	0.0	0.0

The profile of the lone pair orbital may be illustrated by plotting its probability density $|h_l|^2$ against distance in the direction of its maximum. Figure 3 shows the $|h_l|^2$ curve of SF_4, the most interesting feature being a maximum at $r_{max} = 0.635$ Å. As suggested previously[6], 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[6]. 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
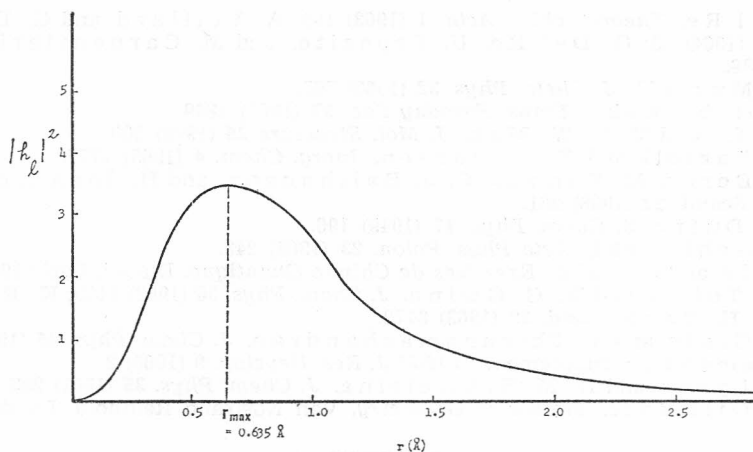
Figure 3. Profile of SF_4 lone pair ($| h_1 |^2$ in arbitrary units).

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[14] 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 $< 3d\,(S)\,|\,2p\,(F) >$ (1.646 Å) and $< 3d\,(S)\,|\,2p\,(F) >$ (1.545 Å).

Finally, it is mentioned that applying the method desribed 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[4,15].

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[16], it appears worthwhile to pursue this method further, so that the lone pair orbitals of various molecular systems may be studied and compared.

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SAŽETAK

Hibridizacija maksimalnog prekrivanja u molekulama PF_5 i SF_4

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

Izračunani su hibridi maksimalnog prekrivanja za molekule PF_5 i SF_4 primjenom matrične metode Murrell-Golebiewski. Lokalizirana orbitala koja opisuje osamljeni par elektrona u molekuli SF_4 dobivena je s pomoću zahtjeva simetrije i ortonormiranja hibrida. Pokazano je da hibridizacija u molekuli PF_5 u prvoj aproksimaciji ima oblik sp^3d. Odstupanje od toga kanonskog oblika vrlo je malo. Osamljeni par elektrona u molekuli SF_4 sadržava izrazito visok udjel d-orbitala.

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   N. T. HONG KONG