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Domain-averaged Fermi holes – a new means of visualization of chemical bonds. Bonding in hypervalent molecules

R. Ponec, J. Roithová

Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Prague 6, Suchdol 2, 165 02, Czech Republic

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Abstract. The nature of bonding in several hypervalent molecules was analyzed at the *ab initio* SCF level using the recently proposed methodology based on the analysis of domain-averaged Fermi holes. The results of the analysis demonstrate that, for sufficiently flexible basis sets, the expansion of the valence shell does indeed take place for second row central atoms in PF_5, SF_4, and SF_6. On the other hand, no such expansion was observed for the first row N atom in NF_5.

Key words: Domain-averaged Fermi holes – Chemical bonding – Hypervalence – Valence shell expansion

Introduction

Since its introduction some decades ago [1–4], the concept of hypervalence, denoting the apparent expansion of the valence shell of the central atom in molecules like XeF_2, ClF_3, SF_4, SF_6, PF_5, etc., has become part of general chemical terminology. Despite wide acceptance of this concept, the nature of bonding in hypervalent systems is still the subject of continuing discussions [5–15]. The main debate concerns the question of whether the Lewis octet rule is violated in these systems, or, what is equivalent, whether the expansion of the valence shell takes place. The first explanation of the valence shell expansion was based on the idea of participation of *d* orbitals in hybridization [5, 6]. This explanation is not, however, attributed too much importance now since according to *ab initio* calculations *d* orbitals usually act as polarization rather than true valence functions. In order to explain the valence shell expansion without invoking the idea of *d*-orbital participation, the concept of 3-center 4-electron bond was proposed [16–18]. Another argument against valence shell expansion was raised some time ago by Cioslowski and Mixon [12]. Their argumentation arises from the fact that bonds in hypervalent molecules are usually very polar with most of the charge concentrated on electronegative ligands. As a consequence of this polarity, the number of electrons in the valence shell of the central atom is considerably reduced so that the Lewis octet rule is not effectively violated. In terms of this approach, most of the molecules regarded as hypervalent should be considered as ''normal''. The situation is, however, slightly more complex since, for example, Bader's analysis revealed the existence of six and/or five bond paths in SF_6 and PF_5 molecules, respectively [19, 20], which again is rather consistent with the expansion of the valence shell. Such an expansion seems to be supported also by the results of recent SC-VB calculations [20–24], in which the so-called democracy principle was formulated. According to this principle, (almost) all electrons of the central atoms can participate in bonding if provided with a sufficient energetic incentive. The mechanism of this participation consists in that the electrons of the central atoms, originally residing in formally doubly occupied, free electron pairs decouple so that each of the resulting singly occupied orbitals can be engaged in bonding to ligands. Although the resulting bonds are very polar, the number of electron pairs around the central atom effectively increases and hypervalency results. Similarly, the importance of ''increased valence structures'' is advocated also by Harcourt [25, 26].

In view of these contradictory opinions we have recently proposed a new approach based on the analysis of the so-called domain averaged Fermi holes [27–29] which, we believe, can throw some new light on the problem of hypervalent bonding. Since, however, this approach was originally applied only at the level of the simple semiempirical AM1 method [29] which certainly does not meet the contemporary computational standards, we report in this study the extension of this approach to the level of *ab initio* SCF methods. The

Correspondence to: R. Ponec
e-mail: rponec@icpf.cas.cz
Tel: +420-2-20390271; Fax: +420-2-20920661
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primary aim of this study is to analyze how the picture of bonding changes in response to the systematic variation of the basis set from the minimal STO-3G to the rather flexible 6-31G** basis. As will be shown, while in the minimal and split 3–21G basis the picture of bonding is very close to what was found in a semi-empirical AM1 study [29], the inclusion of *d* orbitals in the 6-31G** basis considerably changes the valence state of the central atom which in most cases becomes consistent with the idea of valence shell expansion. In the following part the results of our calculations will be reported.

Theoretical

The concept of Fermi hole was introduced in early 1930s by E. Wigner [30] as a means of describing the effects of mutual coupling of electrons of the same spin in solid state physics. The applications to chemistry are not only more recent but also much more scarce and only few systematic studies of Fermi holes were reported so far [31–34]. In addition to these earlier studies we proposed some time ago a new possibility of exploitation of Fermi holes in chemistry [27–29]. This application is based on the concept of the so-called domain-averaged Fermi hole, which is defined as Eq. (1):

$$h_\Omega(r_1) = \rho(r_1) - P_\Omega(r_1) \tag{1}$$

where $P_\Omega(r_1)$ is the conditional probability of finding one electron of the pair in r_1, provided the second, reference electron is allowed to be anywhere in the region Ω. This domain-averaged Fermi hole satisfies the universal normalization condition, Eq. (2), which holds irrespective of the form of the domain Ω.

$$\int h_\Omega(r_1)\mathrm{d}r_1 = 1 \tag{2}$$

Although the validity of Eq. (2) is not affected by the size and the form of the domain, some choices of Ω are of special importance to chemistry. Such choice relies on the Bader's virial partitioning of the function $\rho(r)$ into domains associated with individual atoms [35]. A natural choice of the domains is thus to identify them with Bader's atomic regions. The simplest possibility, which will be used in this study, is to identify Ω with the domain of a single atom. In this case, as we have seen recently [27–29], the domain-averaged Fermi holes provide information about the valence state of a given atom in a molecule. The quantity which provides this information is not, however, the Fermi hole Eq. (1) itself, but the closely related quantity called the "charge-weighted" Fermi hole defined as Eq. (3)

$$g_\Omega(r_1) = N_\Omega h_\Omega(r_1) \tag{3}$$

The proportionality factor N_Ω is equal to the number of electrons in the domain Ω [Eq. (4)].

$$N_\Omega = \int_\Omega \rho(r_1)\mathrm{d}r_1 \tag{4}$$

The philosophy underlying the introduction of these "charge-weighted" Fermi holes is the following. The "normal" Fermi hole, Eq. (1), was derived from the conditional probability, describing the distribution of the first electron of the pair provided that the second one is known to be anywhere in the domain Ω. The localization of one and just one electron on the domain Ω is, however, an artificial act which does not reflect the fact that in the real molecule the domain is populated by N_Ω electrons rather than by one. The proportionality factor in Eq. (4) is thus nothing but a statistical correction for the actual number of electrons in Ω.

As we have already stressed in [29], the "charge-weighted" Fermi holes can also be obtained alternatively by appropriately integrating the exchange part of the density matrix [36], Eq. (5):

$$g_\Omega(r_1) = \rho(r_1)\int_\Omega \rho(r_2)\mathrm{d}r_2 - 2\int_\Omega \rho(r_1, r_2)\mathrm{d}r_2 \tag{5}$$

They are also closely related to the inter-loge correlation terms $F(\Omega,\Omega')$ introduced by Bader [37], Eq. (6).

$$F(\Omega, \Omega') = \int_{\Omega'} g_\Omega(r_1)\mathrm{d}r_1 \tag{6}$$

In this connection it is also interesting to remark that in the case of SCF approximation, the Eq. (3) can be alternatively rewritten in the simple form, Eq. (7):

$$g_\Omega(r_1) = 2\sum_i^{occ}\sum_j^{occ} \langle i \mid j\rangle_\Omega \varphi_i(r_1)\varphi_j(r_1) \tag{7}$$

where $\varphi_i(r_1), \varphi_j(r_1)$ are occupied molecular orbitals and $\langle i \mid j\rangle_\Omega$ denotes the overlap integral over the region Ω, Eq. (8).

$$\langle i \mid j\rangle_\Omega = \int_\Omega \varphi_i(r)\varphi_j(r)\mathrm{d}r \tag{8}$$

After this introductory review of basic concepts, let us also briefly review the methods of the analysis of these Fermi holes. Although they are derived from an inherently two-electron quantity, namely the pair density, these holes themselves are one-electron quantities like the ordinary density $\rho(r)$ so that all the methods applicable to the analysis of $\rho(r)$ can be applied here. One of these methods, which was also used in previous studies [27–29], is the diagonalization of the matrix G_Ω which represents the hole in the AO basis. Particularly interesting were the results of such an analysis in the case of hypervalent molecules [29]. It was shown that the resulting picture of bonding straightforwardly reflected the presence of 3-center 4-electron bonds as a typical structural feature of hypervalent systems [7, 16–18, 25]. Although providing a clear and simple picture of bonding in the studied molecules, the main disadvantage of the study [29] was that it was performed only at the level of the semiempirical AM1 method which, of course, does not meet contemporary computational standards. For this reason and in order to make the results more reliable, we have decided to reconsider the approach again and to perform the analysis at the level of *ab initio* SCF theory. The aim of this extension is not

only to reach a better and more realistic description of bonding in hypervalent molecules but also to study how the results of the analysis depend on the quality of the basis set. Particular attention will be devoted to the explicit evaluation of the frequently discussed role of *d* orbitals in the expansion of the valence shell.

Computations

Although the above presented methodology was formulated quite generally and can be applied at any level of the theory (including post HF methods), some specific approximations were nevertheless used in this study. This concerns, above all, the integration over Bader's regions which was approximated, like in our previous studies [27–29], by appropriately restricting the summations over the basis functions. Within this approximation, which is reminiscent of the well-known Mulliken-like partitioning of electron density [38], the electron is expected to be in a domain of the atom A if it resides in an orbital centered on this atom. Thus, e.g., the integral $\langle i \mid i \rangle_\Omega$ over the atomic domain of the atom A, is approximated as Eq. (9)

$$2\sum_{i}^{occ}\langle i \mid i\rangle_\Omega = 2\sum_{i}^{occ}\sum_{\mu}^{A}\sum_{\nu} c_{\mu i}c_{\nu i}S_{\mu\nu} = \sum_{\mu}^{A}\sum_{\nu} P_{\mu\nu}S_{\nu\mu}$$
$$= \sum_{\mu}^{A}(PS)_{\mu\mu} = Q(A) \qquad (9)$$

Another approximation used in this study concerns the pair density which was generated from *ab initio* SCF wave functions. The resulting approach was applied to the series of several hypervalent molecules involving SF_4, SF_6, PF_5, NF_5, and ClF_3. The wave functions necessary for the generation of pair densities and Fermi holes were obtained using the PC-Gamess program [39] in STO-3G, 3-21G, and 6-31G** bases. The molecules were in all cases considered in molecular geometries completely optimized at each particular level. The calculated values of geometrical parameters are summarized, together with the corresponding experimental data, in Table 1. The Fermi holes were generated and analyzed using our own Fortran codes.

Before presenting the results of our calculations it is necessary to mention at this place one specific feature of the Fermi holes generated at the *ab initio* level. This feature is closely connected with the use of the Mulliken-like approximation of integrals over the Bader's atomic domains. In this case, namely, the integrals of the type $\langle i \mid j \rangle_\Omega$, which appear in Eq. (7) are approximated as Eq. (10)

$$\langle i \mid j\rangle_\Omega = \sum_{\mu}^{A}\sum_{\nu} c_{\mu i}c_{\nu j}S_{\mu\nu} \qquad (10)$$

which, unfortunately is not symmetrical in μ and *v* as it is in the case of explicit Bader's integration. As a consequence, the matrix G_Ω which represents the Fermi hole in AO basis is not symmetrical. In order to remedy this artifact of the approximation, Eq. (10), the matrix of the Fermi hole must be artificially symmetrized according to Eq. (11)

$$\langle i \mid j\rangle_\Omega = \frac{1}{2}\left\{\sum_{\mu}^{A}\sum_{\nu} c_{\mu i}c_{\nu j}S_{\mu\nu} + \sum_{\nu}^{A}\sum_{\mu} c_{\mu i}c_{\nu j}S_{\mu\nu}\right\} \qquad (11)$$

Such a symmetrization was not necessary in the case of the semiempirical method [29] since, because of the orthogonality of the AO basis, the expression $\langle i \mid j \rangle_\Omega$ is symmetrical with respect to μ and *v*. The symmetrization of the hole can also be avoided by working with symmetrically orthogonalized basis sets.

Having specified the necessary computational details, let us proceed now to the presentation of the results of our calculations on individual systems. In the following part the results will be summarized.

Results and discussion

SF_4

As the first example let us discuss the molecule of sulfur tetrafluoride, which, according to Musher's classification [1], belongs to the hypervalent molecules of the first type (HV_I). These molecules are characteristic of being formed from existing "normal" molecules by the addition of two monovalent (or single divalent) ligands in a manner which preserves the structure of the original molecule. A specific feature of this type of molecules is the existence of two types of bonds. One of them, corresponding to equatorial SF bonds, is strongly reminiscent of the SF bonds in the parent SF_2 and classified as more or less "normal" 2-center 2-electron bonds. On the other hand, two axial SF bonds are quite different (they differ already in the bond length) and are classified as genuine hypervalent bonds. The existence of this qualitative difference between axial and equatorial SF bonds was straightforwardly reflected in our previous study [29], in which the Fermi holes derived from semiempirical AM1 pair densities were analyzed. Thus, for example, the diagonalization of the Fermi hole associated with the central S atom yielded 4 nonzero eigenvalues of which one was close to 2 and the inspection of the corresponding eigenvector showed that it corresponds to a σ-free electron pair on S. In addition, there was a pair of degenerate eigenvalues equal to 0.694 and one eigenvalue equal to 0.677. The detailed inspec-

Table 1. Calculated values of geometrical parameters of selected hypervalent molecules[a]

Molecule	Parameter	STO-3G	3-21G	6-31G**	Experimental
SF_4	SF_{ax}	1.717	1.677	1.632	1.646
	SF_{eq}	1.717	1.615	1.544	1.578
	FSF_{eq}	138.9	107.4	102.7	101.5
	FSF_{ax}	138.9	162.8	169.9	173.1
SF_6	SF	1.688	1.612	1.554	1.564
PF_5	PF_{ax}	1.662	1.604	1.568	1.58
	PF_{eq}	1.656	1.580	1.535	1.53
NF_5	NF_{ax}	1.500	1.549	1.531	–
	NF_{eq}	1.439	1.425	1.326	–
ClF_3	ClF_3	1.760	1.757	1.672	1.697
	ClF_1	1.771	1.673	1.579	1.598
	F_1ClF_3	77.8	83.6	86.3	87.5

[a] Bond lengths in Angstroms, bond angles in degrees

tion of the corresponding eigenvectors assigned the degenerate pair to broken valences of two equatorial SF bonds and the remaining eigenvector was very reminiscent of "pure" 3*p* orbital oriented along two axial SF bonds. These results could be interpreted at both qualitative and quantitative level. Thus, for example, the substantial deviation of the above 3 eigenvalues from unity clearly suggests considerable polarity of both equatorial and axial SF bonds [29]. Another interesting conclusion could also be deduced from the qualitative inspection of the form of corresponding eigenvectors. Especially interesting in this respect is the situation with the eigenvector of the sulfur Fermi hole associated with the eigenvalue 0.677. As already stated above, this eigenvector is strongly reminiscent of a 3*p* orbital oriented along the axial SF bonds. This result is very interesting since the situation in which one orbital participates in two adjacent bonds was anticipated a long time ago by Pimentel [16] and Hach and Rundle [17] as a paradigm for 3-center 4-electron bonding and it is also interesting that the existence of this bonding, specifically localized in the axial FSF fragment was indeed confirmed [29] by the values of the so-called 3-center bond indices [40–43] resulting from the recently proposed non-linear population analysis [44–46]. In this connection it is also worth mentioning that the same situation characteristic for the Pimentel, Hach and Rundle model of 3c-4e bonds was also analyzed some time ago by Halgren et al., who proposed the term fractional bonds [47].

Having summarized the results of previous calculations [29], let us proceed now to the presentation of the *ab initio* analysis. The results are summarized in Table 2. As it is possible to see from this Table, there is a close parallel between the results in the split 3-21G (and also STO-3G) basis with those from the previous semiempirical analysis. Thus, for example, the diagonalization of the Fermi hole associated with central S atom yields 9 nonzero eigenvalues, of which 6 are close to two. Five of them, which were absent at the semiempirical level, correspond to core electron pairs of filled K and L shells on S so that there are again 4 four nonzero eigenvalues characterizing the valence shell of S similarly as in [29]. One of them, with the value close to 2, corresponds to the free electron pair on S. The remaining 3 nonzero eigenvalues are again distributed in one degenerate pair equal to 0.707 and a single value of 0.653. The detailed inspection of the form of the associated eigenvectors shows that the degenerate pair corresponds to two broken valences of equatorial SF bonds while the remaining one is again reminiscent of a sulfur 3*p* orbital participating in two axial SF bonds. Such a situation is again characteristic of 3-center 4-electron bonding and, as it is possible to see in Table 3, the existence of this bond is indeed confirmed by the axial FSF 3-center bond index, which exceeds in absolute value the analogous index in the $F_{eq}SF_{eq}$ fragment. This picture of the valence state of the central sulfur atom is also supported by the comparison of the above eigenvalues with those resulting from the diagonalization of the Fermi hole associated with individual fluorine atoms. Thus, for example, there is an approximate complementarity between the eigenvalue 0.653 with the value 1.626 resulting from the diagonalization of the Fermi hole associated with the corresponding axial fluorines ($0.653 + 2 \times 1.626 \cong 4.$), and similar complementarity exists also for the eigenvalues corresponding to equatorial S-F bonds ($0.707 + 1.489 \cong 2$). Although this approximate complementarity holds in this case with comparable accuracy as in the case of semiempirical AM1 and minimal STO-3G basis sets, the bonding sit-

Table 2. Nonzero eigenvalues of semiempirical and *ab initio* SCF domain-averaged Fermi holes associated with the atomic region of central atom and ligands for SF_4 molecule in several basis sets

Basis	Region	Degeneracy	Eigenvalue
AM1	S	1	~2.0
		2	0.694
		1	0.677
	F_{ax}	3	~2.0
		1	1.658
	F_{eq}	3	~2.0
		1	1.512
STO-3G	S	6	~2.0
		2	1.018
		1	1.360
	F_{ax}	4	~2.0
		1	1.203
	F_{eq}	4	~2.0
		1	1.203
3-21G	S	6	~2.0
		2	0.707
		1	0.653
		2	0.055
		1	0.086
	F_{ax}	4	~2.0
		1	1.626
	F_{eq}	4	~2.0
		1	1.489
6-31G**	S	6	~2.0
		2	0.585
		2	0.401
		3	0.066
		3	0.040
	F_{ax}	4	~2.0
		1	1.643
	F_{eq}	4	~2.0
		1	1.495

Table 3. Calculated values of 3-center bond indices for selected molecular fragments of SF_4 molecule from *ab initio* SCF non-linear population analysis in several basis sets

Basis	Fragment	3-center bond index
AM1	$F_{ax}SF_{ax}$	−0.082
	$F_{eq}SF_{eq}$	−0.054
STO-3G	$F_{ax}SF_{ax}$	−0.042
	$F_{eq}SF_{eq}$	−0.042
3-21G	$F_{ax}SF_{ax}$	−0.058
	$F_{eq}SF_{eq}$	−0.031
6-31G**	$F_{ax}SF_{ax}$	−0.022
	$F_{eq}SF_{eq}$	−0.020

uation in the more flexible 3–21G basis set is nevertheless slightly more complex. This can apparently be attributed to the fact that because of greater flexibility of the basis, the final picture of bonding is a bit more complex and, in addition to above discussed 9 nonzero eigenvalues associated with the sulfur Fermi hole, there are in fact another 3 nonzero eigenvalues (2×0.055, 1×0.086). As, however, these eigenvalues are much smaller than the previous ones, we have neglected them in the first approximation. Similarly, the presence of additional eigenvalues can be observed also for the Fermi holes associated with the fluorine atoms but again, due to their negligible values, they can be neglected. The final picture of bonding, characteristic of the presence of two polar equatorial S-F bonds together with even more polar axial 3c-4e FSF bond is thus very reminiscent of what was observed at the semiempirical AM1 level.

This picture of bonding, which we originally believed to be characteristic of the SCF level of theory [29] changed, however, quite dramatically in the case of the 6–31G** basis, in which *d* orbitals on both S and F atoms are considered. As a result of this inclusion, the picture of the valence state completely changes. This can straightforwardly be demonstrated by the inspection of the number and the form of the eigenvectors of the sulfur Fermi hole corresponding to nonzero eigenvalues. Thus, in contrast to previous cases where the diagonalization of the Fermi hole associated with the central sulfur yielded 4 (AM1) or 9 (STO-3G, 3-21G) (essentially) nonzero eigenvalues, 10 essentially nonzero eigenvalues were obtained now. Six of them are again close to 2 and they correspond to 5 core and 1 free σ electron pair on S. In this respect, the results are very similar to what was observed previously. What has changed considerably, however, is the number and the character of the remaining eigenvectors describing the valence shell of sulfur. Thus while in semiempirical, STO-3G and 3-21G calculations where there were 3 such eigenvalues, 4 eigenvalues (2×0.585, 2×0.401) were obtained in the 6-31G** basis. The inspection of the form of the corresponding eigenvectors demonstrates that the pair of eigenvalues 0.585 is associated with two broken valences of two equatorial SF bonds, while the remaining pair corresponds to two broken axial SF bonds. Both these eigenvalues display approximate complementarity with the analogous eigenvalues of the Fermi holes associated with the corresponding fluorine atoms ($0.585 + 1.495 \cong 2$ for equatorial SF bond vs. $0.401 + 1.643 \cong 2$ for axial bonds) and similarly as in the previous case, the deviations of the eigenvalues from unity can be interpreted as an indication of the polar nature of the S-F bonds. We can thus see that the final picture of bonding is, in this, case straightforwardly compatible with the existence of four polar S-F bonds and one σ free electron pair around sulfur. This, of course is consistent with the expansion of the valence shell of the central S atom. This result, is very interesting since a similar expansion of the valence shell was so far detected only in spin-coupled calculations by Cooper et al. [23] and we have in fact believed [29] that it was caused by the inclusion of electron correlation in the SC-VB method.

Thus our opinion was supported by the fact that within the spin-coupled theory, the expansion of the valence shell was observed (not only in SF_4), even for a basis set in which *d* orbitals are missing, although in this case nothing similar was observed using our SCF Fermi hole analysis. The above results indicate, however, that the situation is slightly more complex since for sufficiently flexible basis sets involving *d* orbitals, the valence shell expansion can be observed even at he SCF level of the theory. This result is not, of course, too surprising as such since the importance of *d* orbitals for the description of bonding in second row elements is well known and was widely accepted [6–11, 14, 25, 47]. Especially important in this respect is the study by Halgren et al. [47] in which the possibility of *d* orbital-induced valence shell expansion for second row atoms was anticipated. The most interesting point in this respect is the discussion about the mutual interplay between partial involvement of *d* orbitals and the fractional (3c-4e) character of the bonds which is entirely consistent with our results. Thus, e.g., the inclusion of *d* orbitals (even if only marginal) is predicted to decrease the fractional character of axial bonds which in another words means the decrease of the 3c-4e nature of these bonds. This is what is indeed observed in our calculations. Thus, while for less flexible bases the axial SF bonds had the character of 3c-4e bonds, the expansion of the valence shell emerging from the analysis in the 6-31G** basis changes the nature of these bonds which can now be characterized as more or less "normal", albeit still rather polar SF bonds. The above reported change of the nature of bonding can straightforwardly be demonstrated by the values of 3-center bond indices (Table 3) which in the 6-31G** basis clearly display a considerable reduction of 3c-4e character of the bonds, especially in the axial FSF fragment, which according to Halgren [47] is compensated by their transformation into two polar 2c-2e SF bonds. In this respect, our results thus clearly confirm the conclusions of the study [23] that there is no qualitative difference in bonding between "normal" and hypervalent molecules and as it will be demonstrated in the following part, the same conclusion holds also for the bonding in the molecules of SF_6 and PF_5.

Before presenting the results for these molecules, we consider it worthwhile, however, to comment briefly on the existing contradictory opinions about the interpretation of hypervalent bonding especially from the point of view of the frequently discussed concept of valence shell expansion. In general, it is possible to say that the opinions can be divided into two groups which basically differ in the interpretation of the Lewis octet rule. Thus, for example, the group represented by the studies [7, 9, 10, 12] emphasizes the high polarity of the bonds which results in the shift of charge from the central atom so that the octet rule is not effectively violated. As a consequence, the concept of valence shell expansion is refused by this group. Such an interpretation was, however, questioned in the recent study by Gillespie [13] who argued that it in fact contradicts the original Lewis interpretation of the electron pair bond. Such an interpretation speaks of a bond as a shared electron pair only without further discriminating whether the sharing is full

or only partial. In this respect each of the bonds in hypervalent molecules correspond to one shared pair irrespective of the polarity of the bonds and, consequently, the existence of valence shell expansion has to be admitted in molecules like SF_4, SF_6, PF_5, etc. Such an interpretation is also straightforwardly supported by Bader's analysis which revealed, for example the existence of six or five X-F bond paths in SF_6 or PF_5, respectively [19, 20]. Similarly, the idea of the valence shell expansion is supported by the results of spin-coupled calculations [21–24] in which the so-called "democracy principle" was formulated. The detailed mechanism by which this principle operates is that electrons originally residing in free electron pairs on central atoms decouple (under suitable conditions) and the resulting two isolated electrons can be engaged in bonding with the ligands. In this way it is thus possible to explain, for example, the formation of SF_4 from SF_2, SF_6 from SF_4, etc. By repeating this process until the free electron pairs in the valence shell of the isolated atom are exhausted, the existence of six bonds can be admitted, for example, for S which is in fact nothing but an alternative formulation of the duodecet rule proposed by Gillespie [13].

SF_6

As a next example let us report the analysis of the Fermi holes for the SF_6 molecule. According to Musher [1], this molecule is a representative of hypervalent molecules of the second kind (HV_{II}). These molecules are characterized as being formed from existing molecules by the addition of two monovalent (or one divalent) ligands but, in contrast to HV_I type of molecules, the addition of ligands is accompanied by the deep reorganization of geometrical and electron structures so that the resulting geometry is governed by steric factors. As a consequence, the HV_{II} type molecules usually display the highest possible symmetry. Consistent with this expectation, the SF_6 molecule exists in the form of regular octahedron with six equivalent SF bonds. As in the previous case of sulfur tetrafluoride, let us start the analysis by reviewing the results of the previous semiempirical study [29] and let us begin again with the Fermi hole associated with the central S atom. The diagonalization of this hole yielded 4 nonzero eigenvalues which are found in two degenerated pairs (2×0.773, 2×0.677). The eigenvectors associated with the first pair correspond to broken valences of two S-F bonds. The remaining two eigenvectors resemble two equatorially oriented $3p$ orbitals, of which each participates in two S-F bonds. Such a picture of bonding is thus very reminiscent to what was found in SF_4, except that there are now two p orbitals participating in four S-F bonds. But in contrast to SF_4 (HIV_I) molecule, where such participation implied the formation of 3c-4e bonds in the axial FSF fragment, the electron reorganization in SF_6 is much deeper and consistent with the general rule for HV_{II} systems: the molecule adopts the highest possible symmetry. As a consequence, there is no difference between the individual S-F bonds. They are strictly equivalent and display only weak 3c-4e character (Table 4).

A qualitatively very similar picture of bonding resulted also from the analysis of *ab initio* generated Fermi holes in STO-3G and 3–21G bases. The main difference consists only in the presence of 5 additional eigenvalues close to 2, that correspond to filled core K and L shells on S (Table 5). Another slight difference compared to semiempirical results concerns the degree of degeneracy in the remaining nonzero eigenvalues. Thus, while in the semiempirical study two pairs of degenerate eigenvalues were observed, the situation with the *ab initio* analysis is slightly different since four remaining nonzero eigenvalues are composed of a group of triply degenerate values (1.063 in STO-3G basis vs. 0.707 in 3–21G) and single isolated values (1.526 in STO-3G vs. 1.202 in 3–21G). The detailed inspection of the form of the corresponding eigenvectors shows that the isolated eigenvalue is associated with the more or less pure $3s$ orbital on S, while remaining three correspond to $3p_x$, $3p_y$, and $3p_z$ orbitals. This result is very interesting since it demonstrates even more clearly than in the semiempirical study [29] how deep the electron reorganization anticipated by Musher's rule [1] must be, to allow the accommodation of the valence state of the central sulfur to the observed high symmetry.

This picture of bonding changes, again, for the most flexible 6-31G** basis set and, consistent with the duo-

Table 4. Calculated values of 3-center bond indices for selected molecular fragments of SF_6 molecule from ab-initio SCF nonlinear population analysis in several basis sets

Basis	Fragment	3-center bond index
STO-3G	F_1SF_3	−0.058
	F_1SF_4	−0.040
3-21G	F_1SF_3	−0.025
	F_1SF_4	−0.035
6-31G**	F_1SF_3	−0.023
	F_1SF_4	−0.023

Table 5. Nonzero eigenvalues of *ab initio* SCF domain-averaged Fermi holes associated with the atomic region of central atom and ligands for SF_6 molecule in several basis sets

Basis set	Region	Degeneracy	Eigenvalue
STO-3G	S	5	~2.0
		3	1.063
		1	1.526
	F	4	~2.0
		1	1.267
3-21G	S	5	~2.0
		3	0.707
		1	1.202
		3	0.129
	F	4	~2.0
		1	1.516
6-31G**	S	5	~2.0
		6	0.582
		6	0.090
	F	4	~2.0
		1	1.489

decet rule [13], the expansion of the valence shell of the central sulfur atom was observed. As a consequence of this expansion the diagonalization of the associated Fermi hole yielded, in addition to 5 eigenvalues close to 2 (corresponding to 5 core electron pairs on S), the degenerate sextet of eigenvalues equal to 0.582 (Table 5). An examination of the associated eigenvectors shows that they correspond to broken valences of 6 equivalent SF bonds. Moreover, the substantial deviation of these eigenvalues from unity suggests the polarity of individual SF bonds. This interpretation is again supported by the inspection of the eigenvalues and eigenvectors of the Fermi holes associated with individual fluorine atoms. Such an inspection shows that, in addition to 4 nonzero eigenvalues close to 2 (corresponding to core and free electron pairs on F), there is just one essentially nonzero eigenvalue (1.489) corresponding to a broken SF bond. Taking now into account the near complementarity of eigenvalues corresponding to the sulfur and fluorine components of the broken SF bond ($1.489 + 0.582 \cong 2.0$), the final picture of bonding in SF_6 is clearly consistent with the existence of 6 polar electron pair S-F bonds around the central sulfur. This result is again very strongly reminiscent of the picture of bonding suggested by previous calculations by Cooper et al [20–23], and consistent with the duodecet rule [13], as well as with the existence of six S-F bond paths; it clearly suggests the expansion of the valence shell on sulfur. Despite the close similarity to results by Cooper [23], one still has to keep in mind the fact that while in the case of study [23] the expansion was obtained using post-HF spin-coupled calculations, the same picture of bonding was obtained in our case at the SCF level but only if *d* orbitals were included into the basis set.

The importance of *d* orbitals is also strongly supported by the results of the study by Reed and Weinhold [10], who explicitly addressed the problem of the role of *d* orbitals in SF_6 using the formalism of NPA, NHO and NLO analysis [48–50]. Consistent with our findings they also report the existence of six polar NLMO corresponding to six polar S-F bonds. The polarity of these bonds can be estimated, for example, from the population of the fluorine σ NHO component participating in the S-F bond. The reported population of 1.553 [10] is quite comparable with the value of 1.489 resulting from our analysis. We can thus conclude that there is a close parallel between the results of various independent analyses and each of them is consistent with the existence of six more or less "normal", albeit very polar 2c-2e S-F bonds. It is true, however, that Reed and Weinhold [10] rather emphasize the polarity of S-F bonds and consequently they do not speak of expansion of the valence shell.

PF_5

Another example of HV_{II} type systems is the molecule of phosphorus pentafluoride, PF_5. Consistent with the expectation of Musher's rule [1], the molecule exists in the form of a trigonal bipyramid with axial PF bonds only very slightly longer than the equatorial ones. The analysis of the bonding situation in this molecule is very similar to what was found before for SF_6. Accordingly diagonalization of the Fermi hole associated with the central P atom in STO-3G and 3-21G basis yields again 9 essentially nonzero eigenvalues (Table 6) of which 5, with values close to 2, correspond to 5 core electron pairs of phosphorus and the remaining 4 (again with the degeneracy 3 + 1) correspond to nearly pure $3s$ and $3p_x$, $3p_y$ and $3p_z$ orbitals of the valence shell. We can thus see that the picture of the valence state of the central atom is again very reminiscent to what was found in small basis sets for SF_6.

The above picture of bonding changes, however, for the most flexible 6-31G** basis and becomes quite similar to what was reported in both previous cases: expansion of the valence shell of the central atom is observed. This can be again clearly demonstrated by inspecting the eigenvalues of the Fermi hole associated with the central P atom which yields 10 (essentially) nonzero eigenvalues. Five of them, with values close to 2, correspond again to the filled core K and L shells on P. The remaining five eigenvalues (3×0.517, 2×0.492) are then associated with eigenvectors corresponding to five broken valences of P-F bonds. This result, confirming the presence of five polar P-F bonds, thus straightforwardly supports the previous conclusions of Bader's analysis which indeed reveals the existence of five P-F bond paths [20]. Moreover, the presence of five polar P-F bonds is also in complete keeping with the results of the spin-coupled calculations by Cooper et al [23].

In addition to qualitatively confirming the expansion of the phosphorus valence shell, there are also some subtler aspects of a quantitative nature that can be de-

Table 6. Nonzero eigenvalues of *ab initio* SCF domain averaged Fermi holes associated with the atomic region of central atom and ligands for PF_5 molecule in several basis sets

Basis	Region	Degeneracy	Eigenvalue
STO-3G	P	5	~2.0
		3	0.880
		1	1.316
	F_{eq}	4	~2.0
		1	1.296
	F_{ax}	4	~2.0
		1	1.361
3-21G	P	5	~2.0
		3	0.631
		1	0.529
	F_{eq}	4	~2.0
		1	1.590
	F_{ax}	4	~2.0
		1	1.619
6-31G**	P	5	~2.0
		3	0.517
		2	0.492
		3	0.076
		2	0.180
	F_{eq}	4	~2.0
		1	1.539
	F_{ax}	4	~2.0
		1	1.567

duced from our analysis. Thus, for example, according to the actual eigenvalues corresponding to the Fermi hole associated with the central phosphorus atom, individual PF bonds should not be strictly equivalent and a distinction between axial and equatorial PF bonds is indeed visible. However, because the actual differences are very small, the distinction between axial and equatorial PF bonds is not very important and, in fact, near equivalence of all five PF bonds can be expected. Quite in keeping with this expectation are the values of the actual PF bond lengths which clearly reflect near equivalence of axial and equatorial PF bonds. Another general feature which nicely fits with the near equivalency of P-F bonds lengths concerns the negligible 3-center character of any F-P-F fragment (Table 7). This feature, which generally is typical for any HV_{II} type molecules, is pronounced the most strongly just in the 6-31G** basis for which the valence shell expansion was reported.

NF_5

Another example, closely related to previous one, concerns the elusive molecule of NF_5. Although considerable effort has been devoted to its preparation [51–56], all these attempts so far have failed, thus confirming the generally accepted opinion that the N atom is too small to accommodate five fluorine ligands in the first coordination shell [51]. In contrast to fruitless experimental attempts, the theoretical calculations seem to be much less restrictive and the existence of NF_5 as a metastable minimum on the corresponding potential energy hypersurface was recently reported by several groups [57–59]. The possibility of the eventual preparation of this molecule thus cannot be definitely excluded. Stimulated by these computational results we have decided to apply the above reported formalism to the analysis of possible hypervalence in this molecule. Consistent with this intention we have performed *ab initio* SCF calculations in several basis sets (STO-3G, 3-21G and 6-31G**) and in all cases the calculated optimized structures (trigonal bipyramid) corresponded to true metastable minima on the PE hypersurface. Based on the SCF wave functions the pair densities were generated and the corresponding Fermi holes were analyzed at each particular level. The analysis clearly revealed interesting differences in the nature of the valence state of nitrogen atom compared to the closely related PF_5 molecule. The results of the calculations are summarized in Table 8 from which it is evident that these differences are relatively small for the minimal STO-3G and split 3-21G basis and the main factor in which the picture of bonding differs in this case is lower polarity of NF compared to PF bonds. The situation is, however, more interesting for 6-31G** basis, where in contrast to the existence of five polar P-F bonds in PF_5, no valence shell expansion is visible here and the picture of bonding is very reminiscent of what was found for smaller basis sets. We can thus see that although the same flexible basis set involving *d* orbitals was used for both PF_5 and NF_5, the Fermi hole analysis revealed the valence shell expansion only for phosphorus.

Another interesting feature which can be deduced from our results and in which the bonding in NF_5 differs from that in PF_5 concerns the conservation of the differences between axial and equatorial NF bonds. Thus, while equatorial NF bonds can be regarded as more or less normal covalent bonds of relatively small polarity, the axial NF bonds still retain the character of 3-center 4-electron bonds (Table 9). This difference in the character of the bonding is also reflected at NF bond lengths where consistent with what was observed for SF_4, "hypervalent" axial NF bonds are considerably longer than the "normal" axial ones. It is interesting that the same

Table 7. Calculated values of 3-center bond indices for selected molecular fragments of PF_5 molecule from *ab initio* SCF non-linear population analysis in several basis sets

Basis	Fragment	3-center bond index
STO-3G	$F_{ax}PF_{ax}$	−0.026
	$F_{eq}PF_{eq}$	−0.032
	$F_{ax}PF_{eq}$	−0.065
3-21G	$F_{ax}PF_{ax}$	−0.014
	$F_{eq}PF_{eq}$	−0.021
	$F_{ax}PF_{eq}$	−0.040
6-31G**	$F_{ax}PF_{ax}$	~0.0
	$F_{eq}PF_{eq}$	~0.0
	$F_{ax}PF_{eq}$	−0.027

Table 8. Nonzero eigenvalues of *ab initio* SCF domain-averaged Fermi holes associated with the atomic region of central atom and ligands for NF_5 molecule in several basis sets

Basis	Region	Degeneracy	Eigenvalue
STO-3G	N	1	~2.0
		1	1.576
		1	1.115
		2	1.042
	F_{ax}	4	~2.0
		1	1.183
	F_{eq}	4	~2.0
		1	1.060
3-21G	N	1	~2.0
		1	1.570
		1	1.032
		2	0.894
		2	0.032
	F_{ax}	4	~2.0
		1	1.306
	F_{eq}	4	~2.0
		1	1.179
6-31G**	N	1	~2.0
		1	0.830
		3	0.910
		1	0.123
		3	0.067
		3	0.019
	F_{ax}	4	~2.0
		1	1.475
	F_{eq}	4	~2.0
		1	1.263

Table 9. Calculated values of 3-center bond indices for selected molecular fragments of NF_5 molecule from *ab initio* SCF nonlinear population analysis in several basis sets

Basis	Fragment	3-center bond index
STO-3G	$F_{ax}NF_{ax}$	−0.059
	$F_{eq}NF_{eq}$	−0.022
	$F_{ax}NF_{eq}$	−0.043
3-21G	$F_{ax}NF_{ax}$	−0.060
	$F_{eq}NF_{eq}$	−0.026
	$F_{ax}NF_{eq}$	−0.049
6-31G**	$F_{ax}NF_{ax}$	−0.038
	$F_{eq}NF_{eq}$	−0.014
	$F_{ax}NF_{eq}$	−0.033

conclusions about the different nature of axial and equatorial NF bonds was reported also in the recent study [59].

ClF_3

Another example of a molecule resisting the expansion of the valence shell is the molecule of ClF_3, which, according to Musher's classification [1] belongs to the HV_I type systems. Consistent with the general rule for these systems, the molecule adopts a T-shaped geometry. Since the semiempirical AM1 method completely fails to reproduce the experimental geometry it was not possible to perform the analysis of the Fermi hole at the semiempirical level and there are thus no reference data for comparisons like those of the previous cases. This, however, is not very important since the *ab initio* results are very transparent and, as it is can be seen from Table 10, also their interpretation is very easy. The most important result which is immediately visible from this Table is the close qualitative parallel in the nature of the valence shell of the central chlorine atom for all basis sets. Thus, for example, the diagonalization of the Fermi hole associated with the central chlorine yielded in all cases 9 nonzero (or essentially nonzero) eigenvalues. Seven of these nine eigenvalues are very close to 2. Five of these seven eigenvalues correspond to the core electron pairs of filled K and L shells and the remaining two are free electron pairs in the valence shell of chlorine. In addition to these seven core and free electron pairs there are thus only two additional nonzero eigenvalues[1]. The detailed inspection of the associated eigenvectors shows that one of them corresponds to the broken valence of the ClF_1 bond and the remaining one is again reminiscent of a pure $3p$ orbital oriented along the $F_3Cl_2F_4$ fragment. We can thus see that, similar to what was observed for NF_5, the valence state of the central atom does not display any features of valence shell expansion, but the bonding situation is again characteristic of the presence of the axial 3c-4e FClF bond. Consistent with this expectation are also the values of the 3-center bond indices (Table 11) which indeed confirm the existence of this type of bond predominantly in $F_3Cl_2F_4$ fragment.

The reported inability of the chlorine atom to expand its valence shell even after including *d* orbitals into the basis set is very interesting since in the spin-coupled calculations by Cooper et al. [24] valence shell expansion was observed. This again implies that, while in some cases even the small admixture of *d* orbitals is able to induce the expansion of the valence shell already at SCF level, for some other molecules the decoupling of electron pairs required by the democracy principle [23] or duodecet rule [13] critically depends on the inclusion of electron correlation. In this respect it is interesting to mention the study by Magnusson [11], who also emphasized that inclusion of electron correlation may act as an important auxiliary factor to enhance the role of *d*

Table 10. Nonzero eigenvalues of *ab initio* SCF domain-averaged Fermi holes associated with the atomic region of central atom and ligands for ClF_3 molecule in several basis sets

Basis	Region	Degeneracy	Eigenvalue
STO-3G	Cl	7	~2.0
		1	1.382
		1	1.197
	F_1	4	~2.0
		1	1.093
	F_3	4	~2.0
		1	1.204
3-21G	Cl	7	~2.0
		1	0.934
		1	0.884
		1	0.032
		1	0.010
	F_1	4	~2.0
		1	1.274
	F_3	4	~2.0
		1	1.519
6-31G**	Cl	7	~2.0
		1	0.741
		1	0.683
		1	0.112
		2	0.029
		2	0.018
		3	0.067
	F_1	4	~2.0
		1	1.357
	F_3	4	~2.0
		1	1.613

Table 11. Calculated values of 3-center bond indices for selected molecular fragments of ClF_3 molecule from *ab initio* SCF nonlinear population analysis in several basis sets

Basis	Fragment	3-center bond index
STO-3G	F_3ClF_4	−0.098
	F1ClF3	−0.100
3-21G	F_3ClF_4	−0.116
	F_1ClF_3	−0.060
6-31G**	F_3ClF_4	−0.056
	F_1ClF_3	−0.030

[1]This is again strictly true for minimal STO-3G basis; for more flexible basis sets there are also some other nonzero eigenvalues but as they are very small, they can be neglected.

Table 12. Calculated values of atomic valencies of the central atom in the studied molecules

Molecule	Atom	*d* orbital population (6-31G**)	STO-3G	3-21G	6-31G**
SF_4	S	0.396	2.896	2.766	3.260
PF_5	P	0.140	3.845	3.682	4.679
SF_6	S	0.777	3.711	4.000	5.423
NF_5	N	0.124	3.722	3.665	4.189
ClF_3	Cl	0.209	1.838	1.953	2.093

orbitals in facilitating the hypervalent bonding. The fact itself that the actual participation of *d* orbitals can be often quite low is not very important. This problem was specifically addressed in the study by Halgren et al. [47] who critically analyzed the usual argument against the massive participation *d* orbitals in hypervalent bonding which relies on the fact that the population of these orbitals is often much smaller than required by usual hybridization schemes like d^2sp^3, dsp^3, etc. It was shown that even the marginal *d* orbital participation can have important consequences for the character of axial, ''hypervalent'' bonds, especially in reducing their fractional (3c-4e) character and this reduction could indeed be demonstrated on the decrease of the values of 3-center bond indices.

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