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Multicenter bonding and the structure of electron-rich molecules. Model of three-center four-electron bonding reconsidered

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Abstract. The concept of three-center four-electron (3c-4e) bonding, which has often been invoked in attempts to interpret the electronic structure of electron-rich molecules, is scrutinized using various methodologies, including generalized population analysis and the analysis of the so-called domain-averaged Fermi holes. Results for representative examples show clearly how manifestations of the 3c-4e model can depend critically on the quality of the wave function being analyzed. In general, the "existence" of 3c-4e bonding tends to be most compatible with the analysis of wave functions of lower quality; enhancements to the flexibility of the basis and/or the inclusion of electron correlation can lead to dramatic changes, such that the 3c-4e scheme transforms into a pattern of two more or less normal, albeit often very polar, two-center two-electron bonds.

Keywords: Electron-rich molecules – Three-center four-electron bonding – Fermi hole analysis – Generalized populations – Spin-coupled

1. Introduction

The classical Lewis model [1] has of course played a pivotal role in the development of modern chemistry. Vast swathes of chemistry continue to be interpreted qualitatively in terms of (linear combinations of) Lewis structures, with chemical bonds envisaged in terms of electrons pairs shared between two centers. There are, however, many examples for which it proves appropriate to augment this basic motif of two-center two-electron (2c-2e) bonding with patterns that involve more centers and/or more electrons. Perhaps the most usual situation in which one encounters such additional units is with electron-deficient compounds, such as the broad family of boranes, for which it is usual to invoke the idea of the three-center two-electron (3c-2e) bond [2, 3, 4]. On the other hand, electron-rich orbital-deficient molecules, such as the polyhalide anions X_3^-, have been interpreted in terms of three-center four-electron (3c-4e) bonding [5, 6, 7]. Further possible examples of 3c-4e bonds are provided by hydrogen bihalide anions XHX^-, neutral 1,3-dipolar molecules such as diazomethane and N_2O, and the axial units of hypervalent systems such as PF_5 and SF_4 [8, 9, 10, 11, 12].

Recent years have seen significant interest not only in the critical evaluation of earlier empirical models of multicenter bonds, but also in the design of new computational tools for detecting and quantifying multicenter bonding [13, 14, 15, 16, 17, 18, 19, 20]. Two such methodologies will be employed here. The first of these was originally based on the studies of Sannigrahi, Kar and Nandi [21, 22, 23] and of Giambiagi and coworkers [24, 25], in which the so-called multicenter bond indices were proposed. In addition to allowing the straightforward detection of the presence of multicenter bonding in the molecule, the sign of the index also reveals the number of electrons that are involved [26, 27]. Thus, for example, while 3c-2e bonds are characterized by positive values of the three-center bond indices, negative values are meant to be diagnostic of 3c-4e bonding. The second approach that we are going to use for studying multicenter bonding involves analysis of the so-called domain-averaged Fermi holes [20, 28, 29, 30]. This methodology provides information about the actual valence state of the atom in a molecule and it has already proved useful in studies of hypervalence [30, 31].

Following on from recent work in which we examined the phenomenon of 3c-2e bonding [19], the present study focuses on the somewhat more complex issue of 3c-4e bonding. In contrast to 3c-2e bonding, which is almost universally accepted as a "real" bonding mechanism, the situation with 3c-4e bonding is much less clear. Indeed, the apparent presence or absence of 3c-4e bonding can depend dramatically on the quality of the wave function being analyzed: we will show by means of various examples that the "existence" of 3c-4e bonding tends only to be compatible with the analysis of wave

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functions of lower quality. Improving the level of theory, by increasing the flexibility of the basis set and/or by taking account of electron correlation, generally results in a transformation of the 3c-4e bonding into two more or less ordinary, albeit often very polar, 2c-2e bonds. Both of these features will be demonstrated by means of various calculations for the trifluoride F_3^- and hydrogen difluoride FHF^- anions, as representatives of systems for which the first model of 3c-4e bonding was proposed, as well as by examining the typical hypervalent systems SF_4 and PF_5, and the 1,3-dipolar molecule CH_2N_2. In each case, we examine the importance of the flexibility of the basis set to the multicenter bond indices and Fermi hole analysis at the restricted Hartree–Fock (RHF) level, and we examine the effects on multicenter bond indices of including (mostly nondynamical) electron correlation using the spin-coupled (SC) approach.

2 Theoretical background

We present here only relatively brief overviews of the two methodologies that we used for analyzing 3c-4e bonding, because both of them are already well described in the literature [19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32].

2.1 Multicenter bond indices

The formalism of multicenter bond indices was introduced by several independent groups [16, 17, 21, 22, 23, 24, 25], initially on heuristic grounds, and it is only more recently that various alternative formulations were demonstrated to be equivalent [26, 32]. The contemporary theory of these bond indices can be formulated within the framework of the so-called generalized population analysis [19, 33], which is a generic name for the whole family of approaches based on the partitioning of density matrices, and related quantities, into mono-, bi-, tri- and generally k-atomic contributions, which can then be attributed some chemical or physical meaning. The simplest situation is at the level of the RHF approximation, where the partitioned quantity is the identity (Eq. 1), in which P and S are the (normalized) first-order density and overlap matrices, respectively.

$$\frac{1}{2^{k-1}} Tr(PS)^k = N = \sum_A \Delta_A^{(k)} + \sum_{A<B} \Delta_{AB}^{(k)} + \sum_{A<B<C} \Delta_{ABC}^{(k)} + \dots \sum_{A<B<\dots K} \Delta_{ABC\dots K}^{(k)} \quad (1)$$

Thus, for example, the partitioning of the identity (Eq. 1) for $k = 1$ yields monoatomic terms which correspond to gross Mulliken charges on the individual atoms [34]. Similarly, the biatomic terms resulting from the analogous partitioning for $k = 2$ coincide with the so-called Wiberg or Wiberg–Mayer indices [35, 36, 37], whose values, for pairs of classically bonded atoms, are known to match classical bond multiplicities. On the other hand, the corresponding values for pairs of atoms which are not considered to be bonded are usually found to be practically negligible.

The ability to mimic the presence and/or absence of bonding interactions is also observed for terms resulting from the partitioning of the identity (Eq. 1) for higher k. Three-center bond indices are defined simply as the triatomic terms resulting from the partitioning of the identity (Eq. 1) for $k = 3$. The detection of three-center bonding then arises from the empirical observation that values of the three-center bond indices are practically negligible for triads of atoms between which there are no bonding interactions; the only nonnegligible terms correspond to those atomic triads between which three-center bonding might be expected. As an example in this respect we mention the case of diborane, for which the only nonvanishing three-center terms correspond to the two BHB triads, involving the boron atoms and bridging hydrogens, for which the existence of 3c-2e bonding can be anticipated on the basis of the *styx* rules [5, 6, 38].

Probably the simplest way to compute these various bond indices is to partition the relevant overlap integrals according to the centers with which particular basis functions are associated. For rather obvious reasons, we refer to this strategy as a "Mulliken-like" scheme. Instead, we may also incorporate generalized population analysis into the framework of virial partitioning of the electron density, as in the atoms in molecules (AIM) theory introduced by Bader [39]. Such an extension was reported recently by various independent groups [40, 41, 42, 43, 44]. We use the label "AIM generalized" for bond indices generated by such a strategy, and most of the calculations reported here will be of this type.

Much of the experience with practical applications of these various bond indices has been gained from studies at the RHF level, but the generalization beyond the scope of this approximation has also been reported [19,33]. In essence, the original identity (Eq. 1) can be rewritten in the form

$$\int \Delta^{(k)}(r_1, r_2 \dots r_k) dr_1 dr_2 \dots dr_k = N = \sum_A \Delta_A^{(k)} + \sum_{A<B} \Delta_{AB}^{(k)} + \sum_{A<B<C} \Delta_{ABC}^{(k)} + \dots \sum_{A<B<\dots<K} \Delta_{ABC\dots K}^{(k)} , \quad (2)$$

where the expressions for the various $\Delta^{(k)}(r_1, r_2, \dots, r_k)$ [19, 33], which involve higher-order density matrices, are closely related to the expressions that arise for k-particle cumulants λ_k of reduced density matrices [45]. It is the generalization embodied in Eq. (2) that allows us to study here the effects of (mostly nondynamical) electron correlation on the nature of 3c-4e bonding.

2.2 Domain averaged Fermi holes

The analysis of domain-averaged Fermi holes was proposed some time ago [28, 29] as another universal tool for the interpretation and the visualization of molecular structure using terms that are close to classical chemical thinking. The holes are defined by Eq. (3), where $\rho(r_1)$ and $\rho(r_1,r_1)$ are the (diagonal) first- and second-order densities, respectively, and the integration (or averaging) is performed over the finite domain of real space Ω:

$$g_{\Omega}(r_1) = \rho(r_1) \int\limits_{\Omega} \rho(r_2) dr_2 - 2 \int\limits_{\Omega} \rho(r_1, r_2) dr_2 \ . \qquad (3)$$

The form of the hole, $g_{\Omega}(r_1)$, depends, of course, on the somewhat arbitrary choice of the domain Ω, but we have shown that especially useful and chemically relevant information can be obtained by choosing the atomic domains that result from virial partitioning of the electron density $\rho(r_1)$. The hole associated in a given molecule with the atomic domain of a particular atom then provides information about the valence state of that atom in the molecule. In the case of the closed-shell RHF approximation, to which we confine ourselves here, Eq. (3) reduces to Eq. (4), where i and j label doubly occupied molecular orbitals:

$$g_{\Omega}(r_1) = 2 \sum_{i}^{OCC} \sum_{j}^{OCC} \langle \varphi_i | \varphi_j \rangle_{\Omega} \varphi_j(r_1) \varphi_i(r_1) \ . \qquad (4)$$

It is thus straightforward to generate the matrix $\mathbf{G}^{\Omega}$, which represents the hole in the basis of atomic orbitals. The orthonormal eigenvectors of this matrix transform as irreducible representations of the molecular point group, but they may be localized by means of a so-called isopycnic transformation [46] which leaves $g_{\Omega}(r_1)$ unchanged. The resulting nonorthogonal one-electron functions, and their corresponding occupation numbers, provide insight into the electronic structure. Examples of their utility for visualizing bonding can be found in numerous previous studies [20, 30, 31, 47, 48].

The whole formalism was formulated from the very beginning quite generally, with the integration (or averaging) being over real atomic domains, i.e., with an AIM generalized strategy; however, the practical calculations in earlier studies were mostly performed using instead a simple Mulliken-like scheme, in which integrals over real domains were replaced by a Mulliken-like approximation, according to which the electron was assumed to be in the domain of a particular atom when it was described by a basis function centered on that atom. Most of the calculations reported here used the AIM generalized approach, but Mulliken-like quantities were also generated for the purposes of comparison.

3 Computational details

Several types of calculations were performed in this study. In the first step it was necessary to generate the corresponding wave functions and electron densities, which in the second step were subjected to generalized population and/or Fermi hole analysis.

For each of the molecular systems examined here, most of our analysis was performed for RHF wave functions generated using the Gaussian 98 series of programs [49]. In all cases the wave functions were generated for fixed geometries derived from experiment. The resulting Gaussian 98 outputs were, in the second step, interfaced with our own programs (which can be obtained upon request) to performe the subsequent analyses in both the AIM generalized and Mulliken-like forms.

The subsequent effects of taking some account of (mostly nondynamical) electron correlation were investigated using the SC approach [50, 51], which also provides directly a simple pictorial representation of the bonding, which we may compare directly with the corresponding generalized population analysis. The required SC wave functions were obtained in the following manner. First of all, we generated RHF wave functions using the GAMESS-UK package [52] using the TZVP basis that is stored internally in that program. We then localized the valence molecular orbitals using our implementation of the Pipek–Mezey population-localization strategy [53]. In each case, it proved straightforward to identify localized molecular orbitals (LMOs) which describe the bonding. For the purposes of subsequent comparisons, the Mulliken-like three-center index was calculated at the RHF level, but restricting the summations just to those so-called "active" LMOs which describe the bonding.

In essence, the SC wave functions that were used here correspond to replacing the ½N doubly occupied orthogonal active LMOs by a set of N singly occupied nonorthogonal orbitals, which are fully optimized in the underlying atom-centered basis set, without any constraints on their form or on the overlaps between them. Additionally, the spins of these N active electrons are allowed to couple together in all modes that lead to an overall singlet state. In order to facilitate a direct comparison with the corresponding RHF results, we chose not to reoptimize those occupied molecular orbitals and LMOs that were not designated as active and, as in the RHF studies, the geometry was also kept fixed.

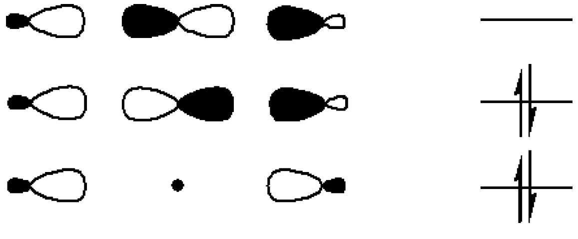
Although no such constraints were imposed during any of the calculations, we found for each of the molecules considered here that the active SC orbitals consist of pairs, each clearly associated with a particular two-center bond, and with predominantly singlet coupling of the electron spins. All of these SC calculations were performed with a version of our code [54] that uses density matrices up to fourth order during the optimization procedure, and so there are essentially no additional costs in extracting all of the required quantities for the computation of the (correlated) Mulliken-like three-center index. As a check on the reliability of the descriptions of the two anions, FFF^- and FHF^-, we also used the CASVB module [55] in the MOLPRO package [56] to perform slightly more sophisticated SC calculations, in which we used a basis set with diffuse functions (6-311++G**) and we relaxed the "inactive" orbitals.

4 Results and discussion

4.1 SF_4 and PF_5

The molecule SF_4, with its disphenoidal geometry, based on a trigonal bipyramid with two axial and two equatorial F atoms and (formally) an equatorial lone pair, was classified by Musher [8] as a hypervalent system of the first kind (HV_I). A characteristic feature of such systems is a significant difference between equatorial and axial SF bonds: while the shorter equatorial bonds are regarded in such a model as more or less normal, albeit very polar, 2c-2e bonds, the nature of the longer axial bonds, called hypervalent bonds by Musher, is somewhat more complex. The bonding pattern assigned to these latter bonds is due in large part to the resemblance of this fragment to the bonding arrangement anticipated by Pimentel [5] and Hach and Rundle [6] in a model considered as a paradigm for 3c-4e bonding. A typical feature of this model, schematically depicted in Scheme 1, is that the central atom contributes a single doubly occupied atomic orbital, of *p* type in our case, which interacts with bonding electrons of both of the axial F atoms so as to form a 3c-4e FSF axial unit. Such descriptions of the bonding in hypervalent molecules were subsequently questioned, and mostly discarded, by subsequent studies that examined more realistic wave functions. It is now accepted that the character of the axial SF bonds in SF_4 is not in fact so much different from that of the equatorial bonds [15, 30, 57, 58, 59, 60]. Rather than invoking notions of 3c-4e bonding, it seems more appropriate to consider a formal expansion of the valence shell at the central atom. The second hypervalent fluoride that we consider here is the trigonal bipyramidal molecule PF_5. According to Musher's classification [8], this molecule is a hypervalent system of the second kind (HV_{II}). A typical feature of such systems is a somewhat smaller difference between the nature of axial and equatorial bonds but, as for SF_4, more recent studies have again put much greater emphasis on the apparent expansion of the octet than on models involving 3c-4e bonding.

Previous analysis of the domain-averaged Fermi holes associated with the central S atom in SF_4 [30] revealed a dramatic change in the nature of the valence state with the basis set used for the construction of the RHF wave function. When using a minimal STO-3G basis set, the resulting picture of the bonding was remarkably reminiscent of the 3c-4e description anticipated from the Pimentel, Hach and Rundle model. On the other hand, the analysis of the Fermi holes when using a more flexible 6-31G* basis was consistent with four rather polar 2c-2e S–F bonds. A key consideration in this "switch" from one picture to another appears to be the availability of suitable d basis functions on the central atom. One of the aims of the present study is to gain deeper insight into this issue, using as our representative examples the molecules SF_4 and PF_5. In so doing, it is important to bear in mind the consensus view that has emerged from most of the reliable ab initio investigations of such systems published in the last 2 or 3 decades: the d basis functions act as polarization functions, albeit to a somewhat greater extent than for first-row atoms, but it is not justified to regard these d functions as valence orbitals. For example, Häser [61] demonstrated using a one-center expansion technique that although the description of the phosphorus valence region in PF_5 is indeed improved by functions of local d character, the corresponding d population is only weakly bound to the P atom, and so it should not be considered as chemically bonding.



Sch. 1.

As a first step to ascertaining the role of the flexibility of the basis set in inducing dramatic changes in the nature of the axial units in SF_4 and PF_5, we start with the AIM generalized Fermi hole analysis of SF_4, examining RHF wave functions calculated with either the minimal STO-3G basis or with the much more flexible TZVP basis set that is stored internally in the GAMESS-UK package [52]. The most striking differences are observed for the hole associated with the central S atom, which yields nine clearly nonzero eigenvalues for the STO-3G basis, as opposed to ten when using TZVP. The eigenvalues (ε) and the numbers of such values (n_ε) are listed in Table 1, and key eigenvectors are illustrated in Fig. 1. Looking first at the results with the minimal STO-3G basis, we find that the first five eigenvalues are all close to 2; these eigenvectors correspond to filled *K* and *L* shells. One of these eigenvectors is illustrated in frame A in Fig. 1a. Such electron pairs are of course mostly irrelevant to the bonding and need not be considered further. The same is true, to a large extent, of the eigenvector with $\varepsilon = 1.854$ (frame D of Fig. 1a) that is linked to the sulfur lone pair. Thus, the bonding is associated in this basis set with the three remaining nonzero eigenvalues. Two of these are degenerate, with $\varepsilon = 0.530$, and the corresponding eigenvectors are very reminiscent of localized orbitals for the equatorial S–F bonds, as shown in frame B of Fig. 1a. We interpret these as the "broken" or free valence of sulfur for equatorial S–F bonds, and an eigenvalue of 0.530 can be regarded as the contribution from the S atom to the shared electron pair of the 2c-2e equatorial S–F bond. As will be shown later, the "missing" electrons to complete each pair come from the relevant fluorine atom. As shown in frame E of Fig. 1a, the remaining eigenvector, with $\varepsilon = 0.600$, is very reminiscent of a S($3p_z$) orbital. Of course, the existence of such an orbital that participates in two axial bonds was anticipated from the Pimentel, Hach and Rundle model of 3c-4e bonding.

We now compare the corresponding description of the hole associated with the central S atom when using the more flexible TZVP basis. As is clear from Table 1 and Fig. 1b, the first six eigenvectors resemble closely those found with the smaller basis set. However, instead of three further nonzero eigenvalues, as before, there are now two degenerate pairs. The first pair of eigenvectors, with $\varepsilon = 0.294$, is again very reminiscent of localized orbitals for the equatorial S–F bonds (frame B of

Table 1. Atoms in molecules (*AIM*) generalized analysis of domain-averaged Fermi holes for SF_4, generated from restricted Hartree–Fock (*RHF*) wave functions with STO-3G and TZVP basis sets; the eigenvalues (ε) and the numbers of such values (n_ε) are listed, and relevant frames in Fig. 1 are identified

Basis	Hole	ε	n_ε	Frame	Interpretation
STO-3G	S	≈2	5	(a) A	Filled *K* and *L* shells
		1.854	1	(a) D	"Lone pair" on S
		0.530	2	(a) B	"Broken" valence of equatorial SF bonds
		0.600	1	(a) E	$3p_z$ orbital on S
	F_{eq}	2.000	1	–	$1s^2$ core electron pair
		≈2	3	–	"Lone pairs" on F
		1.515	1	(a) C	"Broken" valence of equatorial SF bond
	F_{ax}	2.000	1	–	$1s^2$ core electron pair
		≈2	3	–	"Lone pairs" on F
		1.542	1	(a) F	"Broken" valence of axial SF bond
TZVP	S	≈2	5	(b) A	Filled *K* and *L* shells
		1.806	1	(b) D	"Lone pair" on S
		0.294	2	(b) B	"Broken" valence of equatorial SF bonds
		0.237	2	(b) E	"Broken" valence of axial SF bonds
	F_{eq}	2.000	1	–	$1s^2$ core electron pair
		≈2	3	–	"Lone pairs" on F
		1.693	1	(b) C	"Broken" valence of equatorial SF bond
	F_{ax}	2.000	1	–	$1s^2$ core electron pair
		≈2	3	–	"Lone pairs" on F
		1.730	1	(b) F	"Broken" valence of axial SF bond

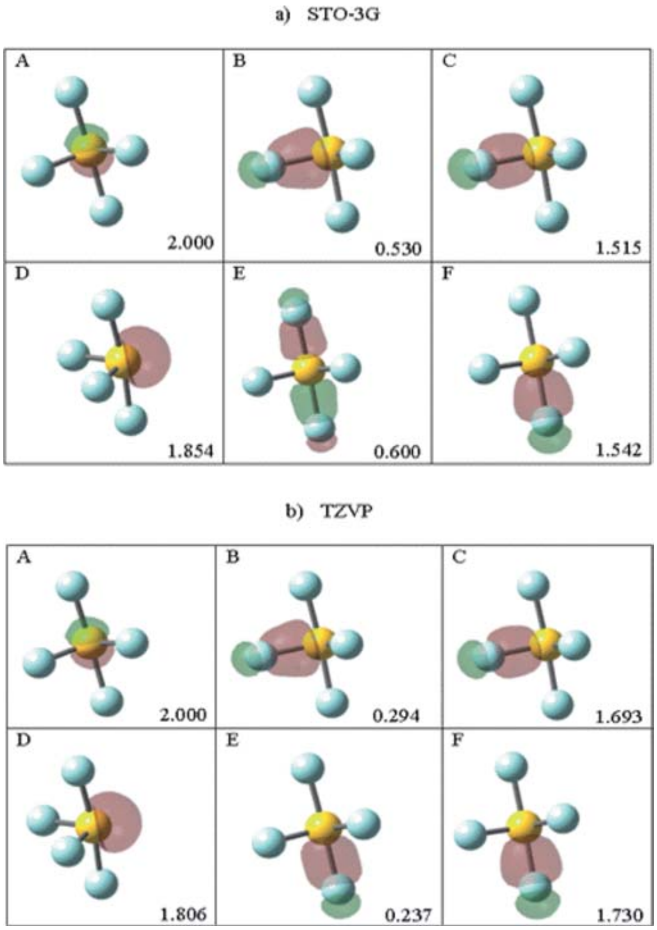


Fig. 1. Selected eigenvectors of the Fermi hole associated with the central S atom and with the axial and equatorial F atoms in SF_4, generated using the atoms in molecules (*AIM*) generalized approach with restricted restricted Hartree–Fock (*RHF*) wave functions for **a** STO-3G and **b** TZVP basis sets. Further details are provided in Table 1 and in the text

Fig. 1b) whereas the second pair, with $\varepsilon = 0.237$, resembles localized orbitals in the axial S–F bonds (frame E of Fig. 1b). We interpret these four eigenvectors in terms of the broken or free valence of sulfur for the equatorial and axial S–F bonds. Such an interpretation is straightforwardly supported by the complementary analysis of the Fermi holes associated with the equatorial and axial F atoms, as summarized in Table 1.

For both basis sets, analysis of the hole associated with one of the equatorial F atoms yields five nonzero eigenvalues, four of which are close to 2. Inspection of the corresponding eigenvectors (not shown in Fig. 1) shows that these latter values correspond to a $F(1s^2)$ core and to the three valence lone pairs. The equatorial bonding to the central atom is thus associated in both basis sets with the remaining eigenvector, with eigenvalues of 1.515 or 1.693. It is clear from the graphical representations (frames C in Fig. 1) that these resemble the functions we identified previously with the sulfur broken or free valence of equatorial S–F bonds, and that we may thus identify these eigenvectors with the corresponding fluorine broken or free valence. Such an interpretation is also supported for both basis sets by the near complementarity of the two contributions, specifically $0.530(S) + 1.515(F) \cong 2(SF)$ for STO-3G and $0.294(S) + 1.693(F) \cong 2(SF)$ for TZVP. This just leaves the holes associated with the axial F atoms to be considered. In the TZVP basis, we find the eigenvector depicted in frame F of Fig. 1b; it resembles clearly those we identified with the sulfur broken or free valence of axial S–F bonds and, indeed, we can see that $0.237(S) + 1.730(F) \cong 2(SF)$. In contrast, the situation with the minimal STO-3G basis is rather different: the Fermi hole analysis corresponds directly to 4c-3e bonding in the axial FSF fragment.

A qualitatively similar situation, characterized by the transformation of 3c-4e bonding into two semilocalized 2c-2e bonds, was also observed in the case of PF_5. As mentioned earlier, this molecule is a hypervalent system of the second kind (HV_{II}), according to Musher's classification [8], and so we expect smaller differences between the character of the axial and equatorial P–F bonds. Nonetheless, we find that the tendency of the axial FPF unit to exhibit the features of 3c-4e bonding for small basis sets is not completely suppressed and, indeed, the description revealed by analyzing the Fermi hole associated with the central P atom is quite similar to the one we have described in detail for SF_4. Thus, for example, we again see nine clearly nonzero eigenvalues with the minimal STO-3G basis set, as opposed to ten when using the more flexible TZVP basis. While in the case of STO-3G the form of the Fermi hole eigenvectors (Fig. 2a) is again reminiscent of the Pimentel, Hach and Rundle model of 3c-4e bonding, the picture of the bonding when using the TVZP basis (Fig. 2b) is clearly consistent with the existence of five very polar 2c-2e P–F bonds.

It is useful at this stage to examine also the values of the corresponding three-center bond indices, whose interpretation relies to some extent on comparing them with the values derived from a simple analytic model of three-center bonding [26]. The solution of that model for a bonding topology corresponding to the Pimentel, Hach and Rundle description of 3c-4e bonding (Scheme 1) yields an idealized value of the bond index equal to −0.375. It is clear from the results in Table 2 that the calculated values show some differences between the AIM generalized indices and those obtained with the more approximate Mulliken-like scheme, with all of them being somewhat smaller in magnitude than the idealized value. Nonetheless, it is also clear that there is a significant reduction in the magnitude of the three-center index for SF_4 when going from STO-3G to TZVP, much as we would now expect. The three-center index for PF_5 has a somewhat smaller magnitude.

Our analysis for both molecules demonstrates that improvement to the quality of the basis set, on replacing STO-3G with TZVP, leads to the transformation of a description based on 3c-4e F*X*F axial units into a rather differerent one that involves two more or less ordinary, albeit very polar, 2c-2e *X*–F bonds. In order to confirm our expectation, following also earlier work [30], that the key factor is the availability of d basis functions on the central atom, we also performed calculations for SF_4 in which we removed from the TZVP basis set the *d* functions on S and/or those on the F atoms. We found that the 3c-4e description emerges whenever there are no *d* functions on the central atom, regardless of whether or not there are any on the F atoms. Further insight is provided by model calculations for both molecules, in which we vary the exponent of the d basis function on the central atom.

Starting with the minimal STO-3G basis, we investigated the influence on the description of the bonding of adding a d basis function on the central atom, with an exponent which we varied systematically between 0.001 and 1. For each case, we used the AIM generalized approach to calculate the three-center index and to examine whether or not the Fermi hole analysis indicated 3c-4e bonding. Our various results are summarized

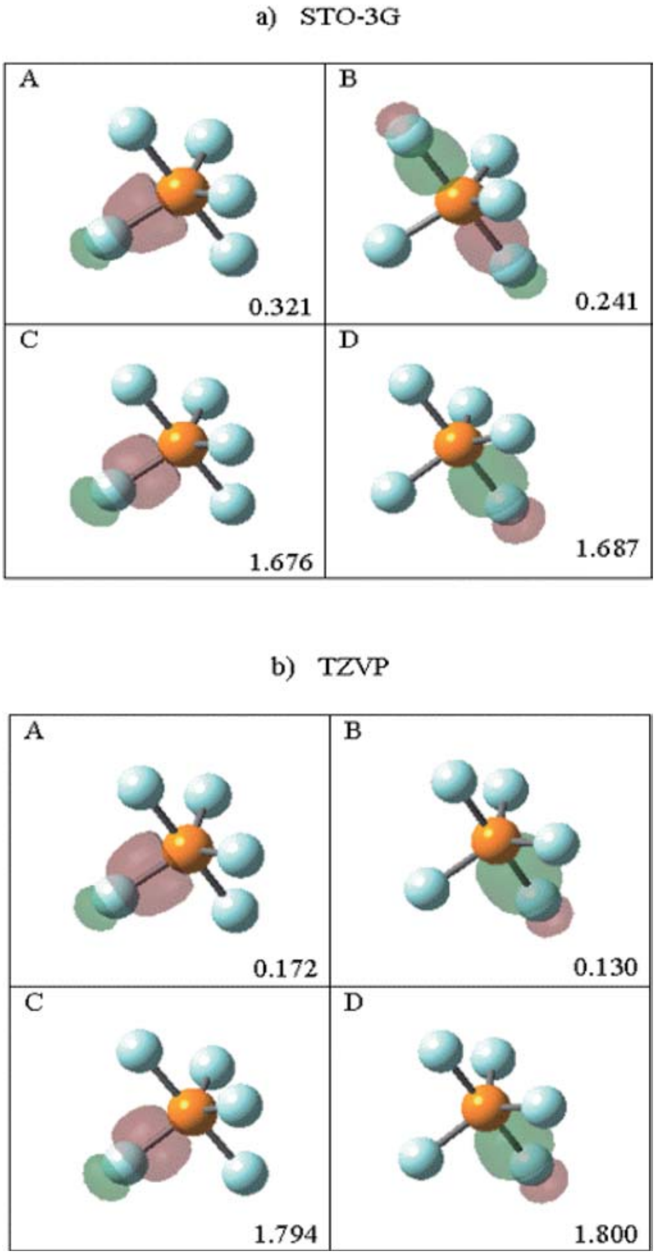


Fig. 2. Selected eigenvectors of the Fermi hole associated with the central P atom and with the axial and equatorial F atoms in PF_5, generated using the AIM generalized approach with RHF wave functions for **a** STO-3G and **b** TZVP basis sets

Table 2. Values of three-center axial FXF bond indices for SF_4 and PF_5, calculated from RHF wave functions with STO-3G and TZVP basis, using both the AIM generalized approach and the more approximate Mulliken-like scheme

Molecule	Basis	Three-center bond index	
		AIM generalized	Mulliken-like
SF_4	STO-3G	−0.056	−0.175
	TZVP	−0.009	−0.046
PF_5	STO-3G	−0.003	−0.043
	TZVP	−0.000	−0.000

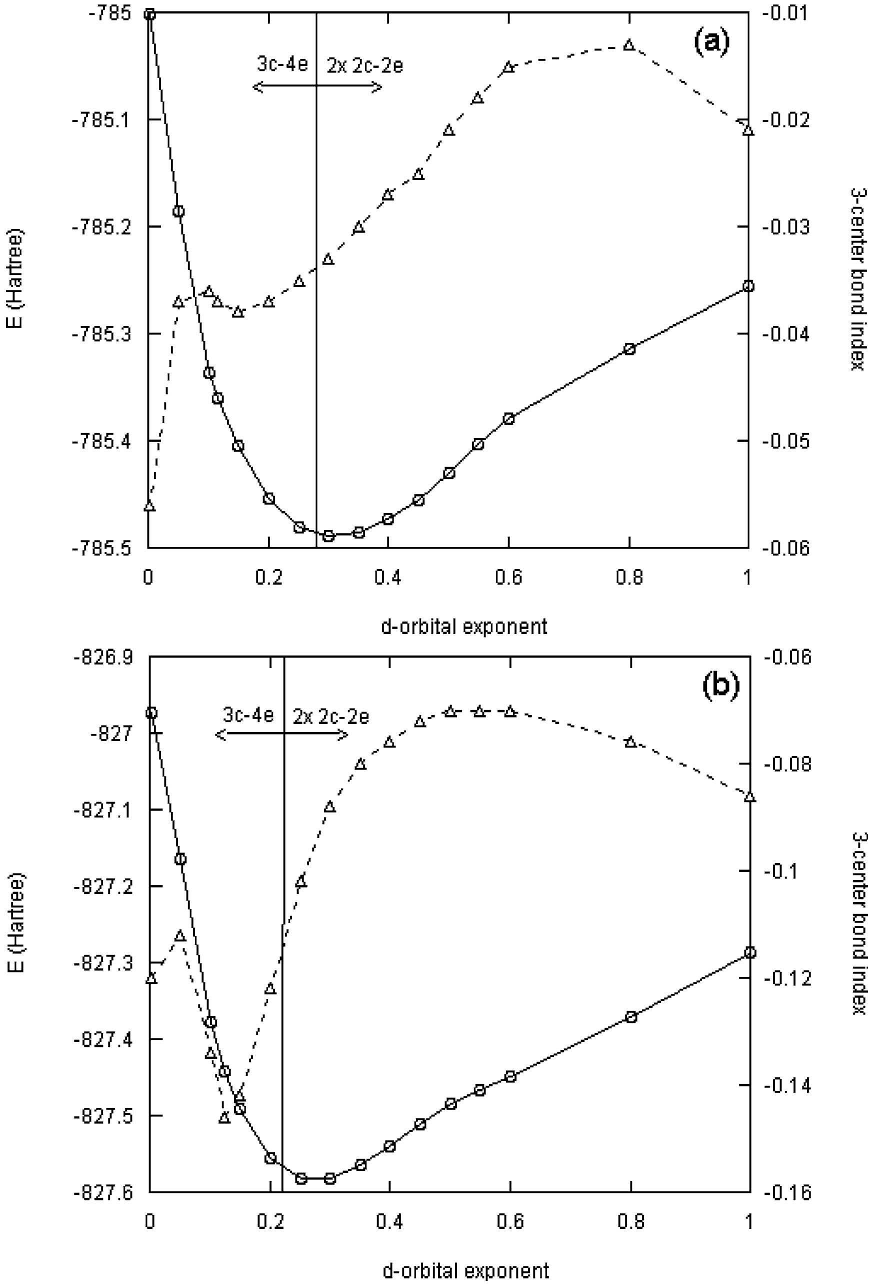


Fig. 3. Dependence on the *d*-orbital exponent of total energies (*full line*) and three-center axial FSF bond indices calculated with RHF wave functions for the STO-3G basis augmented with d functions on the central atom in **a** SF_4 and **b** PF_5

graphically in Fig. 3a for SF_4 and in Fig. 3b for PF_5, in which we have superimposed also the variation of the RHF energy. As the exponent is increased from 0.001, the energy decreases and the 3c-4e description of the bonding eventually "switches off", a little before the minimum energy is reached. For larger exponents in this range, the energy increases again, but the 2c-2e description continues to prevail; however, we checked for both molecules that the 3c-4e description did indeed return when using a much larger exponent of 10. Although it is clear from Fig. 3 that the three-center bond index need not vary monotonically with increasing exponent, we do observe that the switching off of the 3c-4e character, as detected by the Fermi hole analysis, occurs in a region in which the value of the three-center index is headed towards zero.

As the exponent of the added d function increases, the corresponding maximum in its radial distribution function does, of course, move further away from the central atom. By the stage at which the 3c-4e description switches off, that maximum is already a significant proportion of the way along the *X*F bonds. It is, of course, still further away from the central atom at the stage where the variation of the three-center index with a d exponent exhibits a turning point (Fig. 3). All of this appears to be consistent with the conclusion of Häser [61], which we mentioned earlier, that the d population is only weakly bound to the central atom. We note in passing that although we noticed that the more approximate Mulliken-like analysis predicts for both molecules that the switching off occurs at a slightly smaller d exponent, the basic pictures are otherwise rather similar.

Starting from the RHF/TZVP description, it seems unlikely that the inclusion of electron correlation via the SC approach would lead to any dramatic changes to the description of the bonding, and this does indeed turn out to be the case. The SC description of the bonding in SF_4 [58, 59, 60] is found to be based on sulfur sp^x-like hybrids, each of which delocalizes onto a fluorine atom. Each of these singly occupied two-center orbitals overlaps with a singly occupied distorted F(2*p*) function, with the perfect-pairing spin function dominating. There are only modest changes on treating as active also the two nonbonding electrons on sulfur [59]. We can thus see that the SC description of the bonding in the axial FSF fragment corresponds directly to two very polar 2c-2e S–F bonds, just as inferred from the Fermi hole analysis of the RHF/TZVP wave function. The corresponding SC description of the bonding in PF_5 [58,60] turns out to be very similar, in that each of the highly polar P–F bonds is described by the overlap of a P and F hybrid, split almost equally between P and F, and a distorted F(2*p*) orbital, with predominantly singlet coupling of the corresponding electron spins. We find that there are no significant differences between the various P and F hybrids or fluorine orbitals in equatorial and axial positions. It is important to note that the high polarity of the S–F and P–F bonds, observed in the SC description, would be expressed in the language of classical valence bond theory as resonance between large numbers of ionic structures that are based on strictly localized functions, without any active *d* orbital participation in the hybridization scheme. The SC wave function does, of course, provide a much more compact representation of the bonding, with just a single product of fully optimized nonorthogonal orbitals.

4.2 FFF^- and FHF^- anions

The two anions FFF^- and FHF^- are of particular interest as typical representatives of systems that correspond closely to the general paradigm of 3c-4e bonding [14, 15]. Given that an appropriate choice of basis set can be particularly important in studies of negative ions, we selected for our analysis the same 6-311++G** basis set as used in another recent study [15], and we also adopted the same geometries. Of course, when using basis sets that have been extended with diffuse functions, we would not want to place too much reliance on any approach that partitions terms according to the atoms on which basis functions are formally centered. As such, we were reluctant to use Mulliken-like schemes for calculating Fermi holes and bond indices, or the Pipek–Mezey criterion for localizing molecular orbitals, and so we concentrate at the RHF/6-311++G** level on the AIM generalized approach.

We find fairly clear-cut evidence for 3c-4e bonding in the case of FFF^-. Analysis of the hole associated with the central F atom reveals five clearly nonzero eigenvalues. Four of these eigenvalues are very close to 2 and inspection of the form of the corresponding eigenvectors shows that they are very reminiscent of electron pairs in 1*s*, 2*s*, $2p_x$ and $2p_y$ orbitals. The remaining eigenvector, with an eigenvalue of 0.81, corresponds to a $2p_z$ σ orbital oriented along the internuclear axis. The existence of such a function on the central atom is of course very reminiscent of the bonding situation anticipated in the Pimentel, Hach and Rundle model of 3c-4e bonding. Further corroborating evidence comes from the corresponding value of −0.221 for the three-center bond index.

The situation for FHF^- is somewhat less clear-cut. Although the Fermi hole analysis does indeed reveal an eigenvector that is suggestive of 3c-4e bonding, the corresponding eigenvalue is fairly small (0.206). Similarly, the three-center bond index turns out to be practically negligible. A key factor appears to be the extreme polarization of this system, given that integration of the electron density over the domain of the central atom suggests a net charge of +0.777. When examined in isolation from higher moments, AIM charges do, of course, tend to exaggerate the degree of charge separation in polar systems relative to, say, Mulliken charges, but our values for FHF^- do provide some evidence in support of an earlier study [14] in which the dominant contribution to bonding was identified with electrostatic interactions.

We noticed for both of these anions that the Fermi hole analysis at the RHF level and that the corresponding numerical value of the three-center index were relatively little changed on replacing the 6-311++G** basis with TZVP. This provides some justification for carrying out some further analysis based on the various Mulliken-like approximations, using the TZVP basis. Of course, we would not want to place too much trust in individual numerical values, but we do expect that any significant trends will be meaningful, especially in terms of the change to the three-center index on taking some account of electron correlation via the SC approach.

Symmetry-unique TZVP basis LMOs for these two anions are shown in the left-most columns of Fig. 4. As for all of the other systems we considered, we observe that the LMOs are predominantly localized over two centers. Of course, this is not in itself convincing evidence for the lack of 3c-4e bonding because, by construction, the LMOs are necessarily occupied only by two electrons with opposite spins. We performed fixed-geometry SC calculations for both systems, treating as active just the four σ bonding electrons. We label these calculations "frozen core", because none of the inactive orbitals were optimized. Although no such constraints were imposed in these calculations, we find that the converged SC solution for each FXF^- system is composed of overwhelmingly singlet-coupled pairs, with one pair of orbitals associated with each XF subunit. Symmetry-unique SC orbitals ϕ_1 and ϕ_2 are shown for both anions in the central and right-most columns of Fig. 4. Orbitals ϕ_4 and ϕ_3, respectively, are the corresponding symmetry-related orbitals that have not been shown.

For FHF^-, the largest overlap integrals are $\langle\phi_1|\phi_2\rangle = \langle\phi_4|\phi_3\rangle = 0.85$ and $\langle\phi_2|\phi_3\rangle = 0.32$. It is clear from the form of the orbitals (top row of Fig. 4), the pattern of overlap integrals, and the dominant mode of spin coupling that there are no obvious signs of 3c-4e bonding in this system. Instead, there are two 2c-2e F–H

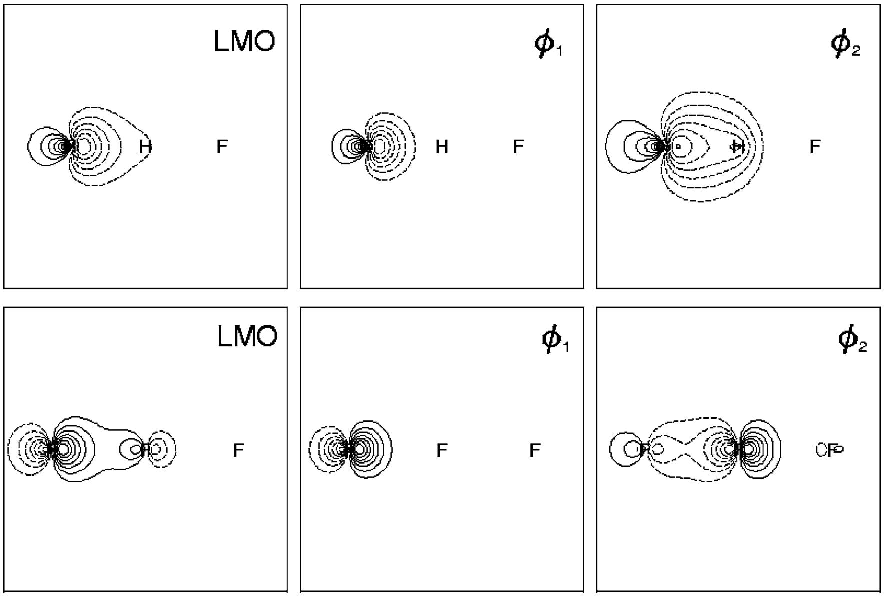


Fig. 4. Contour plots of symmetry-unique localized molecular orbitals (*LMOs*) and frozen-core spin-coupled (*SC*) active orbitals for FHF^- (*top row*) and FFF^- (*bottom row*), calculated using the TZVP basis. Phases were chosen so that the largest magnitude of each function corresponds to a positive value. *Broken contours* correspond to negative values, and the relative phases of different orbitals are arbitrary

bonds that are so polar that one might wonder whether it is appropriate to describe the bonding as being much closer to ionic than to covalent. At the RHF level with this basis set, the Mulliken-like three-center index has an all-electron value of −0.111, and this changes very little (to −0.116) on restricting the summation just to the four electrons that occupy the two bonding LMOs. The corresponding SC value of −0.105 is also rather similar, and this suggests that the description of the bonding at the RHF level is not significantly different from that which emerges as the SC level.

On the other hand, the situation for the much less polar FFF^- ion is somewhat different. We find for FFF^- that the SC orbitals formally hosted on the central atom (ϕ_2 and ϕ_3) show significant delocalization onto one or other of the terminal F atoms, as can be seen from the bottom row of Fig. 4. The largest overlap integrals are $\langle\phi_1|\phi_2\rangle = \langle\phi_4|\phi_3\rangle = 0.62$, associated with each of the two FF subunits, and the corresponding electron spins are very heavily singlet coupled. This has the consequence that although orbitals ϕ_2 and ϕ_3 have a relatively high overlap, $\langle\phi_2|\phi_3\rangle = 0.51$, the corresponding electron spins are not singlet coupled, but they are instead essentially independent (i.e. uncoupled). The remaining overlap integrals have smaller magnitudes, all being somewhat less than 0.1. At the RHF level with the TZVP basis set, the Mulliken-like three-center index for FFF^- has a value of −0.341. On restricting the relevant summation just to the two bonding LMOs, this value becomes −0.376, which is fortuitously close to the idealized value mentioned earlier for 3c-4e bonding. However, the corresponding value at the SC level is dramatically different, being just −0.077. This large change, taken together with the form of the SC solution, suggests that it is not appropriate beyond the RHF level to discuss this system in terms of 3c-4e bonding.

It is particularly important in the present case to assess the extent to which these SC solutions might be affected by the absence of diffuse functions. Additionally, we might wonder whether the choice of a frozen core might lead to increased delocalization of the active orbitals. For these reasons, we carried out additional SC calculations for both anions using the 6-311++G** basis set, fully optimizing the inactive orbitals simultaneously with the active ones and with the total active-space spin function for a four electron singlet. The resulting symmetry-unique active orbitals ϕ_1 and ϕ_2 are shown for both anions in Fig. 5, with ϕ_4 and ϕ_3 being the corresponding symmetry-related pair in each case. There are clearly only small differences in the form of the SC active orbitals for FHF^-, and it turns out that all of the corresponding overlap integrals change only in the third decimal place. Furthermore, the two pairs are still

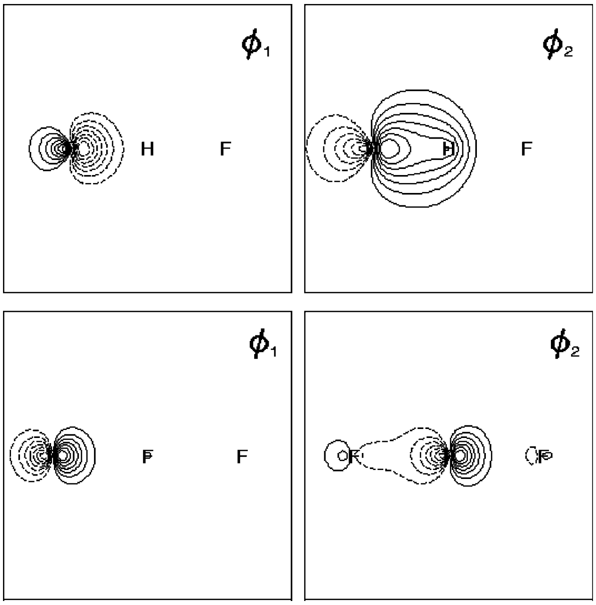


Fig. 5. Contour plots of symmetry-unique fully optimized SC active orbitals for FHF^- (*top row*) and FFF^- (*bottom row*), calculated using the 6-311+G** basis. The orbitals are depicted as in Fig. 4

overwhelmingly singlet coupled, just as in the frozen-core calculation with the TZVP basis set. We may conclude that the changes on including diffuse functions, and on optimizing the inactive orbitals, are rather modest for this system, and that the description of the bonding is very little changed.

There are larger changes for FFF^-, as can be seen by comparing the bottom rows of Figs. 4 and 5. Although orbital ϕ_2 (and its symmetry-related counterpart ϕ_3) is still deformed towards one (or other) of the terminal atoms, there appears to be less delocalization of the active SC orbitals in the more sophisticated calculation. The $\langle\phi_1|\phi_2\rangle$ and $\langle\phi_4|\phi_3\rangle$ overlaps are reduced from 0.62 to 0.53, but the spins associated with these two pairs are still overwhelmingly singlet coupled, as before. The $\langle\phi_2|\phi_3\rangle$ overlap increases from 0.51 to 0.61. Even though this is now the largest overlap integral, we find that the corresponding spins are still essentially independent, i.e., uncoupled. Although there are clearly some differences in detail on going from the TZVP frozen-core SC calculation to the 6-311++G** fully optimized solution, key features of the two descriptions are similar. As was the case for the smaller calculation, it seems inappropriate to invoke notions of 3c-4e bonding in the SC description of FFF^-.

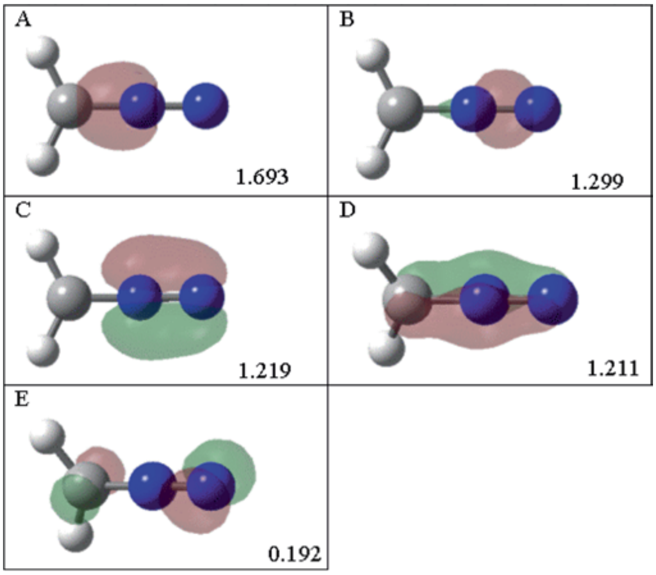


Fig. 6. Eigenvectors of the Fermi hole associated with the central N atom of the CNN fragment in CH_2N_2, generated using the AIM generalized approach for an RHF wave function with the TZVP basis

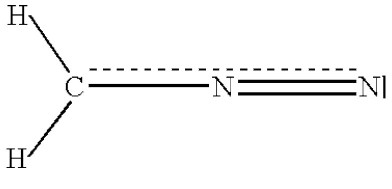
CH_2N_2

As our last example highlighting the sensitivity of the picture of bonding to the quality of the wave function, we examine the 1,3-dipolar molecule diazomethane. This system will be shown to have similarities to the case of the FFF^- anion, but with the obvious difference that the bonding pattern now involves π rather than σ electrons. The first indication of the compatibility of the picture of bonding with the paradigm of 3c-4e bonding comes from our value of −0.208 for the AIM generalized three-center bond index, derived from RHF/TZVP calculation at the experimental geometry.

The existence of 3c-4e bonding in the π system of the CNN fragment is also reflected at the RHF level by the Fermi hole analysis for the central N atom of the CNN fragment. The interpretation of these results, which are summarized in Fig. 6, is quite straightforward and suggests that the first three eigenvectors correspond to the broken valences of σ_{CN}, σ_{NN} and in-plane π_{NN} bonds, respectively. In addition to these three broken valences, which arise from the formal bond splitting accompanying the isolation of the central N atom from the CNN fragment, there are another two eigenvectors whose form is reminiscent of the lowest two occupied orbitals expected for 3c-4e π bonding. On the basis of these results, the structure of the diazomethane molecule can thus be characterized by Scheme 2, in which the 3c-4e bonding is denoted by a broken line extending over the whole CNN fragment. However, as in the case of the FFF^- anion, the bonding situation changes dramatically with the inclusion of electron correlation.

The SC description of the four electron “out-of-plane π system” in CH_2N_2 [51, 60, 62] is not significantly altered if one also treats as active the electrons in the σ-bonded framework and/or in the two electron “in-plane π system” [60]. Each of the four SC active orbitals for the out-of-plane π-electron system takes the form of a deformed $2p_\pi$ function, distorted towards one of the neighboring centers, with one orbital on each of the terminal heavy atoms and two on the central nitrogen atom. Even though the two orbitals associated with the central N atom have a high overlap, the associated electron spins are predominantly independent, i.e., uncoupled. Instead, the overwhelmingly dominant mode of spin coupling corresponds to CN and NN π bonds. Including also the σ and in-plane π systems, the SC description appears to correspond to C=N and N≡N multiple bonds, with a hypervalent central N atom.

For the purposes of the present work, fixed-geometry frozen-core SC calculations were performed for CH_2N_2 using the TZVP basis set, treating as active just the four electrons involved in the out-of plane π system. The qualitative form of the solution coincides, of course, with those described previously [51, 60, 62]. At the RHF level the key Mulliken-like three-center index has an all-electron value of −0.516, which becomes −0.407 on restricting the summation just to the two molecular orbitals of the appropriate symmetry. The corresponding SC value is just −0.062, and the dramatic decrease in



Sch. 2.

the magnitude of this index, taken together with the form of the SC active orbitals and the dominant mode of spin coupling, again calls into question notions of 3c-4e bonding in correlated descriptions of this system.

5 Conclusions

Our generalized population and Fermi hole analysis has shown clearly that in contrast to 3c-2e bonding, which is widely accepted as a "real" bonding mechanism in electron-deficient molecules, the model of 3c-4e bonding that has been invoked for electron-rich molecules is much more complex. A key finding, for the examples that we selected, is that the final picture of the bonding can be very sensitive to the quality of the wave function being analyzed.

Our results for SF_4 and PF_5 highlight how the description can depend critically on the quality of the RHF wave function. For basis sets without d functions on the central atom X, we find that the picture of the bonding in the axial XSX units is reminiscent of the situation anticipated from the Pimentel, Hach and Rundle model [5, 6] of 3c-4e bonding. However, the inclusion of appropriate d polarization functions on the central atom changes the situation dramatically, so that typical features of 3c-4e bonding, such as p orbitals on the central atom which participates in two axial bonds, are no longer observed. Instead, the bonding in these axial units can be better interpreted in terms of a formal expansion of the valence shell of the central atom, and the presence of two very polar 2c-2e X–F bonds. Further improvements to the quality of the wave function, by taking some account of electron correlation using the SC approach, do not lead to any dramatic further changes to the qualitative picture of the bonding.

An earlier study [15] based on analyzing the B3LYP/6-311++G** electron density using standard AIM tools, as well as the topology of the electron-localization function, also found no evidence of 3c-4e bonding for the axial units of SF_4 and PF_5. Those authors studied a range of formally hypervalent linear, T-shaped and bipyramidal molecules, and only found convincing support for the 3c-4e model in the cases of FFF^-, $FClF^-$ and $ClFCl^-$. Our own analysis of the first of these anions also confirmed the presence of 3c-4e bonding, but only at the RHF level of theory. Further improvements to the quality of the wave function, by taking some account of mostly nondynamical electron correlation, produced a somewhat different picture, as evidenced by the form of the SC wave function and by a somewhat drastic reduction in the magnitude of the corresponding three-center bond index. As such, it seems inappropriate to invoke notions of 3c-4e bonding in the SC description of FFF^-.

The other anion that we studied is FHF^-. At the B3LYP/6-311++G** level [15], this system shows some significant differences from the trihalide anions, mostly on account of the strong electrostatic interaction between hydrogen and the two fluorines. Our own results, based on the AIM generalized three-center index and Fermi hole analysis, suggest that this system does not feature significant 3c-4e character even at the RHF/6-311++G** level. There were no noteworthy changes to the three-center bond index on taking some account of electron correlation with the SC approach. On the other hand, we found that the situation for diazomethane resembles closely that for FFF^-, albeit that it is now π rather than σ bonding that is involved. As before, the inclusion of electron correlation leads to a dramatic reduction in the three-center bond index.

Indeed, for all of the systems that we studied, it appears that the 3c-4e scheme does not represent a real bonding mechanism of comparable status to the standard 3c-2e model. It appears instead to be something for which there is only clear evidence when analyzing lower-quality wave functions.

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