Chemical Structures from the Analysis of Domain-Averaged Fermi Holes. Hypervalence and the Nature of Bonding in Isocoordinated Molecules SF_6 and CLi_6

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The nature of bonding in isocoordinated molecules of SF_6 and CLi_6 was analyzed using the recently proposed approach based on the scrutiny of the so-called domain-averaged Fermi holes. It has been shown that although the molecule of SF_6 does not satisfy the charge criterion of hypervalence, the actual picture of bonding is consistent with the traditional hypervalent model assuming the existence of six localized albeit very polar SF bonds around the central atom. On the other hand, while the molecule of CLi_6 represents the ideal candidate for hypervalence according to charge criterion, the picture of bonding is, in this case, considerably different from what the concept of hypervalence is traditionally associated with and can be better characterized by the term hypercoordination.

Introduction

Since its introduction in late sixties,[1−3] the concept of hypervalence was the subject of numerous studies aiming at the rationalization and the explanation of the structure of molecules such as SF_6 and CLi_6 whose structure evidently violates any valence and stoichiometry rules. The question of the crucial importance in this respect is the possibility of the eventual expansion of the valence shell of the central atom or, what is equivalent, the eventual violation of the Lewis octet rule[4] at this atom. Although there is now more or less broad consensus in that the eventual expansion of the valence shell is not due to participation of d-orbitals in ordinary hybridization schemes,[5] the nature itself of hypervalent bonding still remains the subject of continuing discussions. One of the explanations avoiding the participation of d-orbitals of the central atom is based on the Hach, Rundle, and Pimentel model of a three-center four-electron (3c−4e) bond[6,7] and it is true that such a kind of bonding was and still is often considered as a plausible alternative.[8−10] The situation is, however, a bit more complex since according to recent studies[11,12] the existence of 3c−4e bonds can be detected only in calculations using relatively small basis sets. On the other hand, the same calculations using more flexible basis sets are rather consistent with the traditional interpretation according to which the hypervalence is accompanied by the expansion of the valence shell at the central atom.[11] This picture of bonding is, however, opposed by the approach proposed some time ago by Cioslowski and Mixon.[13] These authors argue that because of large electronegativity of the ligands the charge at the central atom in molecules such as SF_6 is reduced so dramatically that the Lewis octet rule is not violated and that speaking of hypervalence is not in this case appropriate. This interpretation of the Lewis octet rule was, however, questioned by Gillespie[14] who argues that the above interpretation contradicts the original interpretation proposed by Lewis. This interpretation speaks, namely, only of bonds as shared electron pairs without any further discrimination whether this sharing is close to even or highly uneven. The fact itself that due to high polarity of bonds in a molecule such as SF_6, the total charge on the central atom is dramatically reduced thus says nothing about the number of shared electron pairs and, consequently, cannot be taken as an argument in favor of nonviolation of the octet rule.

In view of these contradictory opinions we decided to reconsider the problem of bonding in hypervalent molecules and to demonstrate the discrepancies resulting from the straightforward use of the charge criterion[13] of hypervalence. As will be shown, the results of recent analyses based on the interpretation of domain-averaged Fermi holes[11] as well as sophisticated spin-coupled calculations[15] do not support the conclusions of the charge criterion[13] but rather are consistent with the point of view advocated by Gillespie.[14] For this purpose we report the analysis of bonding in two traditionally hypervalent molecules—SF_6 and CLi_6—for which the inconsistency of the corresponding theoretical predictions is especially dramatic.

Theoretical

The methodology of our approach, based on the analysis of the so-called domain-averaged Fermi holes, was introduced some time ago[16,17] as a new powerful means of the interpretation and visualization of molecular structure. As the philosophy underlying the introduction of this new methodology is sufficiently described in our previous studies,[10,11,16,17] we consider it possible to summarize only the basic ideas to the extent necessary for the purpose of this study.

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The domain-averaged, or rather closely related charge-weighted Fermi holes, are defined by eq 1:

$$g_\Omega(r_1) = N_\Omega \rho(r_1) - 2\int_\Omega \rho(r_1,r_2)\, dr_2 \qquad (1)$$

where N_Ω is the mean number of electrons in the domain Ω

$$N_\Omega = \int_\Omega \rho(r)\, dr \qquad (2)$$

and $\rho(r_1,r_2)$is the pair density. These holes are thus closely related to the quantities $F(\Omega,\Omega')$ (eq 3)

$$F(\Omega,\Omega') = \int_{\Omega'} g_\Omega(r)\, dr \qquad (3)$$

but although these quantities were introduced by Bader a long time ago,[18] the usefulness of the quantities $g_\Omega(r)$ for structural elucidation was discovered only very recently.[16,17]

The interesting feature of the holes $g_\Omega(r)$ is that they satisfy the universal normalization condition (eq 4)

$$\int g_\Omega(r)\, dr = N_\Omega \qquad (4)$$

Although this normalization holds irrespective of the size and shape of the domain Ω, there are nevertheless some domains whose relevance for chemistry is of particular importance. Such privileged domains can be, for example, identified with the atomic domains of Bader's virial partitioning of the function $\rho(r)$. As shown in our previous studies, the analysis of the Fermi holes associated with the atomic domains of a single atom provides the information about the valence state of that atom in a molecule, and using this approach the formal expansion of the valence shell of the central atom in several traditionally hypervalent molecules such as SF_4, SF_6, PF_5, etc., has been detected. The detailed procedure of this analysis, which involves as the crucial step also the isopycnic transformation[19] of the hole (eq 1), is sufficiently reported in the original studies.[10,11,16,17] In these studies, however, the analysis was introduced only at simple semiempirical level of the theory, and as the extension from semiempirical to ab initio levels brings into this analysis some new subtle differences, we consider it useful to mention the interpretation of ab initio Fermi holes (eq 1) in more detail.

First of all, it holds that irrespective of the size, form, and the shape of the region Ω, the dimension of the matrix G^Ω is always $K \times K$, where K is the number of basis functions required in a given basis set for the whole molecule. The diagonalization of this matrix thus yields K eigenvalues. Most of them are, however, equal to zero and can be, together with the corresponding eigenvectors, neglected. This neglect can clearly be justified on the basis of the spectral expansion (eq 5):

$$G^\Omega = \sum_i^K n_i|i\rangle\langle i| = \sum_j^{\text{nonzero}} n_j|j\rangle\langle j| \qquad (5)$$

The chemical and physical meaning thus can be attributed only to nonzero eigenvalues and eigenvectors. The number of these nonzero eigenvalues depends in each particular case on the choice of the region Ω. For regions associated with single atoms, the number of nonzero eigenvalues is straightforwardly related to the valence state of that atom in a molecule. At a semiempirical level of the theory, the number of nonzero eigenvalues is strictly equal to the number of basis functions localized on the atom whose associated charge-weighted Fermi hole is analyzed. A little bit more complex situation exists, however, for ab initio atomic Fermi holes generated in flexible basis sets. In this case, the increased quality of the basis finds its reflection in the increase of the number of nonzero eigenvalues, but fortunately this increase does not complicate the final picture of bonding too much. This is due to the fact that some of the nonzero eigenvalues are actually very small so that they can be neglected. This neglect can again be justified on the basis of spectral expansion (eq 5), since it is clear that the dominant contribution to the Fermi hole (eq 1) comes only from the so-called essentially nonzero eigenvalues and the corresponding eigenvectors

TABLE 1: Calculated Eigenvalues and Eigenvectors of Domain-Averaged Fermi Holes for the Molecule of SF_6

atomic domain	eigenvalue	degeneracy	interpretation
S	2.000	1	1s
	1.997	1	2s
	1.996	3	($2p_x$, $2p_y$, $2p_z$)
	0.266	6	σ(S−F)
F	2.000	1	1s
	1.995	1	σ(lone pair)
	1.942	2	π(lone pair)
	1.667	1	σ(S−F)

$$G^\Omega = \sum_i^K n_i|i\rangle\langle i| = \sum_j^{\text{nonzero}} n_j|j\rangle\langle j| \cong \sum_k^{\text{ess}\cdot\text{nonzero}} n_k|k\rangle\langle k| \qquad (6)$$

As shown in the study,[11] the number of these essentially nonzero eigenvalues is again straightforwardly related to the valence state of a given atom in a molecule. In the following part, the results of our analysis will be reported.

Before presenting these results we consider it useful, however, to remind you that although the above analysis was formulated from the very beginning quite generally and can be applied at both HF and post-HF level of the theory, the practical applications are so far a bit restricted. This is due to the fact that the correlated pair density required for the construction of the Fermi holes in the most general case is not at present readily available from existing quantum chemical codes. As a consequence, the analysis has to be so far confined to the SCF level of the theory, where the pair density can straightforwardly be constructed from the first-order density matrix. Nevertheless, we are currently working on the extraction of the correlated pair density from existing quantum chemical codes and we hope to be able to report the results of the Fermi hole analysis at the correlated post-HF level of the theory in due time.

Calculations

Consistent with the methodology recalled above, the calculations performed in this study were of two types. In the first step the wave functions of the studied molecules were generated at the ab initio HF level of the theory. The calculations were performed using Gaussian 98 and PC Gamess programs[20,21] in 6-311G** basis. The output of these programs was used, in the second step, as an input to our own programs in which the required domain-averaged quantities were generated and analyzed. These programs, that can be obtained upon request, require as input yet another file that contains the so-called AOM matrix. In our case, this matrix was generated using a modified PROAIM program,[22] but other alternative programs, as for example MORPHY, could in principle be used as well.

The results of our calculations are summarized in Tables 1 and 2.

Results and Discussion

Having summarized the methodological background as well as computational details of the present study, let us now discuss the results of our calculations.

TABLE 2: Calculated Eigenvalues and Eigenvectors of Domain-Averaged Fermi Holes for the Molecule of CLi_6

atomic domain	eigenvalue	degeneracy	interpretation
C	2.000	1	1s
	1.934	1	2s
	1.784	3	($2p_x$, $2p_y$, $2p_z$)
	1.205	1	“metallic cage”
6Li	1.992	6	1s
	0.790	1	“metallic cage”
	0.215	3	($2p_x$, $2p_y$, $2p_z$)
	0.066	1	2s

SF_6. This molecule is a typical example of the system formally violating the ordinary valence and stoichiometry rule. Existence of these molecules led to the introduction of the concept of hypervalence and, consistent with the classification introduced by Musher,[3] the molecule of SF_6 is classified as the hypervalent molecule of the second type. This classification, which implicitly assumes the existence of six S−F bonds octahedrally arranged around the central atom, is not, however, the only one possible and alternative models have also been considered. An example can be, for example, the idea of the resonance of 15 Lewis structures, none of which violates the octet rule[13] or the model of 3c−4e bonds.[3,6,7] The existence of all these alternative models clearly suggests that no general consensus exists in the question of the hypervalence, and the interpretation of hypervalent bonding thus still waits for the satisfactory solution. This situation is to a considerable extent due to the fact that concepts such as chemical bond, valence, etc., in terms of which chemists are used to think of molecules and their structures, lack strict counterparts in the quantum theory. As a consequence, the interpretation of hypervalence is to a considerable extent the problem of the design of appropriate auxiliary tools allowing the buildup of a link between classical chemical concepts and rigorous but abstract wave functions.

The introduction of one such rigorous criterion of hypervalence was claimed some time ago by Cioslowski and Mixon.[13] This technique is based on the comparison of actual atomic charges with the hypothetical limits based on the model of the resonance of appropriate Lewis structures. Applied to the molecule of SF_6, the criterion allows one to expect the S−F bonds to be 33.3% ionic, which corresponds to atomic charge +2.000 on S, and −0.667 on each of the ligands. As, however, the actual charge on S (+4.26) arising from the rigorous analysis of the wave function[13] considerably exceeds the above limit, the conclusion was that the Lewis octet rule is not effectively violated and that speaking of hypervalence is not appropriate in the case of SF_6. This interpretation is, however, questioned by the results of other alternative techniques. Thus, for example, although the reported NPA charge ($N(S) = +2.90$), which is known to represent usually a reasonable approximation to AIM charge,[23] also leads to the conclusion that the Lewis octet rule should not be violated, the results of the complete NPA analysis are rather consistent with the traditional interpretation of hypervalence, and reveal the existence of 6 polar S−F bonds. This result is very instructive. It suggests, namely, that the criterion of hypervalence based on a comparison of total atomic charges[13] is apparently too crude since it does not take into account subtler details of the distribution of electrons in the valence shell of the central atom—the so-called valence state. This, however, is exactly the essence of the objections raised against the charge criterion by Gillespie and Robinson,[14] who moreover emphasize its incompatibility with the original interpretation of the octet rule by Lewis.

In view of these contradictory opinions we decided to reconsider the problem of the hypervalence of SF_6 and to analyze the bonding in this molecule using recently proposed rigorous methodology based on the analysis of domain-averaged Fermi holes. In previous studies we have demonstrated that, in the case of the hole associated with the atomic region of a single atom, the analysis provides the information about the valence state of that atom in a molecule, and with this approach the existence of six polar 2c−2e S−F bonds could indeed be detected in SF_6.[11] These calculations were, however, based on the Mulliken-like approximation of the integrals over the Bader’s regions, and as this approximation is known to suffer from serious deficiencies,[24] the possibility could not be excluded that the observed picture of bonding reflects only the eventual bias resulting from the approximate character of the analysis. To exclude these uncertainties we report now the results of the analysis of the bonding in SF_6 based on the exact AIM generalized form of the analysis, in which the Fermi holes were averaged over the real atomic domains of individual atoms. In the following part the results of our calculations will be reported.

The most relevant information for the characterization of bonding in SF_6 comes, evidently, from the analysis of the Fermi hole associated with the central S atom. The first information that can be deduced from this analysis concerns the total number of electrons in the AIM region of this atom in a molecule. This value, given as a norm of the corresponding hole (eq 4), is the same quantity that serves as the rigorous criterion for the classification of the violation of the octet rule according to Cioslowski and Mixon.[13] In our case this value is equal to 11.74. This corresponds to the atomic charge +4.26, (reported also in the study[13]), which is again high enough to guarantee the nonviolation of the octet rule according to the charge criterion.[13] To demonstrate the inconsistency of this criterion with the predictions derived from the scrutiny of the valence state, let us report now the results of the analysis of the corresponding rigorous Fermi hole. The results of this analysis are summarized in Table 1. As it is possible to see, the analysis yields in this case 11 (essentially) nonzero eigenvalues. Five of them are very close to 2, and the inspection of the corresponding eigenvectors (one of them is visualized in Figure 1a) clearly shows that they correspond to electron pairs of completely filled K and L shells of S. These electrons are not involved in bonding and need not be considered any longer. The contribution of S atom to bonding in SF_6 thus evidently involves only the remaining 1.76 electrons that contribute to the valence shell. This amount, considered globally, is certainly small enough to guarantee the nonviolation of the octet rule, but this straightforward conclusion is evidently inconsistent with the fact that these valence electrons of S are distributed into 6 equivalent contributions represented by the remaining 6 nonzero eigenvalues of the Fermi hole. This seems to suggest that bonding in SF_6 should involve six equivalent S−F bonds and as it will be shown, this interpretation is indeed straightforwardly corroborated by the inspection of the eigenvectors associated with the corresponding individual eigenvalues. One of them is visualized in Figure 1b and as it is possible to see, its shape is very reminiscent of the localized orbital of one S−F bond. Consistent with the terminology introduced in previous studies,[10,16,17] this eigenvector is interpreted as the “broken valence” of an S−F bond and the corresponding eigenvalue (0.266) is regarded as the contribution of S to the shared electron pair of one S−F bond. This interpretation is also straightforwardly corroborated by the results of the analysis of the Fermi hole associated with individual F ligands. As can be seen from Table 1, the analysis in this case yields 5 (essentially) nonzero eigenvalues, of which 4 are close to two. Inspection of the corresponding eigenvectors shows that they

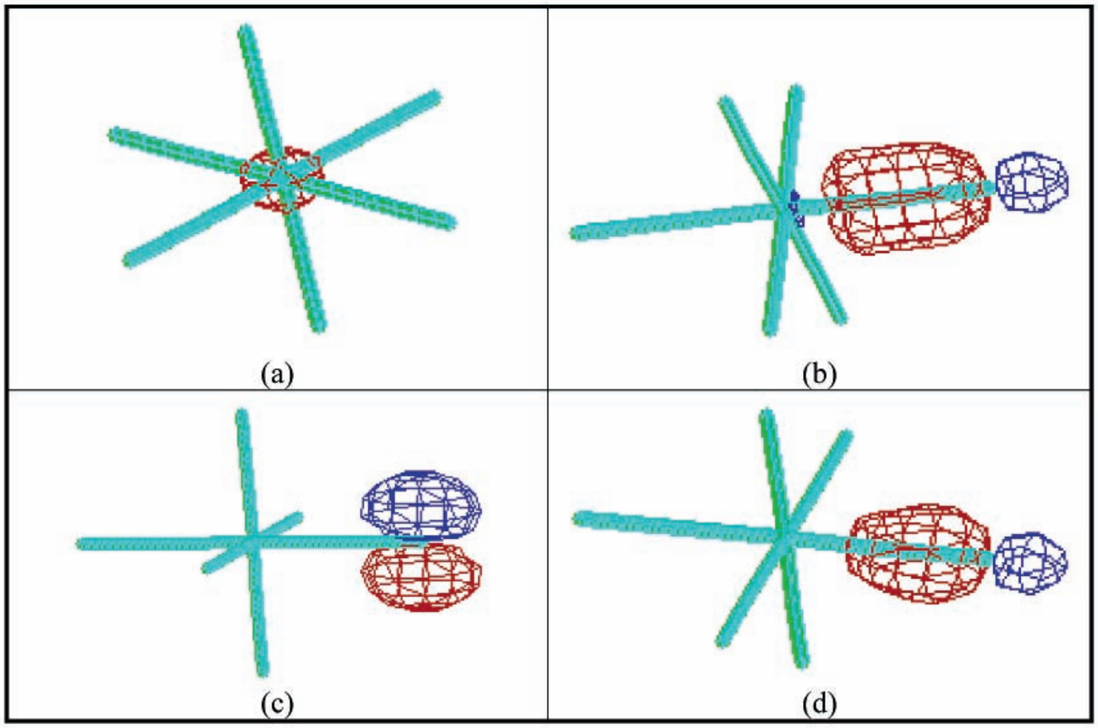

Figure 1. Eigenvectors of domain-averaged Fermi holes for SF_6 molecule. (a) Eigenvector of the Fermi hole corresponding core ($1s^2$) electron pair of the central S atom. (b) One of the six degenerated eigenvectors of the Fermi hole associated with the central S atom corresponding to the "broken valence" of the S−F bond. (c) Eigenvector of the Fermi hole associated with one of the F ligands corresponding to one of the free electron pairs on F. (d) Eigenvector of the Fermi hole associated with one of the F ligands corresponding to the "broken valence" of the S−F bond complementary to 1b.

correspond to a core $1s^2$ electron pair and 3 valence lone electron pairs, respectively (one of them is depicted in Figure 1c). The fluorine contribution to SF bonding is thus evidently due only to the remaining eigenvector, whose inspection demonstrates (Figure 1d) that it is again very reminiscent of the "broken valence" of the SF bond from the previous analysis (Figure 1b). This result is very important. It implies, namely, that due to existence of "common" eigenvector of the Fermi hole associated with two different adjacent atoms S and F (1b, 1d), and due to near complementarity of the corresponding eigenvalues ($0.266 + 1.667 \approx 2$), the S−F bonds in SF_6 have the character of more or less "normal" 2c−2e bonds and the eigenvalues 0.266 and 1.667 can be regarded as the contributions of S and F atoms, respectively, to a shared electron pair of the SF bond.

Moreover, the fact that both eigenvalues considerably differ from unity also clearly suggests that the electron pair of the S−F bond is shared very unevenly so that these bonds have the character of localized, albeit very polar, 2c−2e bonds. This result is again very interesting since contrary to the predictions of the charge criterion of hypervalence,[13] the corresponding picture of bonding is surprisingly consistent with the traditional intepretation of hypervalence, that assumes the existence of six equivalent polar S−F bonds around the central atom.

CLi_6. As a next example of a traditionally hypervalent system, let us analyze the molecule of CLi_6. This molecule is interesting because it represents another representative of the system for which the prediction of charge criterion of hypervalence[13] is inconsistent with the conclusions based on the inspection of the valence state of the central atom. In this case, however, the character of this inconsistency is completely opposite. Thus, for example, due to reversed electronegativity of central atom vs ligands, the AIM charge at the central carbon is so high (N(C) = 10.54) that it even exceeds the limit of completely filled K and L shells. As a consequence, this molecule should represent the ideal candidate for the violation of the octet rule and, consequently, for the hypervalence according to criterion.[13] A more detailed insight into the distribution of the electrons around the central atom shows, however, that the situation is a bit more complex and the final picture of bonding differs considerably from what the concept of hypervalence is traditionally associated with. To reveal the specific picture of bonding in this molecule let us analyze again the valence state of the central carbon atom. The results of this analysis are summarized in Table 2 and in the following part the results of this analysis will be briefly discussed. As can be seen, this analysis yields in this case six (essentially) nonzero eigenvalues. The inspection of the corresponding eigenvectors shows that the first of them, associated with the eigenvalue 2.000, corresponds to a core ($1s^2$) electron pair (Figure 2a). In addition to this electron pair, that is evidently irrelevant for bonding, there is a group of another four eigenvalues whose values are also not very different from 2. The inspection of the form of the corresponding eigenvectors shows that the first of them, associated with the eigenvalue 1.934, apparently corresponds to valence ($2s^2$) electron pair while the remaining three represent practically complete electron pairs in $2p_x$, $2p_y$, and $2p_z$ orbitals, respectively (one of them is depicted in Figure 2b). These electron pairs thus evidently form a spherically symmetrical configuration characterized by a roughly 90% filled valence shell. On the basis of this assignment, a first approximate model can be proposed, according to which the bonding in CLi_6 is predominantly due to electrostatic interactions between the central carbon in the oxidation state close to (−IV) and the "metallic cage" of six positively charged lithium ions held together by 2 electrons. Although it is interesting that practically the same model was proposed some time ago by Reed and Weinhold,[24] the presented analysis of the Fermi hole clearly suggests that the above electrostatic model represents only the first approximation to the actual situation.

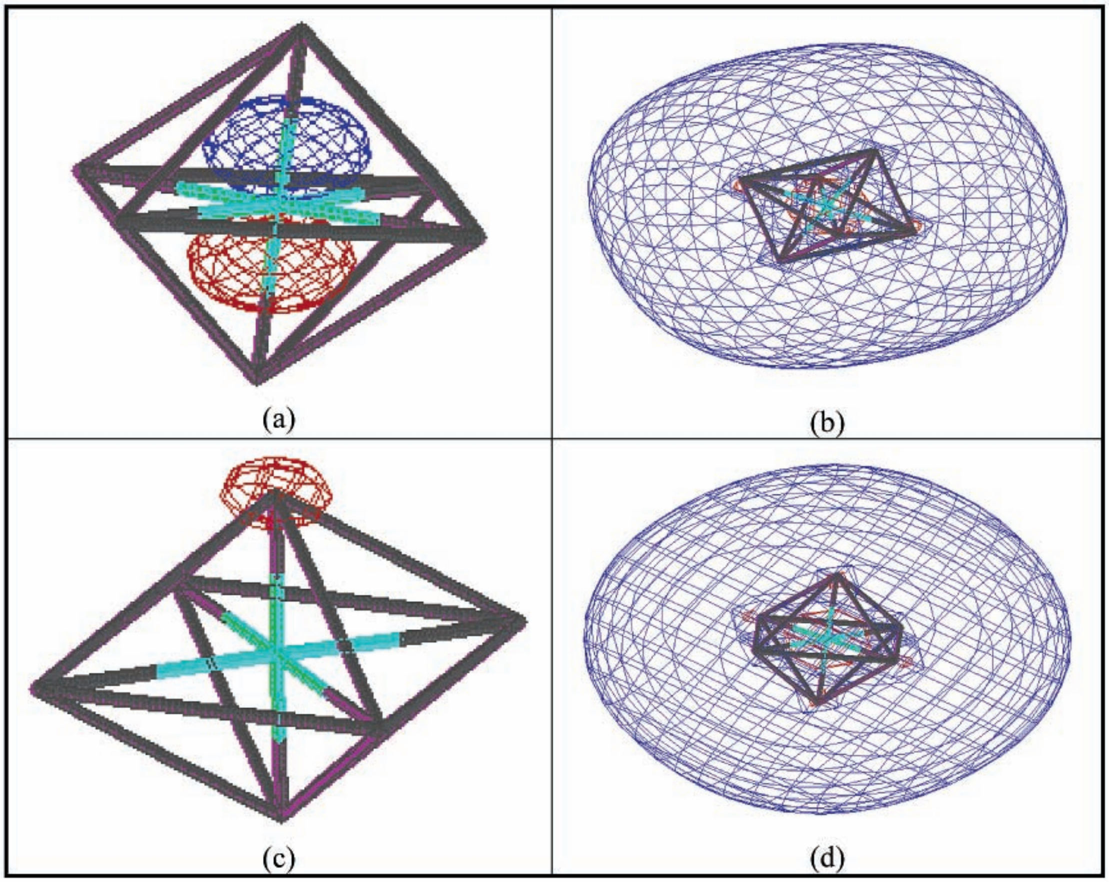

Figure 2. Eigenvectors of domain-averaged Fermi holes for the CLi_6 molecule. (a) One of three degenerated eigenvectors of the Fermi hole associated with the central C atom corresponding to one of the electron pairs in 2p orbitals. (b) Eigenvector of the Fermi hole associated with the central C atom corresponding to the "metallic cage". (c) One of the six degenerated eigenvectors of the Fermi hole associated with the complementary cluster of six Li ligands. The eigenvector corresponds to the ($1s^2$) core electron pair of one of the Li atoms. (d) Eigenvector of the Fermi hole associated with the cluster of six Li ligands corresponding to the "metallic cage" complementary to 2b.

This is due to the fact that this model was in fact deduced only from the incomplete analysis, which does not take into account the remaining nonzero eigenvalue of the carbon Fermi hole equal to 1.205. The inclusion of this eigenvalue does not change, however, the picture of bonding too dramatically and as it will be shown, its main effect is the reduction of the extreme polarity of the electrostatic model and the introduction of a small albeit nonnegligible covalent component into carbon−lithium bonding. This reduction of polarity straightforwardly follows from the inspection of the form of the eigenvector, associated with the additional eigenvalue. This eigenvector is depicted in Figure 2b and as can be seen, its form is very reminiscent of the "metallic cage", whose existence was anticipated already in earlier studies.[24−26] The difference that our analysis contributes to the understanding of the bonding in this molecule concerns the detailed interpretation of this metallic cage. While according to a crude electrostatic model, this "metallic cage" is being completely associated with the cluster of Li ions, our AIM-based analysis clearly suggests that the electron pair of this cage is also shared. The existence of this sharing is also independently supported by the results of the Fermi hole analysis associated with the complementary cage of six Li ions. As can be seen from Table 2, the analysis of this complementary hole yields 11 essentially nonzero eigenvalues. The detailed inspection of the form of the corresponding eigenvectors shows that the first six of them, associated with the eigenvalue 1.991, correspond to core ($1s^2$) electron pairs on individual Li ions (Figure 2c). In addition to these six electron pairs, the next most important contribution comes from the eigenvalue equal to 0.790. The inspection of the corresponding eigenvector clearly shows (Figure 2d) that its form is again very reminiscent of the diffuse orbital of the metallic cage from the previous analysis. The existence of this "common" eigenvector, as well as the near complementarity of the corresponding eigenvalues ($1.205 + 0.790 \approx 2.0$), thus confirms that the electron pair of the "metallic cage" is also shared, and the eigenvalues 1.205 and 0.790 can be regarded as the contributions of carbon and Li cage, respectively, to this pair. The interpretation of the remaining eigenvalues and eigenvectors is also quite straightforward and as it can be found in the detailed study,[27] their inclusion again results only in a small additional reduction of the polarity of C•••Li bonding. We can thus see that in addition to a dominant electrostatic component, suggested already by NPA analysis,[23,24] the bonding in CLi_6 also has a small covalent component that to some extent reduces the polarity of the electrostatic model. This result is very interesting not only since it slightly modifies the conclusion of previous NPA analysis,[23,24] but mainly because it demonstrates that despite formal iso-coordination, the picture of bonding in CLi_6 is dramatically different from what was found in the previous case of SF_6. Thus, for example, the number and the degeneration of nonzero eigenvalues of carbon Fermi hole reveals no evidence for the existence of six central atom••• ligand bonds as detected in the case of SF_6. This primary qualitative difference is also corroborated by the detailed inspection of the form of the corresponding eigenvectors, that clearly imply important differences in the character of central atom•••ligand bonds in both molecules. This difference is due to a specific form of the "common" eigenvector associated with the shared electron pair of “metallic cage”. This eigenvector, depicted in Figure 2d, suggests that bonding in CLi_6 lacks the important traditional attribute of hypervalence, namely, the localized, strongly directional character of bonds between the central atom and ligands that was so convincingly demonstrated in the case of SF_6.

The existence of dramatic differences in the character of bonding in both molecules is not, however, the only result of the above analysis. Another, perhaps even more important, difference concerns the inconsistency of predictions of various criteria of hypervalence. Thus, for example, while the low charge on the central atom is interpreted as an argument against hypervalence in SF_6, the picture of bonding revealed by the inspection of the valence state clearly corresponds to a traditional hypervalent model with 6 localized (albeit very polar) 2c−2e SF bonds.

On the other hand, in the case of CLi_6 the situation is just the opposite. In this case, the reversed distribution of polarity results in the dramatic increase of charge density at the central carbon which is so high that the Lewis octet rule is indeed formally violated and this molecule thus represents a good candidate for the hypervalence according to the criterion.[13] Despite this, however, the actual picture of bonding in this molecule is so different from what the concept of hypervalence is traditionally associated with that it is really questionable to speak of hypervalence and the term hypercoordination seems to be more appropriate to us.

This result is very interesting since it seems to suggest that due to serious internal inconsistencies, the criterion based on the straightforward comparison of atomic charges is apparently too crude to provide a reliable test for the hypervalence. A considerably different picture of bonding, often more consistent with the traditional interpretation of the hypervalence, can be obtained if the nature of the valence state of the central atom is taken into account.

In this connection we consider it worthwhile, however, to say a few words of explanation. This concerns the use of terms such as the violation of the octet rule, valence shell expansion, etc., throughout this study. Here, we would like to stress that although our analysis has clearly revealed the existence of six S−F bonds in SF_6 and in this respect we often referred to terms such as valence shell expansion or the violation of the Lewis octet rule, our understanding of the problem of hypervalence is very close to its interpretation by Gillespie and Robinson.[14] These authors claim, namely, that the often-discussed phenomenon of the violation of the octet rule or the formal expansion of the valence shell for second row atoms should not be considered as something exceptional, since duodecet, rather than octet rule, is to be in this case considered as a natural standard. Consistent with this interpretation are also the results of the sophisticated spin-coupled calculations by Cooper et al.[15] whose the so-called “democracy principle” represents in fact nothing but an alternative formulation of the duodecet rule.

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