On the Role of d Orbitals in SF_6

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Abstract: The role of d orbitals in the bonding of SF_6 is studied through natural population and natural hybrid orbital analysis of ab initio SCF wave functions. The sulfur d orbitals are found to contribute very strongly to the binding energy (250 kcal/mol) and to have a total occupancy of around 0.25e, the valence electron distribution on sulfur being about 32% in 3s, 59% in 3p, 8% in 3d, and 1% in 4p. The occupancy of the two sulfur $3d_\sigma$ orbitals (0.16e), however, is only one-sixth of what would be required for sp^3d^2 hybridization, and the energetic contribution of these orbitals is only two to three times larger than that of the sulfur $3d_\pi$ orbitals. The sulfur d orbitals are important because they allow strong back transfer from the negatively charged fluorine ligands to the strongly positively charged (+2.9e) sulfur, in turn allowing significant contraction of the S–F bonds and greatly increased molecular stability. Application of the method of natural localized molecular orbitals reveals that the σ_{SF} "bonds" have only one-quarter contribution from sulfur orbitals. The results of this study lead to a refined picture of the nature of hypervalency which is in essential agreement with previous discussions given by Rundle, Musher, and Kutzelnigg, among others. Models of SF_6 requiring sp^3d^2 hybridization should be discarded.

I. Introduction

The Lewis–Langmuir octet theory[1,2] and the concept of valence-shell orbital hybridization[3] have been of great value in understanding the nature of the chemical bonding in compounds of elements of the first row such as acetylene, ethylene, and methane. Extending these ideas to the "hypervalent"[4] compounds of the second and higher row non-metals such as PCl_5, SF_6, I_3^-, $SeCl_4$, NSF_3, and XeF_2, however, requires the postulate of a "second valence shell" or "expanded octet",[5,6] and hydridization schemes involving d orbitals[3,7] are invoked for these species.[7-10] Though such a d-orbital hybridization picture has long been criticized on the basis of the large promotion energies involved, the sp^3d and sp^3d^2 models are still employed by many chemists.[11,12]

Pauling[3] introduced hybridization involving d orbitals to describe the bonding in transition-metal complexes but judged that, in non-metallic hypervalent species, ionic resonance forms would be much more important than forms involving sp^3d and sp^3d^2 hybrids.[13] Many workers, particularly Pimentel,[14] Rundle,[15] Pitzer,[16]

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(9) See, e.g.: Gillespie, R. J. *J. Chem. Soc. (London)* **1952**, 1002–1013. Cilento, G. *Chem. Rev.* **1960**, *60*, 147–167. Craig, D. P.; Zauli, C. *J. Chem. Phys.* **1962**, *37*, 601–608, 609–615. Cruikshank, D. W. J.; Webster, B. C.; Mayers, D. F. *J. Chem. Phys.* **1964**, *40*, 3733–3734.

(10) (a) Mitchell, K. A. R. *Chem. Rev.* **1969**, *69*, 157–178. (b) According to Mitchell's eq 6, $r_{max} = 3/\zeta$ measures the size of the 3d orbital (in au). We find $\zeta_{opt} \simeq 2.0$ (see Section II), suggesting that 3d has its maximum overlap in the S–F bonding region. On this topic of 3d orbital diffuseness, see also: Coulson, C. A. *Nature (London)* **1969**, *221*, 1106–1110.

(11) See, e.g.: (a) Cartmell, E.; Fowles, G. W. A. *Valency and Molecular Structure*, 4th ed.; Butterworths: London, 1977. (b) Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper & Row: New York, 1978. (c) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980. (d) Hout, R. F.; Pietro, W. J.; Hehre, W. J. *A Pictorial Approach to Molecular Structure and Reactivity*, John Wiley & Sons: New York, 1984; pp 276–277. (e) Works (a), (b), and (d) favor sp^3d and sp^3d^2 models. Work (c) is somewhat critical of these models in Chapter 5 but seems to endorse them on p 504. Huheey writes (p 718), "The question of d orbital participation in nonmetals is still an open controversy.... Inorganic chemists of a more theoretical bent tend to be more skeptical, feeling that the arguments regarding promotion energies and poor overlap have not been adequately solved. On the other hand, chemists interested in synthesis and characterization tend to favor the use of d orbitals in describing these compounds, pointing to the great heuristic value that has been provided by such descriptions in the past and feeling that until rigorous ab initio calculations (not likely in the near future) on these molecules show the absence of significant d orbital participation it is too soon to abandon a useful model."

(12) Maclagan, R. G. A. R. *J. Chem. Educ.* **1980**, *57*, 428–429. Critical of the sp^3d^3 model for SF_6, it points out the fact that this model is taught in most elementary valence courses. Note that Pauling does not mention SF_6 in ref 3, contrary to Maclagan's assertion, and furthermore that his remarks regarding the importance of ionic resonance structures in SF_6 are consistent with Pauling's remarks concerning PCl_5 and PF_5 in ref 13 and in his general chemistry textbooks.

(13) Pauling, L. *The Nature of the Chemical Bond*, 2nd. ed.; Cornell: Ithaca, 1940; pp 92–93. See also the 3rd. ed.; Cornell, Ithaca, 1960; pp 145–146, 177–178.

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Table I. SCF Calculations on SF₆, Dunning and Hay Double-ζ Basis on Sulfur, Split-Valence Double-ζ on Fluorine, Plus Various d Orbitals on Sulfur[a]

calc. no.	d functions on sulfur	R(S–F)	E(total)	ΔE	q_s[b]
1	none	1.572	−993.67259	−101	2.903 (2.513)
2	Gaussian, exp = 0.54	1.572	−994.03852	128	2.921 (1.748)
3	STO-3G-3d, ζ = 1.57	1.572	−994.03685	127	2.962 (1.138)
4	STO-3G-3d, ζ = 2.00	1.572	−994.06499	145	2.900 (1.578)
5	STO-3G-3d, ζ = 2.50	1.572	−994.00706	109	2.953 (2.076)
6	same as calc no. 4, split (2,1)	1.572	−994.07249	150	2.875 (1.483)
7	none	1.676[c]	−993.71928	−72	2.666 (2.399)
8	STO-3G-3d, ζ = 2.00	1.560[c]	−994.06570	145	2.917 (1.551)

[a] R values in Å, total energies in au, atomization energies (ΔE) in kcal/mol. [b] Charge on sulfur atom, natural population analysis. The Mulliken charge is shown in parentheses for comparison. [c] Optimized.

and Musher,[4] have presented models for hypervalent bonding which do not require d-orbital participation. Kutzelnigg[17] has recently reviewed the theory of hypervalency, coming to the conclusion that, though ab initio calculations show the energetic importance of central-atom d orbitals, a model of excess-electron, multicenter bonding is closer to reality than a hybridization model involving d orbitals. There is in addition much experimental evidence[18-21] that points in favor of models of hypervalency not requiring d-orbital participation.

Recently, we have developed a method for analyzing wave functions of arbitrary form in terms of intrinsic atomic hybrids: the method of natural hybrid orbitals (NHOs).[22-24] We find that wave functions for nonhypervalent molecules have NHOs with hybridizations that are qualitatively in accord with chemical intuition, with trends in line with Bent's rule.[25] For example, CH₄ at the SCF level with a double-ζ plus polarization basis set has four symmetry-equivalent NHOs on carbon with sp$^{2.99}$d$^{0.01}$ hybridization. The form of the NHOs is not very sensitive to basis set extension and does not appreciably change with electron correlation.[22b,23,26] The NHOs are ideally suited for forming a set of intrinsic bond orbitals (natural bond orbitals, NBOs). Associated with the NHO method is the method of natural population analysis (NPA; see Appendix)[24] which is based on an orthogonal set of intrinsic atomic orbitals (natural atomic orbitals, NAOs) whose form and populations are stable with respect to basis set extension. The NPA method avoids the artifacts that plague Mulliken population analysis[27] and yields results in qualitative accord with chemical intuition.[24] Furthermore, the relationship of NAOs, NHOs, and NBOs to localized molecular orbitals (LMOs) can be conveniently studied through the method of natural LMOs (NLMOs).[28]

With these powerful new tools in hand, we sought to examine the prototype hypervalent molecule SF₆, particularly with a view to determining quantitatively the role of d orbitals in the bonding. This work thus serves as an important extension of previous ab initio analyses of SF₆ based on Mulliken population analysis.[29-34]

We shall first summarize the ab initio SCF calculations performed on SF₆, focusing on the variation of the total energy with respect to the form of the d orbitals employed in the basis set, and then present results of natural population, natural hybrid orbital, and natural localized molecular orbital analysis of the wave functions. Out of these results, a refined picture of the nature of hypervalent bonding arises which we shall compare with those given by previous workers.

II. SCF Calculations

Ab initio SCF wave functions for SF₆ were calculated with use of the MELD computer programs[35] as modified by one of the authors for the Harris/7. In all calculations, the standard contracted Gaussian basis set of Dunning and Hay[36] was employed, which is double-ζ on sulfur and split-valence double-ζ on fluorine. To this sp basis set were added one or two sets of Cartesian d orbitals on sulfur.[37] We first varied the form of the sulfur d orbitals in order to estimate their energetic importance. This was done with a fixed S–F bond length of 2.97 au (1.572 Å). Since the sp basis is held fixed, this procedure will, if anything, tend to overestimate the role of d orbitals. The results are shown in Table I. Initially, an uncontracted Gaussian of exponent 0.54 was added, this being the value employed by von Niessen et al.,[31] and leading to a drastic energy lowering (229 kcal/mol). We therefore tried to improve the form of this orbital by replacing it with a linear combination of three Gaussians fit to a Slater 3d orbital (STO-3G)[38] and varying the Slater exponent. We started with a Slater exponent of 1.57 as was employed by Gianturco et al.[29] Evaluation of the energy with added STO-3G-3d functions of Slater exponent 1.57, 2.00, and 2.50 led to the finding that the optimum Slater exponent is in the region of 2.0 (see Table I).[10b] Finally, the STO-3G-3d function was split in a (2,1) fashion, leaving the most diffuse 3d Gaussian uncontracted. This, however, lowered the energy by only 4.6 kcal/mol whereas the unsplit 3d orbital set lowered the energy by 246 kcal/mol with respect to the sp basis.

The STO-3G-3d orbital set of Slater exponent 2.0 is therefore satisfactory for the purpose of estimating the importance of sulfur

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Table II. Natural Atomic Orbital[a] Populations on Sulfur in SF_6 (See Table I for Specification of Basis Sets and Geometries)

calc. no.	3s	$3p_x$	3s + 3p	$3d_{x^2-y^2}$	$3d_{xy}$	tot 3d	4s	$4p_x$
1	1.0199	0.6743	3.0429	0.0000	0.0000	0.0000	0.0048	0.0163
2	0.9700	0.6152	2.8156	0.0704	0.0223	0.2077	0.0049	0.0168
3	0.9299	0.6132	2.7695	0.0736	0.0215	0.2117	0.0065	0.0167
4	0.9825	0.6088	2.8089	0.0811	0.0243	0.2351	0.0047	0.0168
5	0.9380	0.6168	2.7884	0.0722	0.0188	0.2008	0.0064	0.0168
6	0.9905	0.6067	2.8106	0.0782[b]	0.0318[b]	0.2518[b]	0.0055	0.0170
7	1.1863	0.7011	3.2896	0.0000	0.0000	0.0000	0.0030	0.0137
8	0.9671	0.6066	2.7869	0.0819	0.0254	0.2400	0.0049	0.0170

[a] The basis AO coefficients of all NAOs of calculation 8 are given in the supplementary material. [b] $4d_{x^2-y^2}$: 0.0012. $4d_{xy}$: 0.0013. tot 4d: 0.0063.

Table III. Percentage Distribution of Valence and Rydberg NAO Occupancy on Sulfur in SF_6[a]

calc. no.	tot occ	3s	3p	$3d_\sigma$	$3d_\pi$	4s	4p	5p
1	3.0972	32.93	65.31	0.00	0.00	0.15	1.58	0.02
2	3.0786	31.50	59.94	4.57	2.17	0.16	1.64	0.01
3	3.0383	30.61	60.55	4.84	2.12	0.21	1.65	0.01
4	3.0996	31.70	58.92	5.23	2.35	0.15	1.63	0.01
5	3.0466	30.79	60.74	4.74	1.85	0.21	1.65	0.01
6	3.1254	31.69	58.24	5.00[a]	3.05[a]	0.18	1.63	0.01
7	3.3338	35.58	63.09	0.00	0.00	0.09	1.23	0.00
8	3.0834	31.36	59.02	5.31	2.47	0.16	1.65	0.01

[a] See Table I for specification of basis sets and geometries. Note that the hypothetical sp^3d^2 model would predict a distribution of 16.67% 3s, 50.00% 3p, and 33.33% $3d_\sigma$. [b] $4d_\sigma$: 0.08. $4d_\pi$: 0.12.

3d orbitals in the SCF wave function for SF_6. We optimized the bond length of SF_6 with and without this function, obtaining the values 1.560 and 1.676 Å, respectively, compared with the experimental value[39] of 1.561 Å. [We note that Bartell et al.[34] obtained 1.649, 1.589, and 1.656 Å with the STO-3G, STO-3G*, and 4-31G basis sets, respectively.] The atomization energies with and without d orbitals at these optimum geometries are +145 and −72 kcal/mol, to be compared with the experimental value[32] of 464 kcal/mol. Lazzeretti et al.,[40] using a very extensive basis set in the best SCF calculation on SF_6 to date, obtained a total energy (−994.327 au) which is about 230 kcal/mol below the Hartree–Fock limit for the separated atoms. Hay[32] obtained atomization energies at the SCF, GVB, and GVB-CI levels of 125, 186, and 220 kcal/mol, respectively, his SCF energy being −994.029 au.

III. Natural Analysis of Wave Functions

The SF_6 wave functions were analyzed by natural population, natural hybrid orbital, and natural localized molecular orbital analysis.[22-24,28,41] A brief outline of natural population analysis and determination of the underlying NAOs is presented in the Appendix.

A. Comparison with Mulliken Populations. The much smaller basis set sensitivity of natural populations in comparison to Mulliken populations can be seen from Table I, where the charge on sulfur by both methods is given. At the fixed S–F bond length of 1.572 Å, the natural charge on sulfur varies over a range of only 0.087 with the six basis sets, in contrast to the Mulliken charge whose variation is more than 15 times larger (1.37). [Previously published Mulliken charges on sulfur in SF_6 also vary strongly with basis set,[29,31,32,34] from +0.39 to +2.10.] Note in particular calculations 2 and 3 from Table I. Though the energy changes by only 0.0017 au, the Mulliken charge on sulfur changes by 0.610e; by contrast, the corresponding natural charge changes by only 0.041e. The spurious sensitivity of Mulliken populations to basis set changes is further aggravated by the appearance of unphysical orbital "populations" that are negative or greater than two. Indeed, it is possible that individual orbital Mulliken populations can take on any value between −∞ and +∞.[27b] In most of our calculations, we obtained Mulliken populations slightly greater than two for the fluorine 1s AOs and one or more negative

AO populations on sulfur. We were surprised to see how negative some of the Mulliken populations for the sulfur 6s AO became: −0.83 in calculation 3 and −0.34 in calculations 4 and 8 (see Table I). The sulfur 6s and 7s AOs in the calculation reported in ref 37 also had Mulliken populations of −0.06 and −0.69. Natural populations, on the other hand, are always between zero and two. These results add further support to the conclusion[24] that natural population analysis provides a more realistic and stable measure for comparing electron distributions in different systems and should be preferred to the traditional Mulliken population analysis for this purpose.

There is a third deficiency of Mulliken population analysis which is pertinent in the present case, having to do with the overestimation of the covalent character of compounds having significant ionic character (particularly organolithium compounds[24,42]). Consistent with the results observed in other systems, we find from the natural population analysis of Table I that the SF_6 molecule has significantly greater ionic character than that represented by Mulliken analysis. The natural charge on sulfur is nearly +3, indicating that sulfur donates about half an electron to each fluorine. It is interesting to note the opposing trends in natural and Mulliken charges on sulfur with respect to bond length (using the STO-3G-3d, ζ = 2.00 set): At R(S–F) = 1.466, 1.572, and 1.677 Å, the natural charges are 3.006, 2.900, and 2.710, whereas the Mulliken charges are 1.259, 1.578, and 1.737, respectively. Thus, the underestimation of the ionic character of SF_6 by the Mulliken analysis becomes more severe as the interatomic overlap increases, as would be anticipated.

The natural populations have the additional feature that the orbital populations refer to an intrinsic set of natural atomic orbitals (NAOs) instead of to the non-orthogonal basis AOs.[24] In a double-ζ basis set, for instance, there is no single Mulliken population that can be associated with the sulfur "3s orbital" (since at least two basis AOs are contributing strongly to this function) whereas one will have a distinct sulfur 3s NAO in the natural population method which roughly corresponds in form to the 3s Hartree–Fock orbital of the isolated sulfur atom. As the wave function is improved to the Hartree–Fock limit, the form and occupancy of the NAO functions is found to converge smoothly toward limiting values,[22b] in contrast to the Mulliken populations where the electrons become distributed over most of the basis AOs, even those of negligible energy contribution.

B. Natural d-Orbital Populations in SF_6. In Table II, we summarize the sulfur 3s, 3p, 3d (and 4d), 4s, and 4p NAO occupancies (natural populations) for the eight calculations of Table

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I. In all cases, the sulfur 1s, 2s, and 2p NAOs were nearly fully occupied, with the total occupancy of these five core orbitals being at least 9.9999, the occupancies of the 5s, 6s, 7s, and 8s NAOs being 0.000002 or less, and the 5p orbitals each having a maximum occupancy of 0.0002. From Table II, the total occupancy of the sulfur d orbitals is around 0.25. This is much less than the Mulliken population analysis result of Hay[32] of 0.78 in a similar basis set and also the STO-3G* Mulliken analysis result of 1.63.[34] In Table III, the percentage distribution of the sulfur "valence" electrons (excluding the core electrons) in 3s, 3p, 3d, 4s, and 4p is given. The 3d populations are divided into two sets, $3d_\sigma$ ($3d_{x^2-y^2}$ and $3d_{z^2}$) and $3d_\pi$ ($3d_{xy}$, $3d_{xz}$, $3d_{yz}$), according to whether the orbital contributes to σ or to π bonding between sulfur and fluorine. As can be seen, the maximum $3d_\sigma$ occupancy corresponds to 5.3% of the sulfur valence electrons, less than one-sixth of the 33% valence occupancy that would be required by the sp^3d^2 hybridization model for SF₆. A significant finding from Table III is that the $3d_\pi$ population is more sensitive to the form of the sulfur d orbitals than is the $3d_\sigma$ population, the variations in the former case being around four times as large as in the latter case. We also find that the $3d_\pi$ occupancy is more sensitive to geometry variations and appears (with the STO-3G-3d, $\zeta=2.00$ set) to achieve a distinct maximum at a bond length of about 1.54 Å, whereas the $3d_\sigma$ occupancy continues to slowly increase with bond contraction at least down to 1.47 Å. Note from Tables I–III that splitting the d orbital (calculation 6)), though having little effect on the total energy and the total 3d occupancy, significantly lowers the ratio between the $3d_\sigma$ and $3d_\pi$ populations.

Elementary perturbation theory suggests[24] that the energy lowering (ΔE) associated with charge (q) transferred between filled and empty orbitals of energy difference $\Delta\epsilon_{CT} = \epsilon_{empty} - \epsilon_{filled}$ may be approximated as

$$\Delta E_{est} \simeq q\Delta\epsilon_{CT} \qquad (1)$$

Using diagonal Fock matrix elements from our largest calculation (calculation 6), one can thereby estimate for the charge transfer (CT)[43] into the sulfur $3d_\sigma$ NAOs [$q_\sigma = 0.156$, ϵ(S $3d_\sigma$) = 1.05, ϵ(F p_σ) = −0.87] that $\Delta E(3d_\sigma) \simeq 0.30$ au $\simeq 190$ kcal/mol. Similarly, the transfer into the sulfur $3d_\pi$ NAOs [$q_\pi = 0.096$, ϵ(S $3d_\pi$) = 0.56, ϵ(F p_π) = −0.75] leads to the estimate $\Delta E(3d_\pi) \simeq 0.13$ au $\simeq 79$ kcal/mol. The total estimate (269 kcal/mol) for the CT energy into d orbitals of sulfur is in qualitative agreement with the calculated contribution of the d orbitals (250 kcal/mol) from Table I. These considerations suggest that eq 1 can give a useful qualitative estimate of the energetic importance of the d orbital occupancies (0.25e) of SF₆ and of the relative energetic importance of d_σ and d_π contributions to the bonding. We should also mention that the diagonal Fock matrix elements of the sulfur 3d NAOs are much higher than those for the 3s and 3p NAOs: −0.75, −0.19, +0.56, and +1.05 au for 3s, 3p, $3d_\pi$, and $3d_\sigma$, respectively. This is the reason that sp^3d^2 hybridization does not occur in SF₆.

C. Natural Bond Orbitals of SF₆. After formation of the NAOs (and natural population analysis), the next step of our procedure is to search for an optimal set of one- and two-center natural bond orbitals (NBOs). Each two-center "bond" NBO is formed as a linear combination of *orthonormal* natural hybrid orbitals (NHOs) from distinct atomic centers, and each one-center "lone pair" NBO is an unmixed NHO. In this manner, one obtains an optimized description of the wave function which often corresponds closely to the chemist's idealized Lewis structure.

In the case of SF₆, however, this procedure does not give rise to a satisfactory Lewis structure. For the present discussion it is essential to mention from the description of the NBO procedure[22a] that, prior to the formation of the final NBOs, the set of hybrid orbitals on each atomic center must be symmetrically orthogonalized. (Hybrid orbitals on different centers are automatically orthogonal by virtue of the orthogonality of the NAOs from which they are formed.) Now, in the NBO search for

two-center bond orbitals, a function of high occupancy (1.9996) is found on each S–F bond, strongly (73.8%) polarized toward fluorine, but the component sulfur hybrid ($sp^{1.23}d^{0.09}$) of each "bond" has high overlap with hybrids directed to other fluorine atoms and is rejected by the standard NBO projection threshold. [This threshold (0.5) serves to prevent acceptance of hybrids whose "high occupancy" is merely due to high overlap with hybrids previously found and thus to ensure that the accepted hybrids will not lead to numerical singularity in the overlap matrix during the subsequent orthogonalization process. The standard program threshold value is conservatively low for "normal" first-row molecules, typical projection values being 0.9 or higher.] Throughout the following discussion we shall make reference to the results from our best STO-3G-3d calculation (calculation 8 of Table I), though the results for the other wave functions were qualitatively similar.

To investigate the sulfur hybrids further, we altered the NBO program by lowering the projection threshold to 0.45, so that six S–F functions were accepted, thereby forcing the construction of six orthonormal NHOs on sulfur. Since the six hybrids ($sp^{1.23}d^{0.09}$) initially found are highly non-orthogonal, their form is drastically altered through the required orthogonalization. The orbital space of at least six NAOs is required in forming a set of six orthonormal NHOs. This, combined with the octahedral symmetry of SF₆, has the consequence that the six resulting hybrids of sulfur are precisely of sp^3d^2 character, *regardless of the magnitude of the contribution of d orbitals to the original nonorthogonal hybrids, as long as this contribution is non-zero.* When the orthogonalized sulfur hybrids are recombined with the corresponding fluorine σ hybrids, a set of six σ_{SF} NBOs is formed. However, the occupancy of these NBOs is low (1.919), and the orbitals are again highly (83.0%) polarized toward fluorine. The off-diagonal density matrix elements between the six sp^3d^2 sulfur hybrids are quite large, so that the actual NAO populations do not correspond, even approximately, to the ratios $n_s:n_p:n_d = 1:3:2$ that would be suggested by the classical picture of promotion and hybridization. Thus, although a connection can be drawn to the picture of sulfur sp^3d^2 hybridization, the NBO procedure indicates that its validity is not comparable, e.g., to that of sp^3 hybridization in methane. Rather, the picture is one of extreme polar character of S–F "bonds" and of sulfur d_σ and d_π orbitals contributing in proportions quite different from that associated with idealized sp^3d^2 covalent bonding.

D. Natural Ionic Hybrids of SF₆. Since no NHOs leading to a satisfactory Lewis structure could be found, we lowered the occupancy threshold for the NBO search to 1.50 (from the usual value of 1.90), until a set of nonbonding hybrids was obtained which restored the symmetry between fluorine atoms. This corresponds to an *ionic* representation of the bonding, with four lone pairs on each fluorine and no S–F bond NBOs. In this case the NHOs and NBOs are identical since no bonds are formed. We consider these "ionic NHOs" to provide the best simple set of orbitals for describing the bonding in SF₆. The sulfur NHOs are found to be simply the sulfur NAOs since the atom is in an environment of octahedral symmetry. On each fluorine, there is a doubly occupied (1.99999) core orbital, two π-type lone pairs of occupancy 1.974 with pure p character (p_π), and two σ-type lone pairs, one pointed away from sulfur (s_σ: occupancy 1.983, 81.54% s character) and one pointed toward sulfur (p_σ: occupancy 1.553, 81.47% p character). The fluorine Rydberg NHOs have small occupancies (0.0004 and less), in contrast to the more highly occupied 3d, 4s, and 4p NHOs (NAOs) on sulfur (see Table II).

E. Natural Localized Molecular Orbitals. The final step of our wave function analysis package is the formation of natural localized molecular orbitals (NLMOs) from NBOs (or, in this case, NHOs). This procedure is quite simple, involving a controlled diagonalization of the NBO density matrix, carried out in such a way as to preserve any symmetry present in this matrix.[28] We have shown that NLMOs strongly resemble LMOs produced by other procedures (such as that of Foster and Boys[44] or of

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(43) In the following, "p_σ" and "p_π" refer to fluorine lone pair NHOs (see Section IIIC).

(44) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 300–302.

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Table IV. Occupied Natural Localized Molecular Orbitals (NLMOs) in SF_6, Calculation 8 (see Table I)[a]

NHO[c]	F s_σ ϕ_7[d]	F p_π ϕ_8[e]	σ_{SF} ϕ_{10}[f]	σ_{SF} ϕ_{30}[g]
F_2 s_σ	+0.9958			
F_2 p_{π_y}		+0.9935		
F_2 p_σ			+0.8722	−0.0457
F_3 p_σ	−0.0309		+0.0212	−0.0457
F_4 p_σ	−0.0108	−0.0391	−0.0433	−0.0457
F_5 p_σ	−0.0108	+0.0391	−0.0433	−0.0457
F_6 p_σ	−0.0108		−0.0399	+0.8731
F_7 p_σ	−0.0108		−0.0399	+0.0221
S_1 $3s$	+0.0303		+0.2842	+0.2784
S_1 $3p_x$	−0.0339		+0.3709	
S_1 $3p_y$		+0.0804		
S_1 $3p_z$				+0.3709
S_1 $3d_{xy}$		+0.0564		
S_1 $3d_{x^2-y^2}$	+0.0182		+0.0995	
S_1 $3d_{z^2}$	−0.0105		−0.0567	+0.1157
S_1 $4s$	−0.0201			
S_1 $4p_x$	+0.0617		+0.0112	
S_1 $4p_y$		−0.0128		
S_1 $4p_z$				+0.0112

[a] Eleven of the occupied NLMOs were composed at least 99.995% from a single NAO (sulfur 1s, 2s, $2p_x$, $2p_y$, $2p_z$, and the six fluorine 1s NAOs) and correspond to core LMOs. The NHO contributions to the remaining NLMOs with coefficients greater than 0.01 are given (i.e., all contributions greater than 0.01%). The sulfur NHOs are NAOs, and the fluorine NHOs are defined in the text.[b,c] The origin of the small difference between ϕ_{10} and ϕ_{30} is explained in ref 46. [b] See the supplementary material for the basis AO coefficients of all NAOs and the NAO coefficients of all NHOs of calculation 8. [c] S_1 is at the origin, and F_2–F_7 are along the $+x$, $-x$, $+y$, $-y$, $+z$, $-z$ axes, respectively. [d] The other five F s_σ NLMOs are symmetry equivalent to ϕ_7. [e] The other eleven F p_π NLMOs are symmetry equivalent to ϕ_8. [f] The other three σ_{SF} NLMOs in the xy plane are symmetry equivalent to ϕ_{10}. [g] The other σ_{SF} NLMO along the z axis is symmetry equivalent to ϕ_{30}.

Edmiston and Ruedenberg[45]) which localize the canonical molecular orbitals. In addition, the NLMO procedure is quite efficient and leads to direct insight into the origin of "delocalization tails" of the LMOs.

To apply the NLMO procedure, the NBOs must first be divided by occupancy into strongly and weakly occupied sets (A and B, respectively), the number of NBOs in the A set being equal to the number of occupied MOs. The sulfur core and the fluorine core and lone pair NHOs will thus constitute the A set, while the sulfur valence and all other NHOs constitute the B set. The NLMO procedure was then found to lead to the results shown in Table IV.[46]

The NLMO set for SF_6 is found to be rather similar in form to the NHO set except for six of the NLMOs. These six NLMOs are found to correspond to six S–F "bonds", mainly having contributions from sulfur 3s, 3p, and 3d NHOs (total, 23% on sulfur, including 1.3% from 3d) and from the p_σ lone pair on one of the fluorines (76%), with much smaller contributions from the other five fluorine p_σ lone pairs (total, almost 1%).[47a] The strong

(45) Edmiston, C. E.; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *34*, 457–465.

(46) (a) These six σ_{SF} NLMOs display C_{4v} instead of O_h symmetry (see Table IV). This arises from the fact that the matrix elements in the NBO (NHO) density matrix between the p_σ lone pairs of the fluorines in the xy plane with the sulfur d orbitals are not degenerate with those of the p_σ lone pairs of the fluorines along the z axis. Hence, in the NLMO procedure (which is a sequence of symmetrized Jacobi rotations of "degenerate" off-diagonal elements, see ref 28) slight inequivalencies between the two sets of σ_{SF} LMOs can arise. These two sets are, however, nearly identical (as can be seen in Table IV): rotating ϕ_{30} by 90° about sulfur gives a function that has an overlap integral with ϕ_{10} of 0.9949. In a basis set without sulfur d orbitals, the six σ_{SF} NLMOs are symmetry equivalent. (b) For comparison, we also computed NLMOs starting from the "sp³d²" NBOs mentioned in Section IIIC and found the results to be nearly identical with the "ionic" NLMOs of Table IV, even though the starting points are quite different. For example, the overlap integral between σ_{SF} NLMOs of "sp³d²" and "ionic" origin is 0.99994, and the hybrid composition ($sp^{1.71}5d^{0.166}$) of the "sp³d²" σ_{SF} NLMO is essentially identical with that shown in Table IV. The only significant difference is that the "sp³d²" set displays O_h symmetry, wheres the "ionic" set displays C_{4v} symmetry, as discussed above.

polarity of the σ_{SF} LMOs for SF_6 has been previously noted by von Niessen et al.[31] and by Kutzelnigg,[17] who employed the Boys localization method. The hybridization on sulfur in the σ_{SF} NLMOs is $sp^{1.7}d^{0.16}$ (on the basis of the contributions of the sulfur 3s, 3p, 3d NAOs to the NLMO), the d orbital contribution to these sulfur hybrids being a little less than 6%, again only about one-sixth of that required by sp^3d^2 hybridization. This is somewhat less d orbital participation than the $sp^{1.5}d^{0.44}$ hybridization suggested by Hay's analysis[32] (which presumably was based on Mulliken population analysis applied to the sulfur basis AO contributions to the sulfur hybrid orbital) of the generalized valence bond (GVB) wave function for SF_6. The NLMOs for each of the p_π fluorine lone pairs have 0.6% and 0.3% contributions, respectively, from sulfur $3p_\pi$ and $3d_\pi$ orbitals, indicating the presence of a small amount of p_π–p_π and d_π–p_π bonding in SF_6.[47b]

Since the six S–F "bond" NLMOs are so highly polarized toward fluorine, it is better to picture them in terms of isolated fluorine lone pair orbitals having strong "delocalization tails" into available sulfur 3s, 3p, 3d NAOs. The small sulfur contributions to these NLMOs cannot be represented (even approximately) by a set of six orthonormal valence hybrids participating in covalent bonding. Rather, since these sulfur valence NHOs serve only as acceptors for small fractions of an electron from each fluoride lone pair donor orbital, the Pauli principle permits each sulfur NAO to serve as a "delocalization tail" for all of the NLMOs (as permitted by symmetry). Sulfur d orbitals also serve as available acceptor orbitals for this purpose, making a quantitatively important contribution to the molecular binding energy but *without* being required in the high proportions needed for sp^3d^2 covalent bonding. The high ionic character of SF_6 (corresponding to the large electronegativity difference of S and F, and reflected in the large natural charges of Table I) is thus indicated to be the predominant feature of the bonding in this molecule.

IV. Discussion

From our analysis, the electronic structure of SF_6 may be pictured in the following way: Take as the starting "zeroth-order" point an ionic octet model for SF_6, where each ion (F^- and S^{6+}) has a full or empty valence octet. Such a model yields the correct MO occupancies by symmetry species for SF_6. The bare ionic structure is modified by the transfer of about half an electron from the "p_σ" lone pair on each fluoride ion into the empty 3s and 3p orbitals of S^{6+}. This results in what may be called a "first-order" picture of SF_6 [$S^{3+}(F^{0.5-})_6$], in reasonable accord with the calculated natural charges of Table I. This picture not only emphasizes the significant ionic character of SF_6, but also that the coordination number of sulfur is not restricted by the number of hybrid orbitals that the atom can form. Indeed, for analogous tellurium salts the coordination number can be as high as eight, since salts of TeF_7^- and TeF_8^{2-} are known to exist.[33a,48] Just as in the case of CLi_6,[49,50] the picture is that of fairly ionic donor–acceptor bonding with central atom orbital hybridization being irrelevant.

This "first-order" model of SF_6 employs only valence s and p functions, the contribution of d orbitals being secondary. We have previously noted that SF_6 is unstable with respect to the separated atoms at the SCF level in the absence of sulfur d orbitals (Table I), so that this "secondary" contribution is obviously of qualitative importance. Electron correlation, however, might lead to sufficient

(47) (a) These contributions from the five "nonbonded" fluorine p_σ lone pairs are S–F antibonding in character. Since the sulfur hybrids contributing to the six σ_{SF} NLMOs are mutually non-orthogonal, these contributions are necessary in achieving orthogonality between the six σ_{SF} NLMOs. (b) As seen from Table IV, there are also contributions to the F p_π NLMOs from p_σ lone pairs on two of the other fluorines. These are of σ_{SF} antibonding character, revealing that there is a competition between σ and π bonding in SF_6. We thank Prof. Robert Weiss for pointing out this aspect of the S–F π bonding.

(48) Muetterties, E. L. *J. Am. Chem. Soc.* **1957**, *79*, 1004. Selig, H.; Sarig, S.; Abramowitz, S. *Inorg. Chem.* **1974**, *13*, 1508–1511.

(49) (a) Schleyer, P. v. R.; Würthwein, E.-U.; Kaufmann, E.; Clark, T.; Pople, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5930–5932. (b) Schleyer, P. v. R. in *New Horizons of Quantum Chemistry*; Löwdin, P.-O., Pullman, B., Eds.; D. Reidel Publishing Co.: New York, 1983; pp 95–109.

(50) Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1985**, *107*, 1919–1921.

stabilization that SF_6 could be weakly bound (but with a longer S–F bond length) *without* the contribution of sulfur d orbitals.

It should be considered, however, that there will be strong F–F repulsion in SF_6 due to the *twelve* F–F contacts that exist, the F–F distances being 2.22 Å, compared to the F–F van der Waals contact distance of roughly 2.7 Å. This repulsion is further increased by the large negative charge on each F atom. It is relevant to note that the bond lengths in SF_6 are about 0.2 Å shorter than expected for S–F single bonds.[11c] How does this short bond length come about? In a "second-order" picture of SF_6, one should also allow for charge transfer from the p_σ lone pairs of the fluorines into the sulfur d_σ orbitals of roughly 0.16e and CT from the fluorine p_π lone pairs into the sulfur d_π orbitals of roughly 0.09e. The tremendous stabilization gained through this 0.25e charge transfer (ca. 0.4 au) greatly aids in overcoming the F–F repulsions, allowing the S–F bonds to contract significantly and achieve the experimentally observed "short" bond length. Although quite different in magnitude, the n→d CT delocalization in SF_6 is in some ways analogous to the n→σ* CT interaction that we have shown to be the dominant source of stabilization in hydrogen bonding.[23,26a,51] In the latter case, the energy separation $\Delta\epsilon_{CT}$ is around 1.0 to 1.5 au and the quantity of charge transferred is much smaller (on the order of 0.01e), leading to energy stabilizations of the order of 6 kcal/mol (cf. eq 1). This allows the H-bonded species to overcome the significant steric repulsion present in the equilibrium geometry.

There is indeed a more significant and direct connection between hydrogen bonding and hypervalency having nothing to do with d orbitals. A particularly simple hypervalent species is the bifluoride ion FHF^- where hydrogen is hypervalent. In this species, the hydrogen bonding between F^- and HF is so strong that the potential energy surface has only a single minimum corresponding to two equivalent F–H bonds. Pimentel[14] was the first to present a qualitative 3-center- 4-electron (3c-4e) MO treatment of this ion and also of the related trihalide ions such as I_3^- and ICl_2^- in which iodine is hypervalent. In this treatment there are doubly occupied three-center bonding and nonbonding MOs, the latter having no contribution from the central atom and hence being localized on the two "ligands." (In FHF^-, the H atom contributes an s orbital to the 3c bonding MO, whereas in the trihalide ions, the central iodine atom contributes a p orbital.) Electronegative ligands and an electropositive central atom are thus essential for this model. We note here that these two MOs can be unitarily transformed to form two symmetry equivalent LMOs which are ligand lone pairs that have delocalized to some extent onto the central atom. Pimentel and McClellan[52] later showed that this 3c-4e MO description can be extended to the more general case of unsymmetrical H bonds. It is easily determined that their description of the H bond in terms of two MOs is related by a unitary transformation to the two LMOs (σ_{AH} and $n_B + \lambda\sigma_{AH}$*) of the n→σ* CT description of H bonding. We think that it is important to recognize the essentially similar electronic features of H bonding and hypervalency through the unified viewpoint given here.

The 3c-4e MO description of the trihalide ions has also been emphasized by Rundle,[15] and this model was also applied to the analogous compound XeF_2 by Pitzer[16] and (quantitatively) by Coulson.[53] Kiang and Zare[54] discussed how this model could be extended to describe the bonding in SF_6 as involving three orthogonal 3c-4e F–S–F bonds. Their discussion, however, left out consideration of bonding involving the sulfur 3s orbital, as only the sulfur 3p orbitals were utilized in the bonding. Rundle[15] presented the MO description for SF_6, noting that d orbitals on sulfur were not required. It is instructive to discuss the relationship

between the 3c bonding model of SF_6 and the SF_6 MOs. There are six occupied MOs in SF_6 to be formed from the sulfur valence orbitals and the fluorine p_σ lone pairs. From the three sulfur 3p orbitals interacting with the six p_σ orbitals, one can form the three 3c F–S–F bonding and nonbonding orbitals along the three coordinate axes. The F–S–F bonding orbitals correspond to three t_{1u} MOs. The three F–S–F nonbonding orbitals (which have no contribution from sulfur orbitals) can be transformed to form an a_{1g} MO and two e_g MOs. Now, the only one of these six MOs with which the sulfur 3s orbital can mix is the a_{1g} MO. Allowing this mixing to take place, we have a set of MOs like those in Rundle's diagram. This exercise is useful in pointing out the strong bonding between the sulfur 3s orbital and the symmetric (a_{1g}) combination of the three F–S–F nonbonding orbitals. Furthermore, the sulfur $3d_\sigma$ orbitals can mix with the two e_g combinations of the three F–S–F nonbonding orbitals.

Let us therefore discuss explicitly the relationship of our description of the bonding in SF_6 with the MO picture. We start with the ionic $S^{+6}(F^-)_6$ model of SF_6. We first delocalize the a_{1g} combinations of the fluoride p_σ lone pairs into the empty sulfur 3s orbital and then the three t_{1u} p_σ combinations into the empty sulfur 3p orbitals, yielding our "first-order" picture of SF_6-$[S^{3+}(F^{0.5-})_6]$. (There is in addition a minor amount of delocalization from the t_{1u} combinations of the fluoride p_π lone pairs into the sulfur 3p orbitals.) Our "second-order" picture of SF_6 then involves delocalizing the two e_g p_σ combinations into the sulfur $3d_\sigma$ orbitals and futhermore the t_{2g} combinations of the fluorine p_π lone pairs into the sulfur $3d_\pi$ orbitals. This delocalization of fluorine lone pairs into sulfur 3s, 3p, and 3d orbitals is just what occurs during the construction of the occupied NLMOs for SF_6 from the fluorine NHOs and the sulfur NAOs. It seems in many ways simpler than the MO or 3c bonding pictures of SF_6 to consider the NLMO picture of six fluoride ions strongly delocalizing onto a cationic sulfur core.[55] From this perspective, the electronic structure of SF_6 is somewhat analogous with that of CLi_6,[50] except that in CLi_6, the electronegativity relationship between the core and the ligands is *inverted*. In the latter case one also has the possibility of a bonding a_{1g} lithium "cage" MO with negligible C–Li antibonding character.[49,50] It is relevant to note that the analogous a_{1g} MO in SF_6 is the LUMO, and it has as its dominant contribution the sulfur 3s NAO with significant antibonding contributions from the fluorine p_σ lone pair NHOs. This LUMO is responsible for the large cross section for absorption of low-energy electrons and high-electron affinity (around 1 eV) which SF_6 exhibits.[56] The S–F bond length stretches by 0.14 Å upon formation of SF_6^- from SF_6,[56] demonstrating the antibonding character of this a_{1g} MO.

Musher[4] has presented a model of hypervalent bonding in SF_6 that started by forming six non-orthogonal sp^2 hybrids on sulfur, each directed at one of the six fluorines. He then proposed solving the twelve-electron SCF problem for the sulfur 3s and 3p orbitals and the fluorine p_σ lone pairs and transforming the resulting six doubly occupied MOs into equivalent orbitals (LMOs). He argued that each of these LMOs will be predominantly composed from a single sulfur sp^2 hybrid and from the p_σ orbital on the fluorine at which this hybrid is directed, with relatively small contributions from the other five sulfur hybrids and from the other five p_σ lone pairs. This LMO picture, of course, is directly related to the NLMO description of SF_6, the only difference being that the sulfur orbital contribution to the NLMOs was described in terms of 3s, 3p, and 3d NAOs instead of non-orthogonal sp^2 hybrids. The linear combinations of sulfur NAOs contributing to each of the σ_{SF} NLMOs, however, determine a set of six non-orthogonal sulfur orbitals of hybridization $sp^{1.7}d^{0.16}$, in reasonable qualitative accord with Musher's six sp^2 sulfur hybrids. Thus, Hay's assertion[32] that

(51) Weinstock, R. B.; Weinhold, F., University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-661, 1981 (unpublished). Curtiss, L. A.; Pochatko, D. J.; Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *82*, 2679–2687.

(52) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, 1960; pp 236–238.

(53) Coulson, C. A. *J. Chem. Soc. (London)* **1964**, 1442–1454.

(54) Kiang, T.; Zare, R. N. *J. Am. Chem. Soc.* **1980**, *102*, 4024–4029.

(55) The fact that these two descriptions are equivalent for hypervalent "excess-electron" species rests on the fact that both the 3c bonding and nonbonding MOS are occupied, allowing a unitary transformation to two more localized orbitals (LMOs). In electron-deficient compounds such as boranes, however, only the 3c bonding MO is occupied, and hence the 3-center character of the bonding cannot be removed by unitary transformation in this case.

(56) Hay, P. J. *J. Chem. Phys.* **1982**, *76*, 502–504.

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there is little evidence to support Musher's scheme is a mis-statement, since his own GVB orbitals for the S–F bonds yield six non-orthogonal $sp^{1.5}d^{0.44}$ hybrids on sulfur, in rough correspondence with the Musher picture. Musher demonstrated for the specific case of SF_4 that his scheme is equivalent to that of Rundle and Pimentel for 3c-4e bonding. This suggests that the various pictures of hypervalency are complementary, providing different routes to an essentially equivalent representation of the SF_6 bonding, with no suggestion of sp^3d^2 hybridization.

V. Conclusion

We have described a quantitative analysis of the bonding in SF_6, using for this purpose ab initio SCF wave functions of reasonable quality and the recently developed methods of natural population, natural hybrid orbital, and natural localized molecular orbital analysis. We find that the essential features of the bonding are well-described by an ionic donor–acceptor $S^{3+}(F^{0.5-})_6$ picture. Such a model is directly related to the descriptions by Rundle[15] (MO diagram), Musher[4] (non-orthogonal sulfur hydrids), Kiang and Zare[54] (extension of Pimentel's[14] three-center bonding scheme), and Kutzelnigg[17] (strongly polar σ_{SF} LMOs). This model is also essentially consistent with Hay's[32] generalized valence bond calculations which led to the conclusion that "the stability of the hypervalent SF_4 and SF_6 systems is largely due to the incorporation of charge-transfer configurations, with 3d functions on the sulfur playing a lesser role." Interestingly, this is exactly what Pauling[13] presumed many years ago on the basis of empirical arguments. The sulfur 3d functions are, however, quantitatively quite important and must be included in a more refined picture. The role of these d orbitals is in accepting charge from fluorine lone pair orbitals, delocalization into the $3d_\sigma$ functions being two to three times more important energetically than delocalization into the $3d_\pi$ functions. Without the sulfur 3d orbitals, which contribute around 250 kcal/mol to the SCF energy, SF_6 would be much more weakly bound. Also, the shortness of the S–F bonds in SF_6 cannot be rationalized without the strong participation of the sulfur 3d orbitals in the wave function. The total 3d population in SF_6, however, is only around 0.25e, the $3d_\sigma$ population (0.16e) being only one-sixth of what would be required for sp^3d^2 hybridization on sulfur. In fact, central atom hybridization is completely irrelevant to the nature of the chemical bonding in SF_6 (in contrast to, e.g., CH_4), since it is not necessary for sulfur to form six orthogonal hybrids in order to participate in donor–acceptor bonding with six ligands. It is only necessary that the ligands be very electronegative.

We therefore concur with the suggestions of Maclagan[12] and Kutzelnigg[17] that models of sp^3d and sp^3d^2 hypervalent bonding in non-metals should no longer be taught in chemistry courses. However, we suggest with equal emphasis that the *qualitative* influence of d orbitals (our "second-order" picture) in stabilizing hypervalent compounds and in contracting the bonds in such compounds cannot be neglected. We thus concur with Kutzelnigg's remarks on this topic.[17] Many workers, in rejecting the sp^3d and sp^3d^2 models go so far as to state that d orbitals are not qualitatively important in hypervalency of second row atoms (see, e.g., ref 4, 21a, 30, 33a, 54, 57). These workers are, however, quite correct in pointing out (see especially, Musher[4]) that d orbitals are *not essential* for the general phenomenon of hypervalency (our "first-order" picture). This conclusion is bolstered by the wealth of recent experimental and theoretical evidence reviewed by Schleyer.[49b,58]

Finally, in light of our present study of SF_6 and our recent study of CLi_6,[50] it is of interest to reexamine the Lewis–Langmuir octet theory.[1,2] The two main tenets of this theory have been stated by Rundle:[15b] "(1) The chemical bond is the sharing of an electron pair between two atoms and (2) each atom in a molecule achieves a rare gas electron shell by forming chemicals bonds.". From the

consideration of various hypervalent species, Rundle[15b] states, "it appears that Lewis's rare gas or octet rule is stronger than his localized electron pair rule. The deviations from Lewis's rules of valence seem to be that electron pairs can be delocalized so as to lead to bonding among more than a pair of atoms, whereas deviations from the rare gas rule are essentially nonexistent, except for transition metals." In line with Rundle's remark and with the recent findings of Schleyer and co-workers,[49,58] we indeed find that only an octet of electrons is involved in the bonding of the central atom in SF_6 and CLi_6. Valence shell expansion *does not* occur. Rather, our conception of chemical bonds (see rule 1 above) must be modified to allow *partial* (i.e., less than two electron)[58] bonds in cases where a significant electronegativity difference exists between the atoms, i.e., where a nearly ionic ("donor–acceptor" or "coordinate") limit is achieved. Mathematically, this is of course equivalent in the case of "excess-electron" hypervalent bonding (by a unitary transformation from LMOs to three-center MOs) to Rundle's suggestion of allowing multicenter bonding in valence theory.[55] This is also in line with Jørgensen's[19b,59] observation that it is an illusion that N orbitals are needed on a central atom for N bonds. Theoretical analysis of SF_6 and of CLi_6[50] thus leads to a striking *confirmation* of the octet rule and represents a further refinement of the theory of valence that started on March 28, 1902 when Lewis boldly wrote out his drawings of "the cubical atom".[1]

Appendix: Natural Atomic Orbitals and Natural Population Analysis

For completeness, we sketch briefly the methods of natural atomic orbitals (NAOs) and natural population analysis (NPA), full details of which are presented in ref 24 and 41.

The NAOs are closely related to, and derive their inspiration from, Löwdin's natural orbitals (NOs).[60] Indeed, for isolated atoms, the NOs and NAOs coincide. However, in a polyatomic molecule the NAOs retain one-center character, as far as possible, whereas the NOs become delocalized over all nuclear centers, transforming as irreducible representations of the molecular point group. Thus, the NAOs differ from NOs in their monocentric character, but in other respects they share the desirable properties—completeness, orthonormality, maximal occupancy, intrinsic a priori character, etc.—associated with NOs. Like the NOs, the NAOs are optimal with respect to the description of molecular electron *density* (rather than energy), and their determination relies solely on information contained in the one-particle density matrix, unrestricted as to the form of the wave function. The NAOs facilitate chemical analysis of the wave function by maintaining a close connection to the localized "effective" AO basis functions of elementary valence theory, which underlie many chemical concepts.

Just as the NOs arise as eigenfunctions of the full molecular one-particle density operator $\Gamma(r,r')$, so can the NAOs $\phi_i^{(A)}$ be associated with eigenfunctions $\tilde{\phi}_i^{(A)}$ of atomic *blocks* $\Gamma^{(A)}$ of the density operator for a particular atom A. However, these eigenvectors, which serve only as the "parents" of the final NAOs $\phi_i^{(A)}$, cannot serve directly as "atomic orbitals", for two reasons:

(1) The electron density $\rho(r)$ about each center is generally *anisotropic* (in both coordinate and spin space) in the molecular environment, so that the $\tilde{\phi}_i^{(A)}$'s lack the angular and spin symmetries associated with orbitals of free atoms.

(2) The AOs of constituent atoms are *overlapping* in the molecular environment, so that an "atomic eigenvector" $\tilde{\phi}_i^{(A)}$ from one center is partially mixed with those from other centers.

In the numerical NAO procedure, these difficulties are removed in a manner that preserves the relationship to parent eigenvectors $\tilde{\phi}_i^{(A)}$ as closely as possible. The rotational isotropy of coordinate space is restored by averaging atomic density matrix subblocks $\Gamma^{(Alm)}$ of angular symmetry (lm) over all m components, prior to diagonalization. (This also ensures the invariance of the NAO

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(58) Schleyer, P. v. R., Jeremy Musher Lecture on Hypervalent Molecules, Jerusalem, 1985, private communication.

(59) Jørgensen, C. K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon: Oxford, 1962; see especially pp 211 and 226.

(60) Löwdin, P.-O. *Phys. Rev.* **1955**, *97*, 1474–1489.

procedure with respect to rotation of the molecular coordinate system.[24]) The non-orthogonality of atomic eigenvectors on different centers is removed by an "occupancy weighted symmetric orthogonalization" procedure,[23] satisfying

$$\sum_i \tilde{w}_i \int |\phi_i - \tilde{\phi}_i|^2 \, d\tau = \text{minimum} \qquad (A1)$$

where the weighting factor $\tilde{w}_i = \langle \tilde{\phi}_i | \Gamma | \tilde{\phi}_i \rangle$ is the occupancy of $\tilde{\phi}_i$. [In practice, the orthogonalization (A1) is carried out in a 3-step "WSW" procedure, to reduce the implied overcounting that results from employing occupancies of the non-orthogonal $\tilde{\phi}_i$'s as initial weighting factors.[24]] This generalization of Löwdins's symmetric orthogonalization procedure[61] retains the "maximum resemblance" property for orbitals of high occupancy but allows diffuse orbitals of low occupancy to distort as needed to achieve orthogonality. In this way, the character of the free-atom valence shell (the "natural minimal basis set") of each atom is strongly preserved in the molecular environment, leading to orthonormal functions ϕ_i of high occupancy that are optimal for describing the molecular electron density around each atomic center. Typically, a high percentage ($>99\%$) of the electron density is described by the small number of NAOs of the formal "natural minimal basis" set, with much smaller contributions from the extra-valence-shell "Rydberg" NAOs that complete the span of the input AO basis set. Note that each step in the NAO procedure is based on the "maximum occupancy" criterion that distinguishes "natural" orbitals.

In the orthonormal basis of NAOs, the density matrix provides the occupancies that constitute "natural population analysis". The occupancy (natural population) $n_i^{(A)}$ of NAO $\phi_i^{(A)}$ is simply the diagonal expectation value

$$n_i^{(A)} = \langle \phi_i^{(A)} | \Gamma | \phi_i^{(A)} \rangle = (\Gamma^{(A)})_{ii} \qquad (A2)$$

The natural populations rigorously satisfy the Pauli principle

$$0 \le n_i^{(A)} \le 2 \qquad (A3)$$

sum consistently to give the populations $n^{(A)}$ on each atom

$$n^{(A)} = \overset{\text{on } A}{\underset{i}{\sum}} n_i^{(A)} = \text{Tr}(\Gamma^{(A)}) \qquad (A4)$$

and are consistent with the total number (N) of electrons in the molecule

$$\overset{\text{atoms}}{\underset{A}{\sum}} n^{(A)} = N \qquad (A5)$$

We have previously shown[24] that the natural populations are efficiently computed, exhibit good stability with respect to basis set changes, and are in satisfactory correspondence with other theoretical and empirical measures of charge distribution.

The NPA method bears some resemblance to Davidson's[62] use of Hartree–Fock AOs to determine orbital occupancies from the molecular density matrix and to Heinzmann and Ahlrichs'[63] use of "modified atomic orbitals" (MAOs) for the same purpose. The MAOs (like the NAOs) take account of the important *changes* in atomic valence state or AO energy and diffuseness that accompany molecule formation. The Davidson and Heinzmann–Ahlrichs methods satisfy conditions analogous to (A2) and (A3) and would be expected to give results that are qualitatively similar to natural population analysis (significantly improved over Mulliken population analysis in this respect). These methods differ from NPA in being more closely tied to the single-determinant SCF–MO approximation and in generally leaving some portion of the electron density unaccounted for [i.e., inexact satisfaction of (A4) or (A5)]. Very recently, Ehrhardt and Ahlrichs[64] applied the MAO method to SF_6 (using a basis of 5s3p1d on F, 6s4p1d on S) and obtained charges of $+2.67$ on S and -0.44 on F, quite comparable to the NPA results of this paper.

Registry No. SF_6, 2551-62-4.

Supplementary Material Available: The AO to NAO and NAO to NHO transformation matrices from calculation 8 (14 pages). Ordering information is given on any current masthead page.

(61) Löwdin, P.-O. *J. Chem. Phys.* **1950**, *18*, 365–375. Löwdin, P.-O. *Adv. Quantum Chem.* **1970**, *5*, 185–199. Wannier, O. *Phys. Rev.* **1937**, *52*, 191–197.

(62) Davidson, E. R. *J. Chem. Phys.* **1967**, *46*, 3320–3324. Cf. also: Roby, K. R. *Mol. Phys.* **1974**, *27*, 81–104.

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Pauli Forces and the Valence Shell Electron Pair Repulsion Model for H₂O and NH₃

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Abstract: It is shown that the two effects of antisymmetry (Pauli exclusion principle) within the correct SCF wavefunctions cannot "bend" linear H₂O or planar NH₃ without classical electronic coulombic repulsion (CER) between LMO "charge clouds" in the SCF energy expression. These two effects are the orthogonality of the molecular orbitals (MOs) and the electron-exchange interactions between the LMOs. This result is in direct contradiction to the presently accepted valence shell electron pair repulsion (VSEPR) model, which attributes the geometries of molecules to "Pauli forces" between localized electron pairs. It is argued that the Walsh MO energy correlation diagrams, based on the integral Hellmann–Feynman theorem, are a more correct simple model for molecular geometries.

I. Computational Tests for the Dominance of Pauli Forces

Large basis set linear combination of atomic orbitals molecular-orbital self-consistent-field (LCAO MO SCF) wavefunctions give good geometries for closed-shell molecules.[1] They appear to be reliable for the initial examination of the physical effects

determining molecular geometries.

The earliest version of the valence shell electron pair repulsion (VSEPR) model of molecular geometries was due to Sidgwick and Powell.[2] They maintained that one critical factor for angular geometries was the *Coulombic* electron repulsion (ER) between the valence-shell electrons. Our results confirm that conclusion.

(1) See, for example: Schaefer, H. F., III *The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results*; Addison-Wesley: Reading, MA, 1972.

(2) Sidgwick, N.; Powell, H. *Proc. R. Soc. London A* **1940**, *176*, 153.