Chemical Bonding to Hypercoordinate Second-Row Atoms: d Orbital Participation versus Democracy

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Abstract: Spin-coupled theory is used to investigate the bonding in several hypercoordinate and "normal octet" compounds of main group elements. It is found that d basis functions play much the same qualitative role in hypercoordinate and normal molecules, acting as polarization functions. There are no obvious demarcations in the energy penalty per bond of excluding such functions. No evidence is found to support the traditional notions of sp^nd^m hybridization. The spin-coupled approach, also known as the *full*-GVB model, provides a very clear and simple picture of the bonding in all of the molecules studied. In SF_6, for example, the sulfur atom contributes six equivalent, nonorthogonal sp^x-like hybrids, which delocalize onto the fluorine atoms. Each of these two-center orbitals overlaps with a distorted F(2p) function, with the perfect-pairing spin function dominating. The spin-coupled description of PF_5 is entirely analogous, with remarkably little differentiation between axial and equatorial bonds. A key consideration for all of the hypercoordinate species studied is the polarity of the various bonds. It is suggested that less emphasis than hitherto be placed on the "octet rule" and that the so-called *democracy principle* be asserted: any valence electron can participate in chemical bonding if provided with sufficient energetic incentive. This idea is pursued for phosphorus and sulphur halides, for XeF_2, and for the CH_5^-, SiH_5^-, and SiF_5^- ions. It is argued that there are no significant qualitative differences between the hypercoordinate nature of first-row, second-row, and noble gas atoms in appropriate chemical environments.

Introduction

An extraordinary amount has been written in the past sixty years or so on the question of the nature of the bonding in hypercoordinate (or hypervalent) molecules such as SF_6 and PF_5. Although there remain some differences in the emphasis placed on the role played by d basis functions, the consensus view which emerges from most of the reliable *ab initio* investigations published in recent years is that the bonding in a molecule such as SF_6 has very little to do with the availability of d atomic orbitals. Nevertheless, the existence of PF_5, but not of NF_5, is still often rationalized to high school students, and to many undergraduates, in terms of the availability of d orbitals and the possibility of obtaining "an expanded octet". Indeed, models based on d^2sp^3, dsp^2, and dsp^3 hybrid orbitals are still in widespread use amongst professional chemists and are described in many of the most widely used textbooks. It is tempting to speculate as to why such models continue to survive when there is so much theoretical evidence which does not support them.

One explanation, amongst others, is that the overwhelming majority of the recent theoretical evidence comes from calculations based on molecular orbital theory, whereas the general ideas of utilizing d orbitals are much more closely associated with the ideas of valence bond theory. It seems likely that some chemists believe that the quantum chemists' view of d orbital participation is not yet definitive and may change in the future. As pointed out by Kutzelnigg,[1] recent years have seen the vindication by respectable quantum chemical calculations of many of the qualitative concepts which emerged in the early days of theoretical chemistry, although many of the concepts for first-row atoms cannot be generalized successfully to the later main group elements.

The purpose of the present paper is to report an investigation using spin-coupled valence bond theory of the bonding in several compounds of second-row atoms. The spin-coupled wave function,[2] also known as the *full* generalized valence bond (full-GVB) model,[3] represents the proper modern development and generalizations of the ideas of Heitler and London[4] and of Coulson and Fischer[5] to many-electron systems. Being firmly based in valence bond theory, the very compact descriptions of the bonding which emerge in the present study facilitate a direct and, we hope, very convincing description of the bonding. In keeping with the findings of the extensive study by Magnusson,[6] we conclude that d orbitals do *not* play a significant role in the bonding. We find evidence to support the view of Reed and von Schleyer[7] that simple qualitative concepts such as significantly polar bonds are of greater utility than notions of d orbital participation in hybridization. It is interesting to note that Magnusson found energy improvements which are just as large with d functions on peripheral O and F atoms as with d functions on central second-row atoms.[6]

In spite of its continuing overwhelming appeal we suggest that the familiar octet rule should be demoted. We retain only an eight-electron rule (cf. the 18-electron rule of transition metal chemistry), which indicates that a formal electron count of eight around a central atom is favorable. We assert here the new *democracy principle*, which, stated very simply, suggests that "it is the democratic right of every valence electron to take part in chemical bonding if it wants!" Of course, some electrons require a greater energetic incentive than others to take part in bonding. In spite of its simplistic, and somewhat anthropomorphic nature, we find the democracy principle of great utility in describing the

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(1) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.
(2) Gerratt, J.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1968**, *59*, 332.
(3) Ladner, R. C.; Goddard, W. A., III. *J. Chem. Phys.* **1969**, *51*, 1073.
(4) Heitler, W.; London, F. *Z. Phys.* **1927**, *44*, 455.
(5) Coulson, C. A.; Fischer, I. *Philos. Mag.* **1949**, *40*, 386.
(6) Magnusson, E. *J. Am. Chem. Soc.* **1990**, *112*, 7940.
(7) Reed, A. E.; Schleyer, P.v.R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.

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hypercoordinate bonding in fluorides and chlorides of phosphorus and sulfur and in rationalizing the existence of noble gas compounds. In the present paper, we also use the same general language when trying to understand why SiH_5^- is a stable intermediate in certain reactions whereas CH_5^- is only a transition state.[8] Indeed, analogous arguments can be used to describe the bonding in 1,3-dipolar molecules containing first-row atoms, such as diazomethane. All in all, this simple *aide memoire* appears to have much to recommend it.

Spin-Coupled or Full-GVB Model

The spin-coupled description of a molecular system with N active electrons is based on a single product of N singly-occupied nonorthogonal orbitals $\phi_1, \phi_2, ..., \phi_N$ and can be written as follows:

$$\Psi_{SM} = \mathcal{A}(\Psi_{\text{core}}\, \phi_1, \phi_2, ..., \phi_N\, \Theta^N_{SM}) \qquad (1)$$

in which Ψ_{core} describes the inactive electrons. The spin function Θ^N_{SM} takes the form of a linear combination of all linearly-independent N-electron spin eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$ corresponding to quantum numbers S and M:

$$\Theta^N_{SM} = \sum_{k=1}^{f^N_S} c_{Sk} \Theta^N_{SM;k} \qquad (2)$$

The dimension of the spin space is given by

$$f^N_S = \frac{(2S+1)N!}{(^1/_2N + S + 1)!(^1/_2N - S)!} \qquad (3)$$

The coefficients c_{Sk} may be termed spin-coupling coefficients, as they reflect the particular way(s) in which the individual electron spins are coupled together so as to achieve the required resultant. The spin-coupled orbitals ϕ_μ are ultimately expanded in a suitable basis set $\{\chi_p\}$ of atom-centered functions:

$$\phi_\mu = \sum_{p=1}^{m} c_{\mu p} \chi_p \qquad (4)$$

Unlike classical valence bond theory, the spin-coupled approach does not presuppose the form of the orbitals or constrain them to be strictly one-center. Instead, each orbital is allowed to delocalize onto other centers as much or as little as is necessary to minimize the total energy. Even a very small utilization in a spin-coupled calculation of basis functions from other centers can correspond in a classical VB description to the significant utilization of large numbers of ionic structures.

An *ab initio* spin-coupled calculation consists of the variational optimization of all the coefficients $c_{\mu p}$ and c_{Sk} which appear in eqs 2 and 4. In general, this is carried out simultaneously without any constraints on the c_{Sk} and with no restrictions on the overlaps between all N, nonorthogonal spin-coupled orbitals. The spin-coupled model has now been applied to a very wide range of chemical problems. In addition, the spin-coupled wave function turns out be an excellent starting point for constructing very compact, multiconfiguration descriptions of ground and excited states (the spin-coupled valence bond model). Several reviews of spin-coupled and spin-coupled VB calculations are available, including refs 9–11.

An important general finding is that the single-configuration spin-coupled wave function (eq 1) dominates the multiconfiguration spin-coupled VB description of a ground state for all geometries. In this sense, it can be said that the further refinement of the spin-coupled model, by means of additional configurations, does not alter the essential physical picture.

The book by Pauncz[12] provides an excellent account of the most commonly employed algorithms for constructing complete sets of linearly-independent spin functions $\{\Theta^N_{SM;k}\}$. Provided we employ a full set of f^N_S functions, it is straightforward to transform the optimal mode of spin coupling, characterized by the coefficients c_{Sk} in eq 2, from one basis to another.[13,14] In the present work, we find that the Serber basis highlights particularly clearly the most interesting aspects fo the spin wave function Θ^N_{SM}. In this scheme, pairs of electrons are coupled together to generate either singlets or triplets, and then the resulting pairs are coupled sequentially, according to the usual rules for combining angular momenta, so as to obtain the correct values of S and M. The Serber spin functions are orthogonal, and so the contribution made by the spin function with index k in eq 2 to the total spin function is simply c_{Sk}^2. In many of the cases described here, the perfect-pairing Serber spin function dominates. This spin function, which coincides with the perfect-pairing spin functions in the Kotani or Rumer bases, corresponds to coupling together only singlet-coupled pairs of electron spins.

Calculations

One central aim of the present work is to investigate the supposed role of d orbitals in the bonding in hypercoordinate systems. In view of the extensive MO-based work in this area, we decided not to carry out an exhaustive study of the energy improvements that can be achieved with different sets of d functions. Of course, trying to demonstrate that d basis functions do *not* affect the spin-coupled description of the bonding in any significant way is a difficult task, as it could always be argued that the particular set of d functions we have employed is not the most appropriate. We were guided in our choice of basis sets by the very thorough investigations carried out by Magnusson,[6] who demonstrated with SCF calculations that the optimum d exponent(s) for a given element, as well as the energy improvement *per bond*, change very little from "normal" to hypercoordinate systems. In the present work, we have adopted sets of d functions with exponents typical of those used for polarization functions in calculations on molecules containing second-row atoms.

Our spin-coupled calculations for various fluorides and chlorides of phosphorus and sulfur used standard 3-21G basis sets for P/S/F/Cl. These basis sets were augmented with a set of d functions for chlorine with exponent $d_{Cl} = 0.619$. Cartesian functions (i.e. six d components) were used throughout this work. Calculations were carried out both with and without d functions on the other second-row atoms, using $d_P = 0.465$ and $d_S = 0.542$. The geometries adopted[15] for PF_3 (C_{3v}), PF_5 (D_{3h}), PCl_3 (C_{3v}), PCl_5 (D_{3h}), SF_2 (C_{2v}), SF_4 (C_{2v}, disphenoidal), SF_6 (O_h), and SCl_2 (C_{2v}) were all close to those found in standard compilations.

Following standard closed-shell SCF calculations carried out using the GAMESS-UK package,[16] the canonical valence orbitals were localized using an implementation of the population localization criterion of Pipek

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(8) Sini, G.; Ohanessian, G.; Hiberty, P. C.; Shaik, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 1409 and references therein.

(9) Cooper, D. L.; Gerratt, J.; Raimondi, M. *Adv. Chem. Phys.* **1987**, *69*, 319.

(10) Gerratt, J.; Cooper, D. L.; Raimondi, M. In *Valence bond theory and chemical structure*; Klein, D. J., Trinajstić, N., Eds.; Elsevier: New York, 1990.

(11) Cooper, D. L.; Gerratt, J.; Raimondi, M. *Chem. Rev.* **1991**, *91*, 929.

(12) Pauncz, R. *Spin eigenfunctions*; Plenum Press: New York, 1979.

(13) Raos, G.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *Mol. Phys.* **1993**, *79*, 197.

(14) Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *SPINS: A collection of algorithms for symbolic generation and transformation of many-electron spin eigenfunctions*, to be published.

(15) Geometries were taken from prior SCF geometry optimizations using 3-21G+dP+d_{Cl} for PCl_3/PCl_5, 3-21G+d_S for $SF_2/SF_4/SF_6$, and a 3-21G+d_S+d_{Cl} basis for SCl_2. A larger TZVP basis was used for PF_5/PF_3. PF_3: $r(PF) = 1.5645$ Å, $\theta(FPF) = 97.01°$. PF_5: $r(PF_{ax}) = 1.5678$ Å, $r(PF_{eq}) = 1.5317$ Å. PCl_3: $r(PCl) = 2.0463$ Å, $\theta(ClPCl) = 100.20°$. PCl_5: $r(PCl_{ax}) = 2.1456$ Å, $r(PCl_{eq}) = 2.0184$ Å. SF_2: $r(SF) = 1.5891$ Å, $\theta(FSF) = 97.13°$. SF_4: $r(SF_{ax}) = 1.6239$ Å, $r(SF_{eq}) = 1.5587$ Å, $\theta(F_{ax}SF_{ax}) = 170.02°$, $\theta(F_{eq}\text{-}SF_{eq}) = 101.50°$. SF_6: $r(SF) = 1.556$ Å. SCl_2: $r(SCl) = 2.0227$ Å, $\theta(ClSCl) = 102.18°$.

(16) Guest, M. F.; Sherwood, P. *GAMESS-UK User's Guide and Reference Manual, Revision B.0*; SERC Daresbury Laboratory: U.K., 1992.

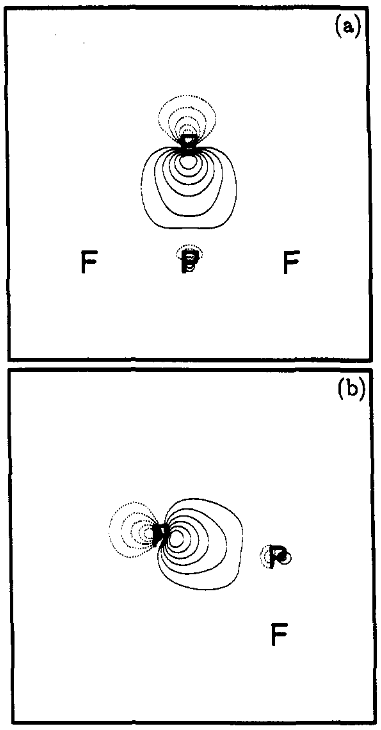

Figure 1. Contour plots[33] of LMOs corresponding to bonds (basis sets include d_P): (a) $P{-}F_{ax}$ in PF_5; (b) PF_3.

and Mezey.[17] In each case, it was straightforward to identify a localized molecular orbital (LMO) corresponding to each phosphorus–halogen or sulfur–halogen bond. For example, one of the LMOs associated with a $P{-}F_{ax}$ bond in PF_5 is shown in Figure 1a; it is very difficult for this system to distinguish between contour plots of LMOs obtained with and without the d functions on phosphorus, or between $P{-}F_{ax}$ and $P{-}F_{eq}$. For comparison, one of the LMOs corresponding to a P–F bond in PF_3 is shown in Figure 1b. Analogous plots for PCl_3 and PCl_5 are presented in Figure 2, and for SF_2, SF_4, SF_6, and SCl_2 in Figure 3. Certainly, it is difficult to make a convincing case from the form of these various LMOs for the active participation of d orbitals in the bonding in the hypercoordinate compounds.

For each system, spin-coupled calculations were carried out explicitly for those electrons involved directly in X–Y bonds (X = P, S and Y = F, Cl). In other words, the XY_2, XY_3, XY_4, XY_5, and XY_6 systems were treated as problems with 4, 6, 8, 10, and 12 active electrons, respectively. The frozen "cores" consisted of the core MOs from the SCF calculations and those valence LMOs which do not correspond to X–Y bonds. The spin-coupled orbitals were then expanded in the basis comprising those LMOs which relate to X–Y bonds, *plus* all virtual orbitals. No constraints whatsoever were placed on the overlaps between the spin-coupled orbitals or on the modes of coupling the individual electron spins so as to achieve a net singlet. In the case of SF_6, for example, this entailed optimizing 12 fully nonorthogonal orbitals and the weights of $f_S^N = 132$ spin functions. All of these calculations were carried out with a version of the spin-coupled codes which relies on the rapid computation of density matrices from cofactors, constructed *in situ* from lower-dimension minors using graphical indexing techniques.[18]

Preliminary spin-coupled calculations were carried out in a similar fashion for XeF_2 ($C_{\infty v}$), with a bond length of 1.99 Å. A 3-21G basis was used for F and for the tightly-held Xe core (1s,2s,2p). Basis functions to describe the 3s–5s, 3p–5p, and 3d–5d electrons on Xe were constructed by least-squares three-Gaussian fits to the "slightly better than double-ζ" Slater basis optimized by Bagus *et al.*[19] in their studies of XeF_2. In particular, the full basis set included three-Gaussian fits to two Xe(5d) Slater-type orbitals, with ζ values of 2.0 and 1.2. It was straightforward to identify two equivalent LMOs well-localized between the nuclei (see

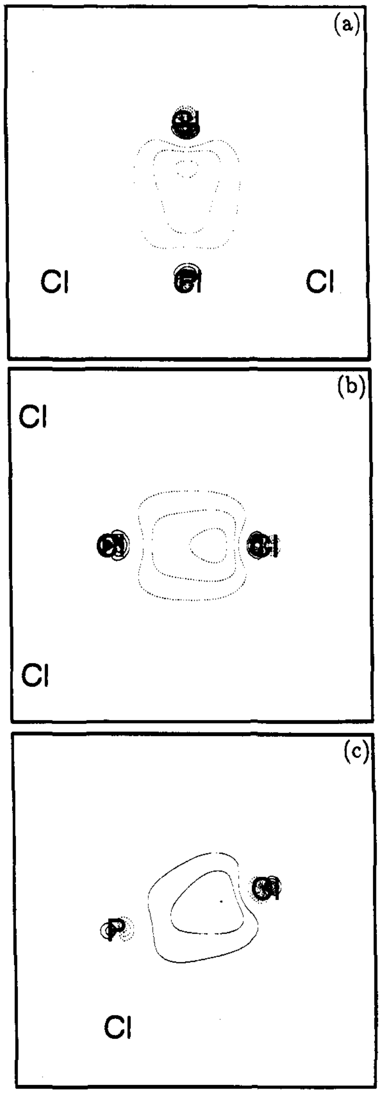

Figure 2. LMOs corresponding to bonds (basis sets include d_P): (a) $P{-}Cl_{ax}$ in PCl_5; (b) $P{-}Cl_{eq}$ in PCl_5; (c) PCl_3.

Figure 4) so that exploratory spin-coupled calculations could be carried out for just four active electrons (cf. SF_2 and SCl_2).

Spin-coupled calculations were also performed for CH_5^- (D_{3h}) and SiH_5^- (D_{3h}) using basis sets of TZVP quality.[20] This was motivated both by the quantitative curve crossing valence bond study of these systems described by Shaik and co-workers[8] and by the fact that these two anions are isoelectronic with the hypothetical hypercoordinate molecules NH_5 and PH_5. All 10 valence electrons were active in the spin-coupled calculations for these anions, with the $C(1s^2)$ and $Si(1s^22s^22p^6)$ frozen cores described by the MOs from a prior SCF calculation. As before, no constraints were placed on the overlaps between the spin-coupled orbitals or on the weights of the linearly-independent singlet spin functions, of which there are $f_S^N = 42$ in the present case. The trigonal bipyramidal SiF_5^- ion was treated in an analogous fashion to PF_5, but with a slightly larger basis set on silicon.[21] To enable comparison with the other systems described in this work, valence LMOs for CH_5^-, SiH_5^-, and SiF_5^- associated with the various bonds are presented in Figure 5.

Results

A. Phosphorus Halides. An appropriate point to start our survey of the spin-coupled results for phosphorus fluorides and

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[17] (a) Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916. (b) Cooper, D. L.; Gerratt, J.; Raimondi, M. *J. Mol. Struct.* (*THEOCHEM*) **1991**, *229*, 155.

[18] Cooper, D. L.; Gerratt, J.; Raimondi, M.; Sironi, M.; Thorsteinsson, T. *Theor. Chim. Acta* **1993**, *85*, 261.

[19] Bagus, P. S.; Liu, B.; Liskow, D. H.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1975**, *97*, 7216.

[20] Trigonal bipyramidal (D_{3h}) geometries were taken from standard closed-shell SCF geometry optimizations using the TZVP basis sets stored internally in the GAMESS-UK package (ref 15). CH_5^-: $r(CH_{ax}) = 1.7319$ Å, $r(CH_{eq}) = 1.0595$ Å. SiH_5^-: $r(SiH_{ax}) = 1.6250$ Å, $r(SiH_{eq}) = 1.5243$ Å. These geometries are very similar to those used in ref 8.

[21] Basis set: 6-31G on Si; 3-21G on F; $d_{Si} = 0.388$. Geometry, optimized at the SCF level: $r(Si{-}F_{ax}) = 1.6524$ Å; $r(Si{-}F_{eq}) = 1.6226$ Å.

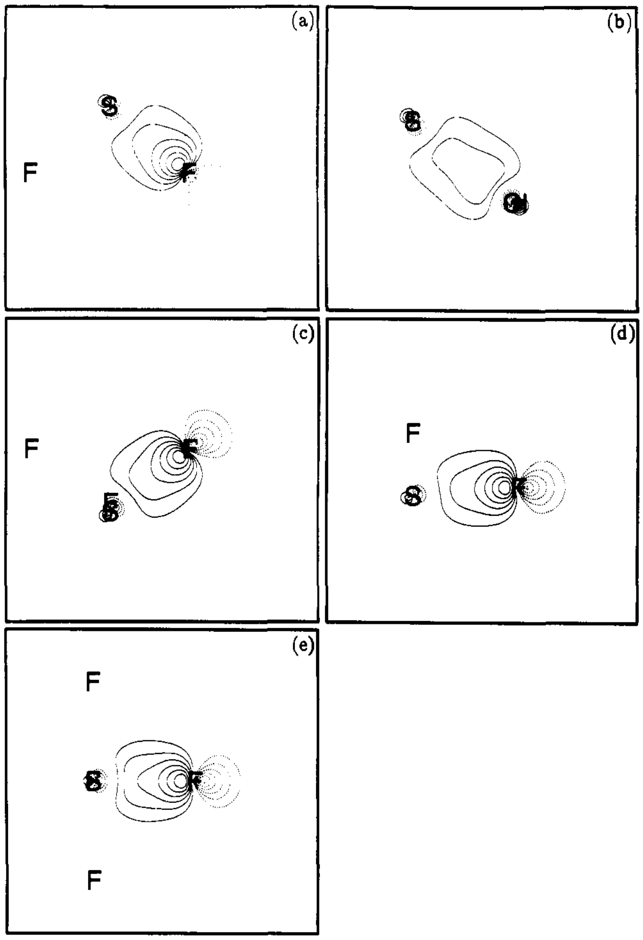

Figure 3. LMOs corresponding to bonds in sulfur halides (basis sets include d_S): (a) SF_2; (b) SCl_2; (c) S–F_{eq} in SF_4; (d) S–F_{ax} in SF_4; (e) SF_6.

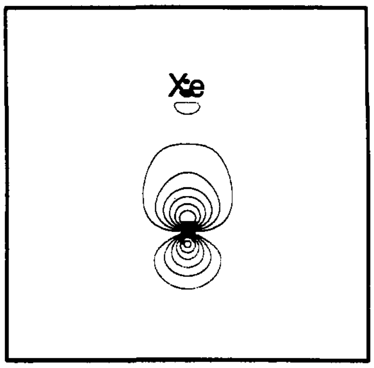

Figure 4. Bond LMO for XeF_2 (with Xe(5d) functions).

chlorides is with the "classical" hypercoordinate species PF_5. In the popular dsp^3 model of the bonding in this trigonal bipyramidal molecule, the three equatorial bonds are considered to be very different from the two axial bonds, being based on P(sp^2) and P(pd) hybrids, respectively. This is in spite of the fact that the two sets of bond lengths are very similar, differing by no more than one might have anticipated from the different steric repulsions experienced by the fluorine atoms in the two types of environment. The two sets of ^{19}F chemical shifts are also remarkably similar. For the dsp^3 model still to be taken seriously, we would expect clear qualitative differences between the spin-coupled orbitals for the two sets of bonds, as well as a clear distinction in the response of these orbitals to the removal of all d functions on phosphorus.

The spin-coupled solution for the 10 active electrons in PF_5 consists, of course, of 10 distinct singly-occupied orbitals, all of

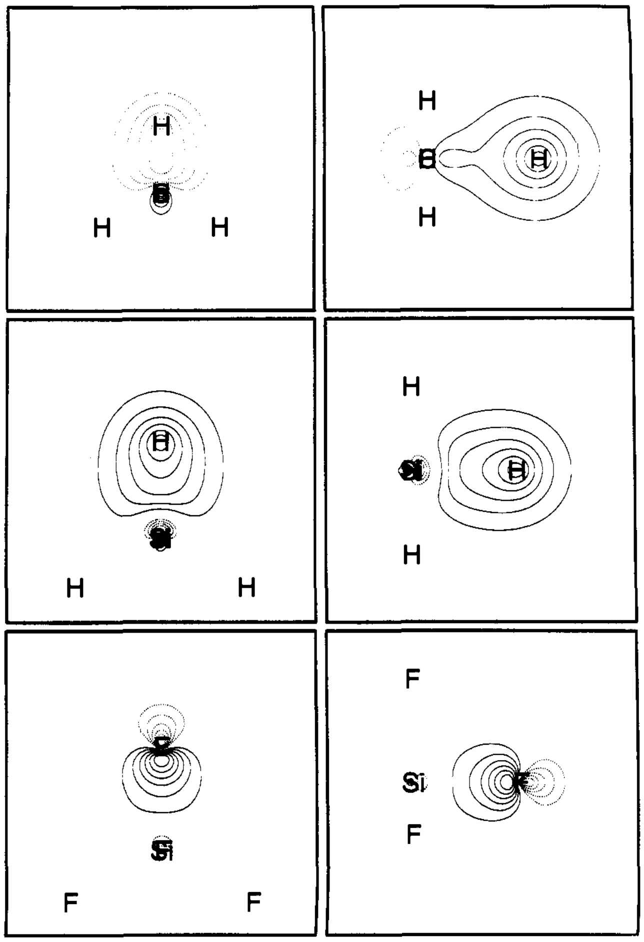

Figure 5. LMOs corresponding to bonds in CH_5^- (top row), SiH_5^- (middle row), and SiF_5^- (bottom row), for basis sets which include d functions. The first column relates to equatorial bonds and the second one to axial.

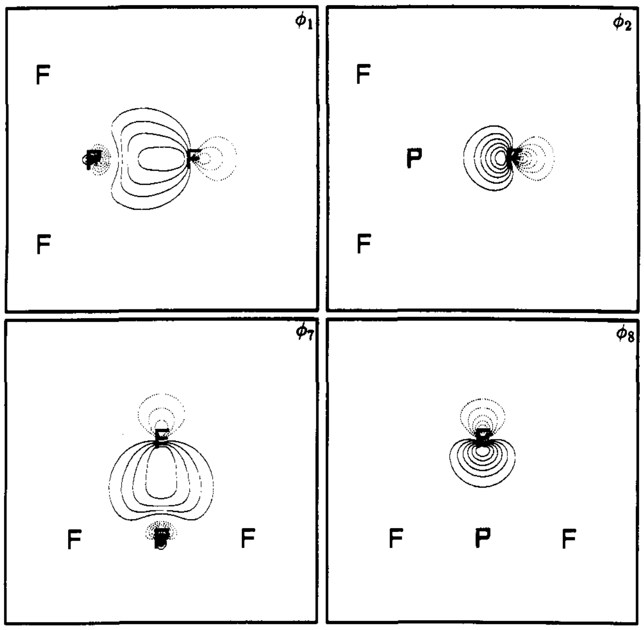

Figure 6. Spin-coupled orbitals for PF_5 (with d_P).

which are allowed to overlap with one another. Although no such constraints were invoked in the calculation, it turns out that the optimized wave function consists of pairs of well-localized orbitals, each associated with a particular P–F bond. This helps make the interpretation of the spin-coupled wave function in terms of classical concepts particularly straightforward. We find that

Table 1. Overlap Integrals between the Spin-Coupled Orbitals for PF_5

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}
				(a) Basis Set Including d_P = 0.465						
ϕ_1	1									
ϕ_2	0.84	1								
ϕ_3	0.14	0.03	1							
ϕ_4	0.03	–0.01	0.84	1						
ϕ_5	0.14	0.03	0.14	0.03	1					
ϕ_6	0.03	–0.01	0.03	–0.01	0.84	1				
ϕ_7	0.23	0.07	0.23	0.07	0.23	0.07	1			
ϕ_8	0.07	0.00	0.07	0.00	0.07	0.00	0.83	1		
ϕ_9	0.23	0.07	0.23	0.07	0.23	0.07	0.05	0.01	1	
ϕ_{10}	0.07	0.00	0.07	0.00	0.07	0.00	0.01	0.01	0.83	1
				(b) No d Functions on Phosphorus						
ϕ_1	1									
ϕ_2	0.83	1								
ϕ_3	0.17	0.05	1							
ϕ_4	0.05	0.01	0.83	1						
ϕ_5	0.17	0.05	0.17	0.05	1					
ϕ_6	0.05	0.01	0.05	0.01	0.83	1				
ϕ_7	0.29	0.10	0.29	0.10	0.29	0.10	1			
ϕ_8	0.10	0.03	0.10	0.03	0.10	0.03	0.83	1		
ϕ_9	0.29	0.10	0.29	0.10	0.29	0.10	0.05	0.02	1	
ϕ_{10}	0.10	0.03	0.10	0.03	0.10	0.03	0.02	0.01	0.83	1

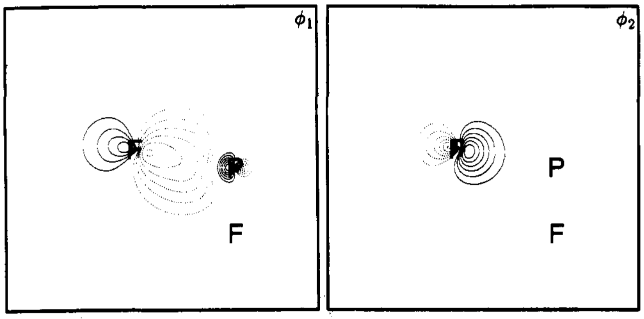

Figure 7. Spin-coupled orbitals for PF_3 (with d_P).

Table 2. Overlap Integrals between the Spin-Coupled Orbitals for PF_3

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
			(a) Basis Set Including d_P = 0.465			
ϕ_1	1					
ϕ_2	0.85	1				
ϕ_3	0.12	0.03	1			
ϕ_4	0.03	0.00	0.85	1		
ϕ_5	0.12	0.03	0.12	0.03	1	
ϕ_6	0.03	0.00	0.03	0.00	0.85	1
			(b) No d Functions on Phosphorus			
ϕ_1	1					
ϕ_2	0.84	1				
ϕ_3	0.15	0.05	1			
ϕ_4	0.05	0.01	0.84	1		
ϕ_5	0.15	0.05	0.15	0.05	1	
ϕ_6	0.05	0.01	0.05	0.01	0.84	1

Table 3. Summary of Calculated Energies for Phosphorus, Sulfur, and Xenon Halides[a]

		total energy/hartree		ΔE_d/eV	
system	basis	SCF	SC	SCF	SC
PF_3	no d_P	–635.769 669	–635.820 884		
PF_3	full basis	–635.932 443	–635.984 869	1.48	1.49
PF_5	no d_P	–833.571 566	–833.657 911		
PF_5	full basis	–833.828 003	–833.917 471	1.40	1.41
PCl_3	no d_P	–1711.180 211	–1711.215 632		
PCl_3	full basis	–1711.309 717	–1711.344 774	1.17	1.17
PCl_5	no d_P	–2625.855 293	–2625.914 685		
PCl_5	full basis	–2626.049 819	–2626.113 000	1.06	1.08
SF_2	no d_S	–593.279 752	–593.327 241		
SF_2	full basis	–593.408 264	–593.454 723	1.75	1.73
SCl_2	no d_S	–1310.286 260	–1310.317 982		
SCl_2	full basis	–1310.399 559	–1310.429 737	1.54	1.52
SF_4	no d_S	–790.964 818	–791.047 458		
SF_4	full basis	–791.201 078	–791.286 751	1.61	1.63
SF_6	no d_S	–988.674 037	–988.799 012		
SF_6	full basis	–989.042 001	–989.173 720	1.67	1.70
XeF_2	no Xe(5d)	–7403.407 105	–7403.458 269		
XeF_2	full basis	–7403.522 070	–7403.571 782	1.56	1.54
SiF_5^-	no d_{Si}	–783.748 209	–783.823 281		
SiF_5^-	full basis	–783.880 737	–783.959 863	0.72	0.74

[a] Further details are given in the text. The quantity labeled ΔE_d is the energy improvement *per bond* due to including a d function on the central atom.

the pairs of orbitals corresponding to equivalent bonds transform into one another under appropriate symmetry operations of the molecular point group, so that the overall wave function belongs to the A_1' irreducible representation of the D_{3h} point group.

Spin-coupled orbitals ϕ_1 and ϕ_2 constitute one of the equatorial P–F bonds; (ϕ_3,ϕ_4) and (ϕ_5,ϕ_6) are the symmetry-related counterparts in the other two equatorial bonds. Similarly, orbitals ϕ_7 and ϕ_8 describe one of the axial P–F bonds, whereas ϕ_9 and ϕ_{10} are the symmetry-related counterparts in the other axial bond. The forms of the four symmetry-unique spin-coupled orbitals are illustrated in Figure 6. These have been taken from those calculations which included a set of d functions on phosphorus. The equivalent contour plots for the calculations which excluded d functions on phosphorus are remarkably similar and consequently have not been presented. Perhaps even more remarkable is the striking resemblance between orbitals ϕ_1 (equatorial) and ϕ_7 (axial), each of which takes form of the admixture of an sp^x-like hybrid on P and a distorted 2p function on F. The "partners" to these two orbitals, i.e. ϕ_2 and ϕ_8, take the form of distorted 2p functions on fluorine. There is certainly no evidence here for significant involvement of d orbitals in the bonding or for any clear distinction between the axial and equatorial bonds. All five P–F bonds are clearly highly polar.

As is to be expected, one of the f_S^N = 42 singlet spin functions overwhelmingly dominates. We find that the perfect-pairing spin function, in which there is a singlet-coupled pair associated with each bond, contributes 99.90% of the total spin function. Removing d functions from phosphorus reduces this contribution only very slightly (99.80% of the total spin function).

The overlap matrices from the two sets of calculations are very informative (see Table 1). First of all, the overlaps within the pairs which constitute a P–F bond show very little variation, and removing d functions from phosphorus makes very little difference. The overlap between orbitals ϕ_7 and ϕ_9, which include contributions from the axial phosphorus hybrids, is very small. The overlaps between the equatorial phosphorus + fluorine hybrids (i.e. $\langle\phi_3|\phi_1\rangle$, $\langle\phi_5|\phi_1\rangle$, and $\langle\phi_5|\phi_3\rangle$) are somewhat larger, but the largest of these overlap integrals occur ***between*** the axial and equatorial hybrids (e.g. $\langle\phi_7|\phi_1\rangle$). All of these "between bond" overlaps were slightly larger in the calculation which excluded d functions.

It is difficult to discern any difference between the parentage of ϕ_1 and ϕ_7, the equatorial and axial phosphorus + fluorine hybrids, which are split almost equally between P and F. Orbitals ϕ_2 and ϕ_8, which are the partners to these hybrids, are almost exclusively fluorine orbitals, with no discernible difference between the two calculations. These various observations reinforce our previous comments about the high polarity of these bonds.

It is very informative at this stage to compare PF_5 with the "normal octet" case of PF_3. We find that the optimal spin-coupled orbitals for the six active electrons in PF_3 take the form of three symmetry-related pairs. Orbitals from the calculations which included a set of d functions on P are shown in Figure 7; those from the calculations which excluded d functions are almost indistinguishable by eye. Orbital ϕ_1 is a combination of an sp^x-like hybrid on P and a distorted 2p function of F. Its partner, ϕ_2, can be recognized as a distorted 2p function on F. Orbitals

Table 4. Overlap Integrals between the Spin-Coupled Orbitals for PCl_3[a]

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
ϕ_1	1					
ϕ_2	0.82	1				
ϕ_3	0.18	0.02	1			
ϕ_4	0.02	−0.07	0.82	1		
ϕ_5	0.18	0.02	0.18	0.02	1	
ϕ_6	0.02	−0.07	0.02	−0.07	0.82	1

[a] The basis set included d_P = 0.465.

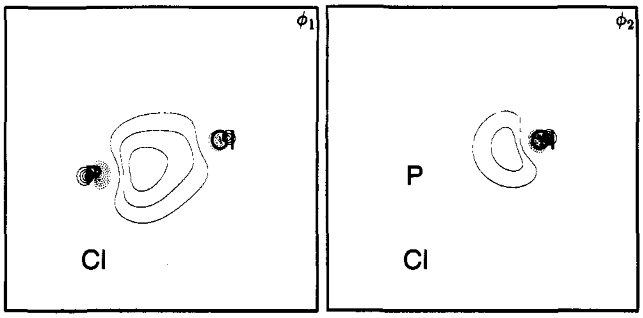

Figure 8. Spin-coupled orbitals for PCl_3 (with d_P).

(ϕ_3,ϕ_4) and (ϕ_5,ϕ_6) are the counterparts of these in the other P–F bonds. Orbital ϕ_1 is fairly equally split between P and F; excluding d functions leads to a small shift toward fluorine.

The perfect-pairing spin function dominates, with a contribution of 99.96% to the total spin function. As for PF_5, this dominance is reduced very slightly on excluding d functions (99.86%). The small changes in the overlap matrices resulting from the removal of the phosphorus d functions (see Table 2) mirror exactly the situation already described for PF_5.

Total SCF and spin-coupled energies from the two sets of calculations, and indeed, for all of the halides described in the present work, are collected in Table 3. The energy improvement, per P–F bond, due to incorporation of the d functions on phosphorus is 1.4 eV in PF_5 but 1.5 eV in PF_3. Not only do we find no evidence to support notions of significant d involvement in the bonding in PF_5, or for any clear distinction in bonding character between axial and equatorial bonds, but it also appears to be the case that the set of phosphorus d functions employed here is no more important to the description of the hypercoordinate molecule PF_5 than it is for that of the "normal" PF_3 molecule.

An energy penalty per bond of 1.5 eV is certainly large, when compared with typical bond energies. However, it is important to bear in mind that the net effect on the calculated energy change in an isodesmic reaction would be very much smaller, simply because of the way in which the energy penalty on removing d functions affects the various reactants and products.

The different electronegativities of fluorine and chlorine atoms are reflected in some significant differences between the spin-coupled descriptions of the phosphorus fluorides and phosphorus chlorides, although our general conclusions regarding d orbital nonparticipation are much the same. In the discussion that follows, all quantities and figures related to calculations which incorporated a set of d functions on phosphorus, unless otherwise stated. The spin-coupled calculations for the six active electrons in PCl_3 converged to three symmetry-related pairs, each associated with a particular P–Cl bond. The overlap integrals are listed in Table 4. The perfect-pairing spin function dominates, contributing 99.22% with d_P and 98.12% without.

Orbital ϕ_1 for PCl_3 is shown in Figure 8. It takes the form of an sp^x-like hybrid on phosphorus, noticeably extended toward a chlorine atom, but without much obvious Cl(3p) parentage. The corresponding orbital in PF_3 (ϕ_1 in Figure 7) has significant F(2p) character, and it is much more obviously delocalized over two atoms. Orbital ϕ_2 for PCl_3 also exhibits significant differences from the corresponding orbital in PF_3; although it is centered on the chlorine atom, this orbital is much more distorted toward the phosphorus atom and it is far more asymmetric than is the case for PF_3. It is possible by eye to distinguish contour plots with and without d_P, but there are no significant changes in shape or degree of delocalization. Removing d functions from phosphorus results in small changes in the overlap matrix, such that $\langle\phi_2|\phi_1\rangle$ = 0.80 and $\langle\phi_3|\phi_1\rangle$ = 0.25, for example. These changes are slightly larger than in the corresponding case of PF_3. Nevertheless, the energy lowering per P–Cl bond on including d_P is only 1.2 eV, to be compared with 1.5 eV for PF_3 (see Table 3).

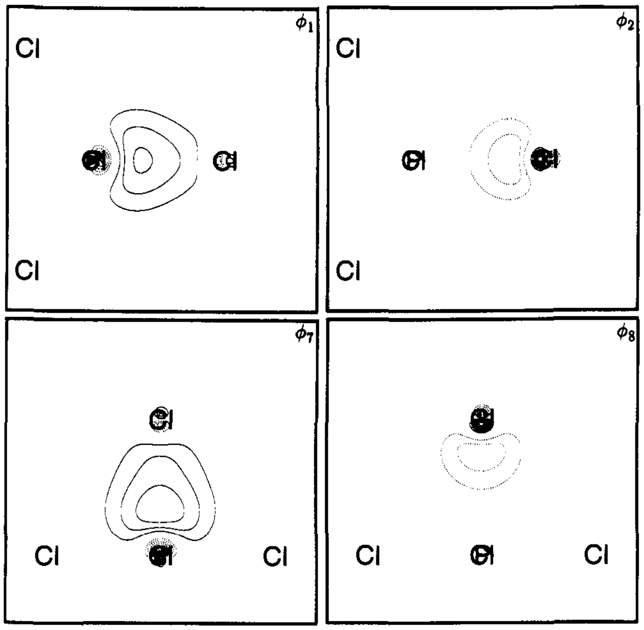

Figure 9. Spin-coupled orbitals for PCl_5 (with d_P).

Table 5. Overlap Integrals between the Spin-Coupled Orbitals for PCl_5[a]

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}
ϕ_1	1									
ϕ_2	0.74	1								
ϕ_3	0.27	−0.01	1							
ϕ_4	−0.01	−0.10	0.74	1						
ϕ_5	0.27	−0.01	0.27	−0.01	1					
ϕ_6	−0.01	−0.10	−0.01	−0.10	0.74	1				
ϕ_7	0.35	0.03	0.35	0.03	0.35	0.03	1			
ϕ_8	0.01	−0.15	0.01	−0.15	0.01	−0.15	0.71	1		
ϕ_9	0.35	0.03	0.35	0.03	0.35	0.03	0.00	−0.05	1	
ϕ_{10}	0.01	−0.15	0.01	−0.15	0.01	−0.15	−0.05	0.08	0.71	1

[a] The basis set included d_P = 0.465.

The qualitative forms of the orbitals for PCl_5 (see Figure 9) are much the same as those just described for PCl_3. In spite of this, the overlaps within "bond pairs" are noticeably smaller than in PCl_3, and there are larger overlaps between the different phosphorus hybrids than was previously the case (Table 5). As shown in Table 3, the energy lowering per P–Cl bond on including the d functions on phosphorus (1.1 eV) is slightly less than for PCl_3. With the orbitals ordered in the same way as for PF_5, the perfect-pairing spin function dominates: 97.53% of the spin function with d_P[22] or 97.41% without. Although high, these contributions are not quite as large as for PF_3, PF_5, and PCl_3. Overall, the differences between PCl_5 and PCl_3 are larger than those between PF_5 and PF_3, but this appears to have much more to do with differences in electronegativity (and, perhaps, with the physical size of the halogen atoms) than with any supposed active participation in the bonding by P(3d) orbitals.

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(22) The next most important contributions, of 0.59% each, correspond to the three equivalent ways of assigning singlet character to one of the equatorial bonding pairs, with *all* of the other pairs triplet-coupled.

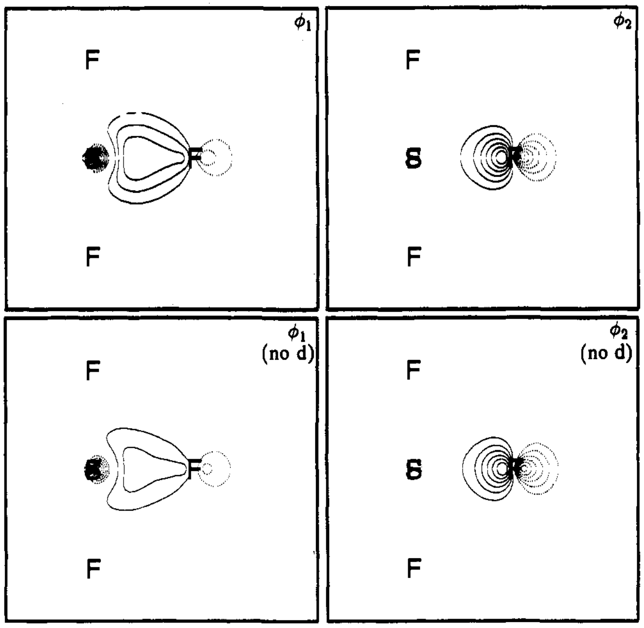

Figure 10. Spin-coupled orbitals for SF_6. d_S was included only for the top two frames.

B. Sulfur Fluorides. The conventional "expanded octet" model of the bonding in SF_6 invokes six equivalent d^2sp^3 hybrid orbitals on the central atom, overlapping with appropriate 2p functions on the peripheral atoms. According to this scheme, d orbital participation should be larger in SF_6 than in PF_5 or SF_4. The geometry of this last molecule is reminiscent of a (distorted) trigonal bipyramid, with a lone pair occupying an equatorial site. It should be particularly interesting to compare the spin-coupled descriptions of the hypercoordinate species SF_6 and SF_4 with the "normal octet" molecule SF_2.

As might be expected from the results already described for PF_3 and PF_5, the spin-coupled calculations for all three sulfur fluorides converged to symmetry-related pairs of orbitals, localized in the various S–F bonds. Spin-coupled orbitals ϕ_1 and ϕ_2 for SF_6 are shown in Figure 10. Orbitals ϕ_3–ϕ_{12} can be obtained from these by symmetry operations of the molecular point group. Orbitals ϕ_1, ϕ_3, ϕ_5, ϕ_7, ϕ_9, and ϕ_{11} are based on six equivalent sp^x-like hybrids on sulfur, but each of them also has significant F(2p) participation. Although these orbitals have obvious two-center character, they exhibit less delocalization onto F than was the analogous case for PF_5. Orbital ϕ_2 (and similarly ϕ_4, ϕ_6, ϕ_8, ϕ_{10}, and ϕ_{12}) takes the form of a distorted 2p function on fluorine and overlaps almost exclusively with the sulfur + fluorine hybrid which points toward it (see Table 6). The six sulfur + fluorine hybrids all overlap with one another ($\langle\phi_1|\phi_3\rangle = 0.28$, increasing to 0.38 without d_S). The perfect-pairing spin function dominates the total spin function, with a contribution of 99.41%. Removing the d functions from sulfur results in small changes in the form of the sulfur + fluorine hybrid orbitals (see Figure 10), in the overlap matrix (see Table 6) and in the contribution from the perfect-pairing spin function (98.85%). These modest changes are entirely analogous to those described earlier for PF_5. As shown in Table 3, the energy improvement per S–F bond on adding d_S is approximately the same for SF_6 and SF_2.

Starting from atomic orbitals 3s, $3p_x$, $3p_y$, and $3p_z$ on sulfur, we can, at most, form *four* linearly independent strictly localized hybrid orbitals, with maximum occupancy corresponding to the eight-electron rule. However, orbitals ϕ_1, ϕ_3, ϕ_5, ϕ_7, ϕ_9, ϕ_{11} in SF_6 are not linearly dependent, precisely because each of them contains a significant amount of F(2p) character. In addition, of course, *radial* correlation in the atomic functions, leading to distinct 3s,3s′ and 3p,3p′ groups of orbitals, reduces the likelihood of linear dependence.

The overlap matrix between the optimal orbitals from spin-coupled calculations on SF_4 with eight active electrons, and including $d_S = 0.542$, is presented in Table 7. We find that the symmetry-related pairs (ϕ_1,ϕ_2) and (ϕ_3,ϕ_4) describe the equatorial bonds, whereas (ϕ_5,ϕ_6) and (ϕ_7,ϕ_8) correspond to the axial bonds. Contour plots of orbitals ϕ_1, ϕ_2, ϕ_5, and ϕ_6 are presented in Figure 11. The perfect-pairing spin function contributes 99.87% of the total spin function. It is clear that our description of the S–F bonds in SF_4 is qualitatively very similar to that for the bonding in SF_6.

The changes resulting from removing the set of d functions from the sulfur atom in SF_4 are somewhat predictable, given the behavior of the other species which we have described. The contour plots of the orbitals change very little, and the weight of the perfect-pairing spin function is very slightly reduced (99.69%). The "bonding" overlaps decrease slightly ($\langle\phi_2|\phi_1\rangle = 0.79$, equatorial, and $\langle\phi_6|\phi_5\rangle = 0.80$, axial). The overlaps between different sulfur + fluorine hybrids increase in magnitude: $\langle\phi_3|\phi_1\rangle = 0.19$, $\langle\phi_5|\phi_1\rangle = 0.27$, and $\langle\phi_7|\phi_5\rangle = -0.21$. The energy lowering per bond due to the inclusion of d_S is 1.6 eV, to be compared with 1.7 eV in SF_2.

The only obvious difference between SF_4 and any of the other fluorides considered so far is the small unfavorable (i.e. negative) overlap between the two axial sulfur + fluorine hybrids ($\langle\phi_7|\phi_5\rangle = -0.15$). By performing an eight-electron spin-coupled calculation in the manner described here, orbitals ϕ_5 and ϕ_7 have both been constrained to be orthogonal to the doubly-occupied sulfur-based LMO occupying the third equatorial site of the distorted trigonal bipyramid. It is plausible, therefore, that the unfavorable overlap could be an artifact of the calculations. With this in mind, we have carried out further spin-coupled calculations for SF_4 with 10 active electrons: the two nonbonding electrons on sulfur were treated on an equal footing with the eight electrons associated with the S–F bonds. Dealing with the extra two electrons does lead to small modifications in the orbital overlaps, but there are no significant changes to the spin-coupled description of the S–F bonds. The overlap between the two axial sulfur + fluorine hybrids remains unfavorable, but the magnitude is reduced ($\langle\phi_7|\phi_5\rangle = -0.05$).

It is convenient to describe together our spin-coupled results for SF_2 and SCl_2, because there are important differences between them. Orbitals ϕ_1 and ϕ_2, for both species, are shown in Figure 12; ϕ_3 and ϕ_4 are the counterparts of these in the other sulfur–halogen bond. The various overlap integrals are recorded in Table 8. The perfect-pairing spin function dominates in each case: 99.94% for SF_2 and 99.50% for SCl_2. The consequences of removing the d functions from sulfur are entirely analogous to those described for all the other systems we have examined.

The spin-coupled description of SF_2 presents no surprises. Orbital ϕ_1 consists predominantly of S(sp^x) plus F(2p), whereas ϕ_2 resembles a distorted 2p function on fluorine. In view of the changes we have already described between PF_5 and PCl_5 or between PF_3 and PCl_3 (Figures 6–9), it is reasonable to envisage that orbital ϕ_1 in SCl_2 will exhibit very little Cl(3p) character. This is indeed the case, although there is somewhat more sulfur character in SCl_2 than there is phosphorus character in PCl_3 and PCl_5. The form of orbital ϕ_2 in SCl_2 is much the same as that of the analogous orbitals in PCl_3 and PCl_5. The differences in the form of ϕ_1 between SF_2 and SCl_2 appear to be larger than those between PF_3 and PCl_3 or between PF_5 and PCl_5. We believe that this behavior can be rationalized, to a large extent, in terms of the different electronegativities of phosphorus and sulfur, such that the S–Cl bond is less polar than are the other sulfur–halogen or phosphorus–halogen bonds we have encountered. This is a general theme to which we shall return later.

The spin-coupled description of the bonding in hypercoordinate species such as PF_5, PCl_5, SF_4, and SF_6 appears to have much more to do with polar bonds than with d orbital participation.

Table 6. Overlap Integrals between the Spin-Coupled Orbitals for SF_6

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}	ϕ_{11}	ϕ_{12}
(a) Basis Set Including d_S = 0.542												
ϕ_1	1											
ϕ_2	0.79	1										
ϕ_3	0.05	0.00	1									
ϕ_4	0.00	0.01	0.79	1								
ϕ_5	0.28	0.07	0.28	0.07	1							
ϕ_6	0.07	-0.02	0.07	-0.02	0.79	1						
ϕ_7	0.28	0.07	0.28	0.07	0.28	0.07	1					
ϕ_8	0.07	-0.02	0.07	-0.02	0.07	-0.02	0.79	1				
ϕ_9	0.28	0.07	0.28	0.07	0.05	0.00	0.28	0.07	1			
ϕ_{10}	0.07	-0.02	0.07	-0.02	0.00	0.01	0.07	-0.02	0.79	1		
ϕ_{11}	0.28	0.07	0.28	0.07	0.28	0.07	0.05	0.00	0.28	0.07	1	
ϕ_{12}	0.07	-0.02	0.07	-0.02	0.07	-0.02	0.00	0.01	0.07	-0.02	0.79	1
(b) No d Functions on Sulfur												
ϕ_1	1											
ϕ_2	0.77	1										
ϕ_3	0.07	0.00	1									
ϕ_4	0.00	0.02	0.77	1								
ϕ_5	0.38	0.12	0.38	0.12	1							
ϕ_6	0.12	0.01	0.12	0.01	0.77	1						
ϕ_7	0.38	0.12	0.38	0.12	0.38	0.12	1					
ϕ_8	0.12	0.01	0.12	0.01	0.12	0.01	0.77	1				
ϕ_9	0.38	0.12	0.38	0.12	0.07	0.00	0.38	0.12	1			
ϕ_{10}	0.12	0.01	0.12	0.01	0.00	0.02	0.12	0.01	0.77	1		
ϕ_{11}	0.38	0.12	0.38	0.12	0.38	0.12	0.07	0.00	0.38	0.12	1	
ϕ_{12}	0.12	0.01	0.12	0.01	0.12	0.01	0.00	0.02	0.12	0.01	0.77	1

Table 7. Overlap Integrals between the Spin-Coupled Orbitals for SF_4[a]

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8
ϕ_1	1							
ϕ_2	0.81	1						
ϕ_3	0.14	0.03	1					
ϕ_4	0.03	-0.01	0.81	1				
ϕ_5	0.20	0.06	0.20	0.06	1			
ϕ_6	0.05	-0.01	0.05	-0.01	0.81	1		
ϕ_7	0.20	0.06	0.20	0.06	-0.15	-0.05	1	
ϕ_8	0.05	-0.01	0.05	-0.01	-0.05	0.00	0.81	1

[a] The basis set included d_S = 0.542.

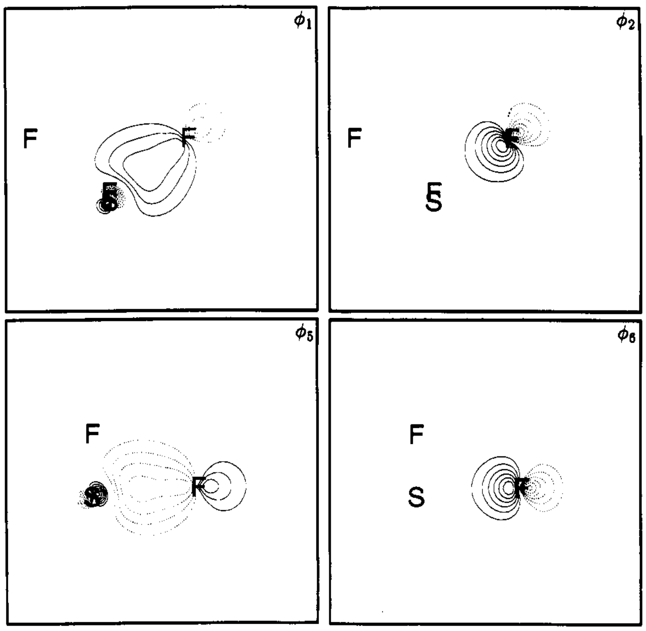

Figure 11. Spin-coupled orbitals for SF_4 (with d_S).

Extrapolating from SF_4 to SCl_4 the differences observed between SF_2 and SCl_2, we were tempted to predict that SCl_4 should not be a hypercoordinate molecule. As such, it came as an unpleasant surprise to learn that SCl_4 is well-known (at least below -30 °C) to inorganic chemists. However, it turns out that this poorly characterized compound is generally formulated as $SCl_3^+Cl^-$, rather than as a disphenoidal hypercoordinate species analogous to SF_4.

C. **Xenon Difluoride.** We have seen that when provided with suitable bonding partners, all five of the valence electrons on phosphorus can take part in covalent bonding using only sp^x-like hybrids. Similarly, the central atom in SF_6 contributes six equivalent sp^x-like hybrids (plus F(2p) character) without any recourse to d orbitals. It appears that all six of the valence electrons can take part in the bonding. Notions of exceeding an octet or of achieving the nearest noble gas configuration appear be of little relevance here. Consequently, it seems entirely reasonable to suppose that even a noble gas atom could be coaxed into forming covalent bonds of a similar nature to those in, say, PF_5 and SF_6. It is well established that ArF_2 does not exist in the gas phase and that KrF_2 is very transient in nature, whereas XeF_2 is quite "stable". With this in mind, we have carried out exploratory spin-coupled calculations for XeF_2 (as a species with four active electrons) to look for similarities with the fluorides of phosphorus and sulfur.

Our spin-coupled calculations for four active electrons in XeF_2 converged to two symmetry-related pairs of orbitals, as one might expect, with the perfect-pairing spin function dominating the total spin function (99.01%). Excluding both sets of 5d functions from Xe reduces this contribution to 97.53% and also incurs an energy penalty of 1.5 eV per Xe–F bond (see Table 3). It is clear from the forms of ϕ_1 and ϕ_2 shown in Figure 13 that there are marked similarities between this spin-coupled description of Xe–F bonds and those of, say, P–F or S–F bonds. The 5d functions on Xe do appear to have a slightly larger qualitative effect on ϕ_1 than do the d functions in the phosphorus and sulfur fluorides, although the changes in the orbital overlaps are fairly small (see Table 9). There is no obvious sign of actual d orbital participation in the bonding: ϕ_1 resembles an admixture of Xe(sp^x) and F(2p), and ϕ_2 takes the form of a distorted 2p function on fluorine. The two-center character of orbital ϕ_1 reflects the highly polar character of these bonds.

A recurring theme in hypercoordinate systems is the occurrence of polar bonds, with electron density shifted away from the central atom onto highly electronegative peripheral atoms. Bearing in mind what we have already said about ArF_2, KrF_2, and XeF_2,

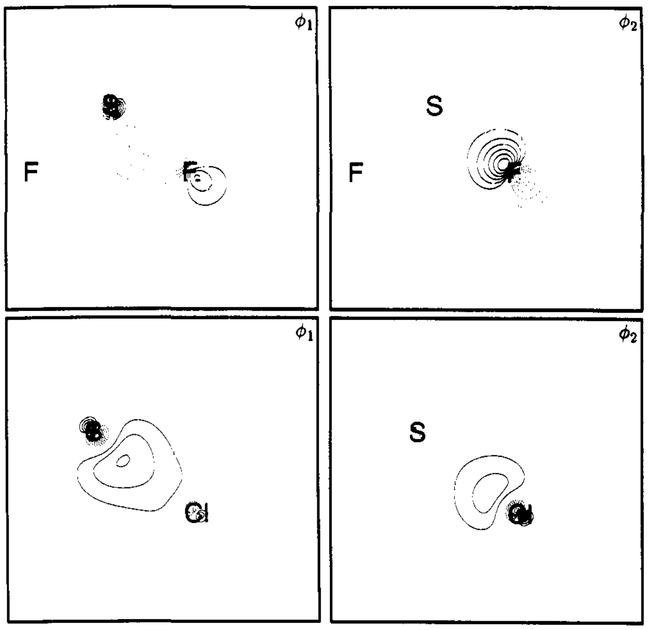

Figure 12. Spin-coupled orbitals for SF_2 (top row) and SCl_2 (bottom row), with d_S.

Table 8. Overlap Integrals between the Spin-Coupled Orbitals for SX_2 Molecules (X = F, Cl)[a]

	ϕ_1	ϕ_2	ϕ_3	ϕ_4
		(a) SF_2		
ϕ_1	1			
ϕ_2	0.80	1		
ϕ_3	0.14	0.03	1	
ϕ_4	0.03	-0.01	0.80	1
		(b) SCl_2		
ϕ_1	1			
ϕ_2	0.79	1		
ϕ_3	0.21	0.03	1	
ϕ_4	0.03	-0.09	0.79	1

[a] The basis set included $d_S = 0.542$.

it is relatively easy to rationalize why $XeCl_2$ and $XeCl_4$ turn out to be too unstable to be properly characterized.

It appears that two fluorine atoms can provide a sufficient energetic incentive for two of the valence electrons in xenon to take part in bonding, *in much the same way* as six fluorine atoms coax sulfur into utilizing all six valence electrons in SF_6. We expect the bonding in XeF_4 to be very similar. However, it turns out that six fluorine atoms cannot provide sufficient incentive for xenon to utilize six of its valence electrons in Xe–F bonds, although a formal oxidation state of +VI is achieved in the XeF_7^- and XeF_8^{2-} ions. XeF_6 is not a standard hypercoordinate species: it is a nonrigid fluxional molecule in the gas phase, and crystals of this compound tend to be based on XeF_5^+ units bridged by F^- ions (cf. SCl_4). High formal oxidation states of +VI and even +VIII, in which the xenon atom can be envisaged to be using all eight valence electrons in bonding, can be achieved with double bonds to oxygen atoms (e.g. $XeOF_4$, XeO_4, SeO_3F_2). This suggests that (doubly-bonded) oxygen atoms are at least as effective partners in hypercoordinate bonding as are fluorine atoms.

One does not have to search very hard in the chemistry of second-row main group nonmetals for hypercoordinate species with polar X=O double bonds in which the central atom utilizes all of its valence electrons in bonding (e.g. H_3PO_4, H_2SO_4, $HClO_4$). One further consequence of this general line of reasoning is that hypercoordinate compounds of first-row atoms are more likely to feature polar X=O double bonds than large numbers of fluorine atoms. The latter situation would, in any case, lead to serious problems of overcrowding. Both arguments support the notion that $NO_2(OH)$ is a much more plausible candidate as a hypercoordinate molecule than NF_5. Of course, molecules such as HNO_3, NF_3O, or $C_6H_5NO_2$ are not conventionally represented with five bonds around the central nitrogen atom, even if the geometries and other properties are consistent with this idea.

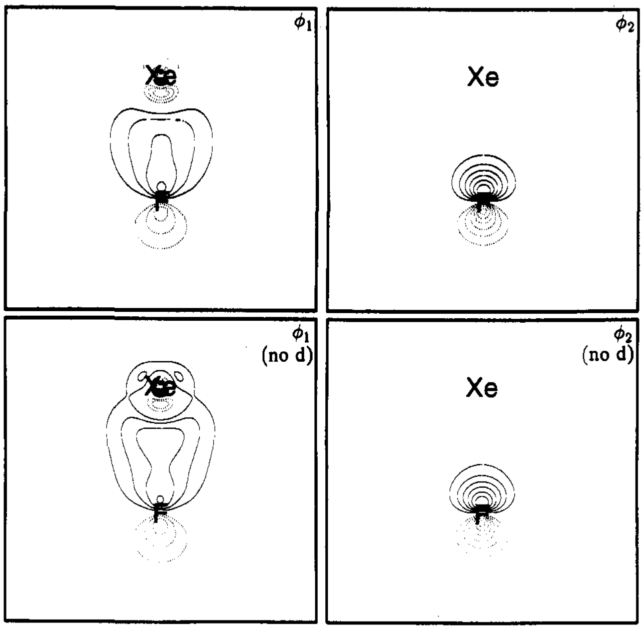

Figure 13. Spin-coupled orbitals for XeF_2. Xe(5d) functions were included only for the top two frames.

Table 9. Overlap Integrals between the Spin-Coupled Orbitals for XeF_2

	ϕ_1	ϕ_2	ϕ_3	ϕ_4
		(a) XeF_2: Full Basis Set		
ϕ_1	1			
ϕ_2	0.77	1		
ϕ_3	0.38	0.10	1	
ϕ_4	0.10	0.06	0.77	1
		(b) XeF_2: No 5d's on Xe		
ϕ_1	1			
ϕ_2	0.77	1		
ϕ_3	0.42	0.12	1	
ϕ_4	0.12	0.12	0.77	1

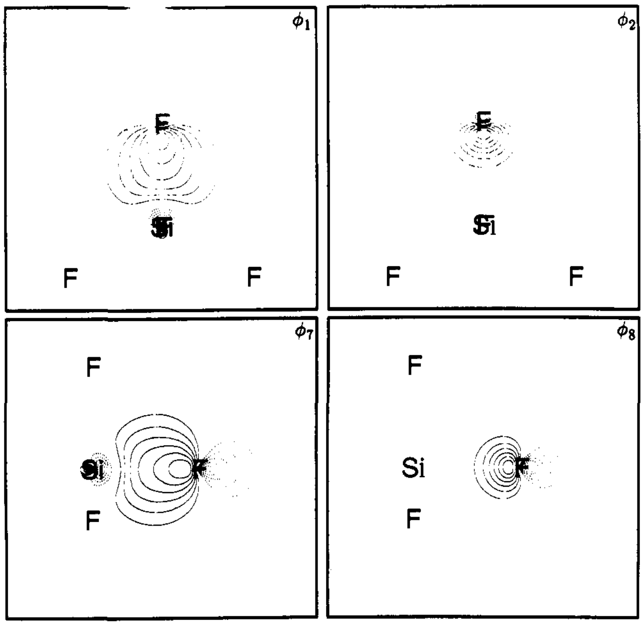

Figure 14. Spin-coupled orbitals for SiF_5^- (with d_{Si}).

Table 10. SCF and Spin-Coupled Total Energies (in hartree) for CH_5^- and SiH_5^- [a]

	SCF	spin-coupled
CH_5^-	−40.587 256	−40.671 455
SiH_5^-	−291.758 268	−291.823 592

[a] Further details of the D_{3h} geometries are given in the text.

Table 11. Overlap Integrals between the Spin-Coupled Orbitals for SiH_5^-

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}
ϕ_1	1									
ϕ_2	0.82	1								
ϕ_3	0.20	0.09	1							
ϕ_4	0.09	0.03	0.82	1						
ϕ_5	0.20	0.09	0.20	0.09	1					
ϕ_6	0.09	0.03	0.09	0.03	0.82	1				
ϕ_7	0.32	0.16	0.32	0.16	0.32	0.16	1			
ϕ_8	0.15	0.08	0.15	0.08	0.15	0.08	0.82	1		
ϕ_9	0.32	0.16	0.32	0.16	0.32	0.16	−0.01	0.00	1	
ϕ_{10}	0.15	0.08	0.15	0.08	0.15	0.08	0.00	0.01	0.82	1

However, we have presented evidence previously that the spin-coupled descriptions of molecules such as HCNO, N_2O, CH_2NHO, and CH_2N_2 correspond to hypercoordinate nitrogen atoms with polar bonds.[23] We believe that there are no significant qualitative differences between the hypercoordinate nature of first-row, second-row, and noble gas atoms in appropriate environments.

D. Hypercoordinate Silicon Atoms. With suitable bonding partners, carbon can use all four of its valence electrons in sp^x-like hybrids. As such, carbon usually satisfies the octet rule by default, although there are a few classes of compounds, such as carbenes, in which some of the valence electrons remain nonbonding. Of course, silicon shows a more marked tendency to be divalent than does carbon.

In order to make carbon or silicon atoms hypercoordinate, we would first need to make available an additional electron. The question then arises as to whether we can (formally) surround C^- or Si^- by sufficient appropriate partners so as to engage all five electrons in bonding. For silicon, for which five or even six surrounding groups create no serious problems of crowding, the answer is most definitely yes. The SiF_5^- ion occurs in various salts, although SiF_6^{2-} tends to be more common. Nuclear magnetic resonance studies of SiF_5^-, at sufficiently low temperatures to exclude fluorine exchange processes, confirm a trigonal bipyramidal structure. Indeed, our spin-coupled calculations for SiF_5^- (see Figure 14) result in a description that is remarkably similar to that presented earlier for PF_5 (Figure 6). The energy penalty per bond of removing the set of d functions from silicon is smaller than in the other systems we have studied (see Table 3). However, it is important to note that we might not be comparing like with like, in that we have used a somewhat larger basis set on silicon than for the central atom in the fluorides of phosphorus and sulfur. Magnusson[6] found that the importance of d functions tends to diminish with increasing quality of s/p basis sets.

The differences in electronegativity between P, S, and Xe on the one hand, and F and Cl on the other, appear to be consistent with the existence or otherwise of the various hypercoordinate halides. With an even less electronegative central atom, it seems feasible that even hydrogen atoms could provide sufficient incentive for hypercoordinate character. This is indeed the case: SiH_5^- and various derivatives are stable intermediates which can be studied, for example, in a flowing afterglow.[24] Streitwieser and co-workers[25] have emphasized the importance of ionic character in a rationalization of the stability of SiH_4F^-, but it is not straightforward to extend the same arguments to SiH_5^-.

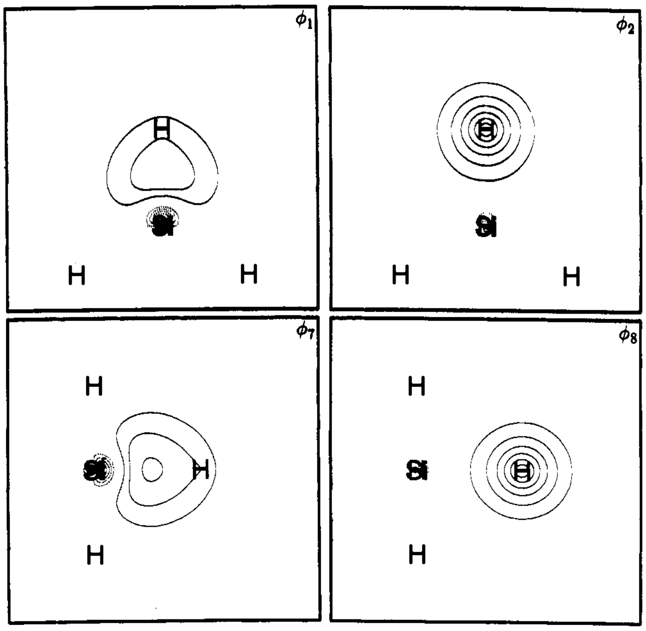

Figure 15. Spin-coupled orbitals for SiH_5^- (with d_{Si}).

It seems entirely natural to the present authors to describe the bonding in SiH_5^- (or SiH_4F^-) in much the same way as we have done for SiF_5^- and PF_5. Because C is less electropositive than Si—it is often assigned the same electronegativity as H—it would be more difficult to rationalize the stability of CH_5^-. Previous work by various authors confirms that CH_5^- is no more than a (high energy) transition state in certain reactions.

According to the quantitative curve-crossing valence bond study of Sini *et al.*,[8] SiH_5^- possesses two resonating axial bonds, one based on $Si(3p_z)$, with the other arising via overlap of H(1s) with an antibonding σ^* orbital of the trigonal SiH_3 moiety. The basic idea is that the fifth valence electron can delocalize into the *equatorial* Si–H bonds. From this model, one might reasonably expect to see significant differences between the spin-coupled descriptions of the axial and equatorial bonds.

In keeping with our findings for other systems, the converged spin-coupled orbitals for SiH_5^- constitute symmetry-related bonding pairs. Total energies are reported in Table 10 and the orbital overlaps in Table 11. Spin-coupled orbitals associated with an equatorial bond (ϕ_1,ϕ_2) and with an axial bond (ϕ_7,ϕ_8) are shown in Figure 15. All five of the $Si(sp^x)$ hybrids are very similar. Although the overlap integrals between the various $Si(sp^x)$ hybrids are relatively high (Table 11), they are all smaller than the corresponding overlaps between $P(sp^x)$ hybrids in PCl_5 (Table 5).

The $Si(sp^x)$ hybrids are fairly large, and each of them extends significantly toward one hydrogen center. The orbitals localized on hydrogen show relatively little distortion from pure H(1s) functions. These observations suggest that the Si–H bonds are relatively polar, with electron density shifted away from the central atom. As is to be expected, the perfect-pairing spin function dominates, contributing 99.10% of the total spin function.

Contrary to our expectations from the work presented in ref 8, it is very clear that the differences between axial and equatorial spin-coupled orbitals in SiH_5^- (e.g. ϕ_1 and ϕ_7) are no larger than those between the equivalent sets of orbitals in either SiF_5^- (Figure 14) or PF_5 (Figure 6). In this sense, SiH_5^- is "just another hypercoordinate molecule", and the present authors are not

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(23) Cooper, D. L.; Gerratt, J.; Raimondi, M. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1187.

(24) Hajdasz, D. J.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 3139.

(25) Gronert, S.; Glaser, R.; Streitwieser, A. *J. Am. Chem. Soc.* **1989**, *111*, 3111.

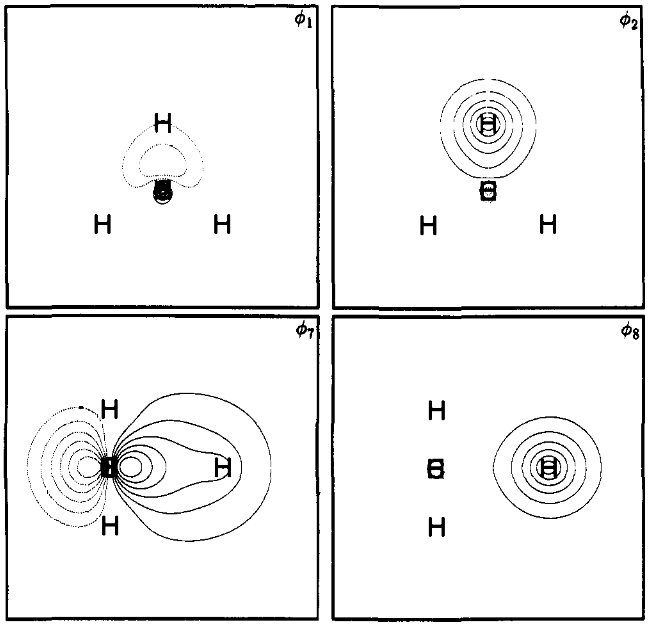

Figure 16. Spin-coupled orbitals for CH_5^- (with d_C).

Table 12. Overlap Integrals between the Spin-Coupled Orbitals for CH_5^-

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}
ϕ_1	1									
ϕ_2	0.73	1								
ϕ_3	0.55	0.14	1							
ϕ_4	0.14	−0.15	0.73	1						
ϕ_5	0.55	0.14	0.55	0.14	1					
ϕ_6	0.14	−0.15	0.14	−0.15	0.73	1				
ϕ_7	0.15	0.07	0.15	0.07	0.15	0.07	1			
ϕ_8	0.14	0.06	0.14	0.06	0.14	0.06	0.75	1		
ϕ_9	0.15	0.07	0.15	0.07	0.15	0.07	−0.50	−0.23	1	
ϕ_{10}	0.14	0.06	0.14	0.06	0.14	0.06	−0.23	−0.22	0.75	1

convinced of the need to invoke delocalization into equatorial bonds to rationalize its stability.

We have already indicated why the supposed stability of CH_5^- would be more difficult to rationalize than the stability of SiH_5^-. It is worthwhile to contrast the spin-coupled description of this high-energy transition state with the description of SiH_5^-. We find that the equatorial bonds in CH_5^- are fairly similar to those in SiH_5^-, but that the axial "bonds" are entirely different (see Figure 16). The sp^x-like character of the axial hybrids on Si is very much reduced, and it is replaced by highly deformed C(2pz) character. In addition, the two carbon axial orbitals have a significant unfavorable (i.e. negative) overlap of $\langle\phi_9|\phi_7\rangle = -0.50$ (see Table 12). The analogous orbitals in SiH_5^- are almost orthogonal to one another (see Table 11). We notice also that the orbitals localized on equatorial hydrogens show more distortion toward the central atom than do those on the axial hydrogens. The form of orbitals ϕ_2, ϕ_4, and ϕ_6, localized on the equatorial hydrogens, is reminiscent of that observed in "typical" C–H bonds.[26]

Perhaps even more striking is the reduced contribution made by the perfect-pairing spin function (90.64%). After the perfect-pairing spin function with five singlet pairs (90.64%), the next most important contributions correspond to combinations of three singlet pairs with two triplet pairs. These two triplets are, of course, coupled to a net spin of 0. The most important of these additional spin functions (3.1%) corresponds to perfect pairing in the equatorial bonds and *triplet* coupling in both axial pairs. There are further contributions of 1.1% each from the three possible ways of assigning triplets to two equatorial pairs, with all the other bonding pairs singlet-coupled. It is clear that our spin-coupled description of the CH_5^- transition state exhibits significant differences from those of the various stable, trigonal bipyramidal molecules we have considered. Indeed, some of these differences are already apparent at the SCF level, from the form of the LMOs in Figures 1, 2, and 5.

Discussion

For many years now, particular forms of wave function have been used to devise models of the bonding in hypercoordinate molecules. The consensus view is that d basis functions are no more important in such systems than they are in so-called "normal" molecules. Nonetheless, many chemists have chosen to ignore all of these findings and to cling to the language of d-orbital participation to "explain" the expansion of the octet. We believe that the present work, being firmly based in the modern development of valence bond theory, may, at long last, provide a simple, convincing alternative for the description of molecules such as PF_5 and SF_6. We stress, once more, that the essential physical picture presented here is unlikely to be altered significantly by further refinement to the spin-coupled wave function.

The various spin-coupled calculations described in this work suggest that there is no clear demarcation between "normal octet" and hypercoordinate systems. Considering, for example, the S–F bonds in sulfur fluorides, it appears that there are no significant qualitative differences between the spin-coupled descriptions of SF_2, SF_4, and SF_6. In all three systems, the bonds arise from the overlap of a distorted F(2p) orbital with a two-center orbital which resembles the admixture of an S(sp^x) hybrid with F(2p). To a large extent, the various systems differ only in the *number* of S(sp^x) hybrids, whose character changes remarkably little. In particular, we can find no evidence to support the notion of S(d^2sp^3) hybridization in SF_6.

The spin-coupled orbitals for the trigonal bipyramidal molecule PF_5 indicate no qualitative difference between axial and equatorial bonds, as might have been expected from the popular dsp^3 model of the bonding. Similar considerations apply to SiF_5^- and SiH_5^-. The five Si(sp^x) hybrids in SiH_5^- are all remarkably similar to one another, as indeed are the five essentially H(1s) orbitals. These observations run contrary to our expectations from a model which invokes delocalization into $SiH_3(\sigma^*)$.[8,27]

Inclusion of d basis functions on the central atom makes no significant qualitative difference to the spin-coupled description of any of the systems studied. In addition, the energy penalty per bond of excluding d functions is much the same for "normal" and hypercoordinate molecules. We find that the d functions play essentially the same role in all of these systems, acting as polarization functions rather than as an essential contributor to the bonding. These findings are, of course, entirely consistent with those reported by Magnusson.[6]

We are not the first group to apply modern valence bond approaches, of the spin-coupled or full-GVB type, to molecules containing hypercoordinate second-row atoms. The most significant work, in this respect, consists of various studies published by Messmer and co-workers.[28] Those authors asserted that the spin-coupled or full-GVB model "is very difficult to implement computationally", and so they imposed the twin, simplifying restrictions of strong orthogonality and perfect pairing (SOPP). Indeed, the vast majority of generalized valence bond calculations in the literature are based on this GVB–SOPP approximation to the spin-coupled or full-GVB wave function. It is important to

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(26) See, for example, Section III.A in ref 11.

(27) We do not wish to find fault with the calculations, but merely to suggest that the qualitative interpretation which arises from them may not be especially useful. It is difficult *a priori* to see why the axial and equatorial bonds should be so similar. Furthermore, it is amusing to speculate on the likely results of "carving up" PCl_5 in an analogous fashion.

(28) (a) Patterson, C. H.; Messmer, R. P. *J. Am. Chem. Soc.* **1989**, *111*, 8059. (b) Patterson, C. H.; Messmer, R. P. *J. Am. Chem. Soc.* **1990**, *112*, 4138. (c) Messmer, R. P. *J. Am. Chem. Soc.* **1991**, *113*, 433.

note that no such constraints have been imposed in the present work, even for systems with 12 active electrons and 132 spin functions. As indicated earlier, such calculations made use of a recently developed strategy which involves efficient fast indexing and processing of cofactors.[18]

The overwhelming dominance of the perfect-pairing spin function in most of the calculations described in the present work suggests that the perfect-pairing constraint would be relatively benign. An important exception is CH_5^-, for which analyzing the full spin space provides significant insight. We note also that the weight of the perfect-pairing spin function tends to decrease slightly on excluding d functions from the central atom. For all of the systems, the contribution of the perfect-pairing spin function is likely to diminish away from equilibrium geometry, particularly as bonds are broken.

Even a cursory glance at the various overlap matrices presented in this work suggests that it would be very much harder to justify the imposition of strong orthogonality constraints. Not only can the overlaps between orbitals involved in different bonds be relatively large, but some of these "between bond" matrix elements provide vital clues to the nature of the bonding. A key conclusion of the GVB–SOPP studies[28] was that "the role of d functions in electronic structure calculations on hypercoordinate molecules ... differs from that in normal molecules". We find no evidence for any of the systems studied in the present work nor, indeed, from work in progress to support this conjecture. The central difference, according to the GVB–SOPP studies, is that d basis functions on hypervalent atoms allow the orbitals to "attain their optimum shapes while remaining mutually orthogonal". Such (strong) orthogonality is, of course, nothing more than a constraint imposed in the GVB–SOPP calculations, purely as a computational convenience. Such restrictions were not invoked here. Although we have found that the exclusion of d functions from the central atoms does tend to increase the "between bond" overlaps, the additional flexibility provided by d basis functions seems to be just as significant in normal molecules as in hypercoordinate ones. We note interesting recent work by Messmer and co-workers, albeit for different molecules, in which the SOPP constraints have been completely abandoned.[29]

As we have indicated, all of the spin-coupled (or full-GVB) calculations in the present work were carried out without preconceptions as to the form of the orbitals, or constraints on the overlaps between them, or restrictions on the spin space. We must, however, recognize that our work is not without some limitations. In particular, the spin-coupled orbitals for the various halides were taken to be orthogonal to the "frozen" LMOs which accommodate the nonbonding electrons on the halogen atoms. Analogous considerations apply, in a few cases, to the central atom (e.g. SF_2). These are restrictions which we intend to relax, to various extents, in future work. However, our experience for many other systems suggests that this is not likely to affect in any significant way the conclusions presented here. Similarly, we do not expect that using larger basis sets would lead to significant qualitative differences. A future publication will deal with systems containing double bonds to oxygen, as well as addressing some of the issues which we have just raised.

For the systems studied in the present work, the bonds from Si, P, S, or Xe to fluorine all appear to have much the same qualitative form. In these cases the key differences can be rationalized very simply in terms of the differences in electronegativity between the various atoms. Indeed, the feasibility of hypercoordinate systems seems to be dependent on the possibility of making significantly polar bonds which shift electron density away from the central atom. With hindsight, therefore, it is not surprising that SCl_2 should be more different from SF_2 than PCl_3 is from PF_3 or that SCl_4 should not feature hypercoordinate bonding. Equally, it is easy to rationalize why SiH_5^- could be a stable intermediate, whereas CH_5^- could not.

Of course, another important consideration when comparing CH_5^- and SiH_5^-, or NF_5 and PF_5, is that problems of crowding are likely to be much more severe for the first-row atoms. However, this should not be taken to mean that first-row atoms cannot be hypercoordinate. We have inferred from the chemistry of xenon that double bonds to oxygen are at least as effective as (two) single bonds to fluorine. Replacing two fluorine atoms by one oxygen atom has the added bonus of reducing steric repulsions around smaller atoms. In this sense, we consider NF_3O to be the closest first-row analogue of PF_5. We have argued in the previous section, as well as in earlier work, that hypercoordinate bonding is common in the chemistry of first-row atoms such as nitrogen.[23] In a very real sense, hypercoordinate bonding to first-row atoms is usually "disguised" by invoking resonance between strict-octet Lewis structures that involve charge separation.

Some authors still insist on using strictly classical valence bond concepts, in which orbitals are *constrained* to use basis functions stemming from only one center. It is easy to envisage the outcome of projecting our spin-coupled wave functions onto such classical VB structures, especially given the highly polar nature of many of the bonds. Instead of any supposed active d orbital participation, one would observe resonance between a large number of structures featuring charge separation, in keeping with previous studies.[30,31] There is nothing wrong with such schemes, except that we believe them to be unnecessarily complicated. We feel that it is much more appropriate to interpret the spin-coupled wave function *directly*, without such manipulations.

Although they are certainly highly polar, the bonds in molecules such as SF_4 and PF_5 do include significant covalent character, in the classical VB sense. This residual covalency plays an important role in determining the preferred geometries of the molecules we have studied. In view of the forms of the optimized spin-coupled orbitals and of the LMOs, it seems particularly appropriate to rationalize the shapes of the various molecules using the simple ideas of the VSEPR model. We intend to investigate in future work the relationship between our spin-coupled results and traditional VSEPR ideas.

Final Remarks

It is clear from this work, from previous work on, for example, CH_2N_2,[23] and from the experimental facts that the time has come for the much-loved octet rule to be superseded. Presented with sufficient energetic incentives, almost *all* valence electrons can take part in bonding. We like to refer to this assertion as the democracy principle. Polar bonds which shift density away from the central atom appear to be favored, particularly if the formal number of bonds is very high. It is thus not suprising that differences in electronegativity can be a useful *first* guide to the possible existence of particular hypervalent species. Of course, it may not be possible in some cases (such as the fluorine atom) to cram round sufficient numbers of sufficiently electronegative atoms to generate a hypercoordinate molecule.

The "constitution" of the democracy principle is founded on the principle of minimizing the total energy. Ultimately, it is this last criterion alone which determines whether a particular atom uses any or all of its valence electrons in chemical bonding. Nonetheless, it is possible to identify factors which are *likely* to be favorable, such as shifting electron density away from the central atom and multiple bonds to electronegative atoms. In some cases, however, more subtle electron correlation effects are important. It remains to be seen, in future work, whether general rules can be formulated which will allow the prediction of which hypercoordinate systems are likely to be "stable".

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(29) Schultz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.*, in press.

(30) Hay, P. J. *J. Am. Chem. Soc.* **1977**, *99*, 1003.

(31) Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1986**, *108*, 3586.

(32) (a) Loades, S. D.; Cooper, D. L.; Gerratt, J.; Raimondi, M. *J. Chem. Soc.*, Chem. Commun. **1989**, 1604. (b) Pages 950–954 in ref 11. (c) Loades, S. D. Ph.D. Thesis, Liverpool University, U.K., 1992.

Taking into account also our spin-coupled calculations for certain systems containing first-row atoms,[23] we find the octet rule to be of somewhat limited value. In particular, we consider it somewhat artificial to *insist* on retaining the octet rule when drawing structures for molecules such as F_3NO, $C_6H_5NO_2$, and CH_2N_2. A representation such as $H_2C{=}N{\equiv}N$, for example, has much to recommend it.

In spite of these various comments, it might be appropriate not to abandon completely the octet rule. A great deal of chemical evidence supports the notion that it can be particularly easy to achieve a (formal) count of four electron pairs around a central atom, often arranged in a tetrahedral or pseudotetrahedral fashion. In this sense it may be useful to retain an "8-electron rule" for main group nonmetals, in much the same way as the "18-electron rule" is useful in transition metal chemistry. A convenient definition of a hypercoordinate main group atom is one which (formally) uses more valence electrons in bonding than is expected from the eight-electron rule.

We find no reason from the present study to invoke d orbitals to describe the bonding in SF_6: the sulfur atom contributes six equivalent, nonorthogonal sp^x-like hybrids which delocalize onto the fluorine atoms. These two-center orbitals overlap with distorted F(2p) functions, with the perfect-pairing spin function dominating. Analogous statements extend to all of the other systems we have studied, whether hypercoordinate or not. Naturally, bonds to chlorine or hydrogen tend to be less polar than those to fluorine, and this is reflected in the amount of sp^x-like character contributed by the central atom. It is important to bear in mind that the conclusions reached in the present work concerning nonparticipation by d orbitals relate only to main group nonmetals. Spin-coupled studies of complexes containing transition metal atoms in low oxidation states have revealed very significant d orbital participation.[33]

The spin-coupled calculations described in this paper for molecules containing second-row atoms will provide little comfort to those who still cling to the idea of active d orbital participation.

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(33) All of the contour plots in the present work depict representations of ϕ, with the positions of nuclei (projected onto the page) indicated by means of their chemical symbols. Each frame presents a view of 9 bohr by 9 bohr. It is convenient to define $F_1 = \min(|\phi_{\min}|, {}^1/_2|\phi_{\max}|/n_{\text{ctr}})$ and $F_2 = |\phi_{\max}|$, where we have used $n_{\text{ctr}} = 6$, throughout. The plots were constructed by requesting n_{ctr} equally-spaced contour heights (—) between F_1 and F_2 and a further n_{ctr} equally-spaced contour heights (- - -) between $-F_2$ and $-F_1$. Adjacent contour heights differ by $(F_2 - F_1)/(n_{\text{ctr}} + 1)$.