7940 *J. Am. Chem. Soc.* **1990**, *112*, 7940–7951

low barriers involved. This has the interesting consequence that H- and C-scrambling in dication **1** occurs in the same energy domain, i.e., ca. 15 kcal/mol (MP4/6-31G**) above **1**.

Comparisons with Other $C_nH_4^{2+}$ Dications. From our theoretical studies on carbodications with four hydrogens, $C_nH_4^{2+}$ (n = 1–6),[13a,e,h,k] ubiquous species in various types of mass spectroscopy,[3] some generalizations emerge:

1. Cumulene dications are minima for all $C_nH_4^{2+}$ dications and the global minima for the smaller members of the family, i.e., $n < 4$.[13a,e]

2. Structures that benefit from aromatic stabilization are favored for systems with more than 3 carbons.[13h,k] These dications disperse the charges better over the molecular framework than is the case with their linear conjugated isomers.

3. All energetically preferred dications have anti van't Hoff stereochemistry, except the cyclobutadiene dication,[13h,l] which enjoys a special type of aromatic stabilization. Illustrative examples are diionized methane, ethylene, propene, and cumulenes in general as well as structures containing three-membered rings, like the vinylidenecyclopropenium and trifulvalene dications.[4] Isomers **1** and **7** are explicit examples of the present study. The two-electron differences between dications and their neutral homologues underlie the reversal of the van't Hoff rule.

4. The methyl-substituted acetylenic-like dications, $CH_3C_nH^{2+}$, are the least favored isomers for all $C_nH_4^{2+}$ dications. Hence, the suggestion in the mass spectroscopic literature[3d] that these species share this common structure is incorrect.

5. All $C_nH_4^{2+}$ species are more compact than the corresponding neutral hydrocarbons. In most cases this results from effective types of hyperconjugation, which also reduces the electrostatic repulsion of charges.

6. All $C_nH_4^{2+}$ dications have significant kinetic stability. Barriers for proton loss steadily increase from the methane dication up to the larger cumulenic-type dications for which such processes become even endothermic. These values, followed by the endothermicities for proton loss (all in kcal/mol), are for CH_4^{2+} 17 and −106,[13a] for $C_2H_4^{2+}$ 16 and −65,[13e] for $C_3H_4^{2+}$ 82 and 11, for $C_4H_4^{2+}$ (D_{2d}) 120 and 54 (3-21G), and for linear $C_5H_4^{2+}$ (D_{2h}) 128 and 71 (3-21G) kcal/mol.[30] Consequently, disproportionation of larger dications gives preferentially larger fragments. As is the case in **4**, the proton dissociates at large distances (i.e., 3.257 Å for $C_4H_4^{2+}$ (D_{2d}) and 3.488 Å for $C_5H_4^{2+}$ (D_{2d})),[30] conforming to the Hammond principle.

Conclusions. The important points deduced from the present study are the following: 1. The allene dication **1** is the singlet global $C_3H_4^{2+}$ minimum. Structures representing hydrogen and carbon scrambling are about 15 kcal/mol less stable at MP4/6-31G**. 2. It appears that all protonated cyclopropenium ion forms will convert to the allene dication with very small barriers. 3. Although the triplet surface was not searched explicitly, the perpendicular allene dication is a minimum, albeit ca. 40 kcal/mol less stable than the planar singlet form. 4. Whereas propyne is the most stable neutral C_3H_4 hydrocarbon isomer and its radical cation is observable in the gas phase, the (triplet) dication is the highest energy form of the $C_3H_4^{2+}$ species studied. 5. The deprotonation barrier of the $C_3H_4^{2+}$ dication is 82 kcal/mol. This process is endothermic by 11 kcal/mol (MP4/6-31G**+ZPE).

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Note Added in Proof. Since this work was submitted, we became aware of a study on the potential energy surface of $C_3H_4^{2+}$: Wong, M. W.; Radom, L. *J. Mol. Struct.* **1989**, *198*, 391. Our dication results are in agreement with their study.

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(30) The 3-21G energies for $C_4H_4^{2+}$ (D_{2d}) and $C_5H_4^{2+}$ (D_{2d}) are 152.033 14 and 189.699 30 au, respectively, and for the corresponding transition structures for deprotonation 151.841 51 and 189.496 07 au, respectively. The 3-21G energy for the related $C_4H_3^+$ fragment is 151.841 51 au and for $C_5H_3^+$ 189.496 07 au.

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Hypercoordinate Molecules of Second-Row Elements: d Functions or d Orbitals?

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Abstract: A new analysis of the d function contributions to the ab initio wave functions of hypercoordinate and normal valency compounds is reported for molecules of first- and second-row elements, all calculated at a comparable level. Energy minimization calculations show that the optimum d function exponent for any element changes very little from one compound to another, even those as different as H_2S and SF_6. There is no support for the view that diffuse d orbitals on the central atom take part in bonding after being contracted in the field of electronegative oxygen or fluorine atoms around the periphery. Although the level of participation of the supplementary functions in the wave functions of the hypercoordinate compounds is greater than in normal valency compounds, there is no difference in the role of the d functions. The effect of the added functions on calculated energy also provides no clear demarcation between the two classes; in S–F compounds, which are typical, the energy improvement per bond is much the same in SF_2 as it is in SF_6. The occupations of the higher order functions are quite strongly dependent on the degree of charge transfer from the central atom and on the number of electron pairs formally arranged around the central atom. d functions added to the basis sets of peripheral atoms like O or F produce just as large an energy improvement as that gained by putting d functions on the central second-row atom. It follows from the evidence that atom-centered molecular wave functions require functions higher in order than s and p functions to properly respond to the rapidly varying molecular potential in the space between the nuclei. Accordingly, any resemblance between d functions in molecular wave functions and the valence d orbitals of excited second-row atoms is an artifact of the electronic structure model; they should not be called "d orbitals".

It is generally agreed that electronic structure calculations on main group molecules would be seriously compromised without d functions in the basis sets of second-row atoms,[1-4] but there is wide disagreement about their role. Structure or reactivity studies

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of sulfur and phosphorus compounds by MO methods frequently refer to the "important contributions to the bonding" made by d orbitals.[5-7] The reasons given are (i) the very large energy depressions obtained by supplementing sp basis sets with d functions, (ii) the distorted molecular geometries obtained from optimization calculations carried out without d functions, and (iii) the size of the d function contributions to indices of bonding.

By contrast, d functions are included in the highest level calculations for the same reasons as f and g functions are used—higher order functions necessary in noncentrosymmetric systems to improve the "completeness" of the basis set.[8,9] No comparisons are made between the molecular wave functions and the orbitals of the component atoms, and any similarity between the d functions in SF_6 and the d orbitals, in, say, the sp^{3}d^2 ^{7}F state of sulfur is ignored. However, this is a policy, not an argument, and the valence orbital hypothesis for d functions continues to be sustained by the sheer size of d function contributions to the wave functions of molecules containing second-row atoms.[7]

Scepticism about valence d orbitals in molecules of main group elements has several roots.[10] One is the ionic character in bonds to oxygen or fluorine from second-row elements, which allows the electron density attributable to the central atom to be accommodated without the need for expansion of the octet.[10,11] Kutzelnigg describes the X–O bond in H_3PO, $H_2P(O)F$, H_2SO, HSOH, HClO, etc. as "semipolar" and finds that "the traditional valence AOs of s and p type are, when appropriately deformed, able to describe the bonding...."[11] Reed and Weinhold have recently shown that the occupancy of the sulfur d functions in SF_6 is far lower than is required by the sp^{3}d^2 hybridization formula, suggesting that it is the Lewis–Langmuir electron-pair model of covalent bonding, not the octet rule, that is broken in this class of molecules.[12] Kiang and Zare took the same approach in a paper on the successive bond dissociation energies of SF_6. They explain the alternating low and high values as a result of the formation of weak two-center three-electron bonds ($F^{-}SF_n^{+}$) and strong three-center four-electron bonds (F:S·F).[13] Reed and Weinhold[12] cite other types of experimental results that fail to support the valence d orbital hypothesis.

Because of the conflict in interpretation of both theoretical and experimental results[12,14] and because much other evidence is equivocal, a systematic examination of the problem is necessary. Are the two views masquerading as distinct hypotheses when they are merely semantic alternatives? Further, is it justifiable to take the middle view ("a role for d functions intermediate between polarisation functions and true valence participation")[15] or is it an illusion?

The competing hypotheses tested in this paper are the following: (a) d functions take a *valence role* (high-lying d orbitals of excited second-row atoms being utilized in σ and π bonding in molecules of main group atoms, especially hypercoordinate species); and (b) d functions are *polarization functions* (compensating for the limitations imposed on the molecular wave function when it is restricted to s and p functions centered on the nuclei).

The two hypotheses are tested by analysis of the RHF wave functions of a comprehensive series of compounds of second-row main group elements not yet studied at a uniform basis set level. Since high-level molecular wave functions for all molecules require functions on the atoms that cannot be related to atomic behavior at all,[16] the variables in the experiment are controlled by inspecting d function utilization in molecules of first-row atoms. In the same spirit, d functions in hypervalent molecules (recently dubbed "hyper-coordinate" to avoid begging the question about expansion of the octet[17]) are compared with d functions in normal valency molecules and around peripheral atoms such as F or O in SF_6 or SO_3. Finally, because a valence role for the d orbitals of second-row atoms is only feasible if the diffuse orbitals of the atom could be suitably contracted in the potential field of the surrounding electronegative elements,[18] this factor is included in the experiments by separately optimizing the d function exponents in all molecules studied.

Method of Calculation

MO wave functions and molecular energies were calculated within the restricted Hartree–Fock formalism with use of the Gaussian 82 and 86

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suites of programs.[19] The calculations were generally performed at the experimental geometries; optimized geometries were used where these were not available. The Dunning–Hay standard "double-ζ" basis sets,[1] with eleven s and seven p functions, were used for Si, P, S, and Cl, contracted in each case to six s and four p functions (11s7p/6s4p). For O and F and other first-row elements, the Huzinaga–Dunning double-ζ (9s5p/4s2p) set[20] was used in all calculations [the (4s/2s) set for H].

Single and multiple sets of gaussian d functions (five functions) were added to the basis sets of all atoms (p functions to H atoms), and the exponents of d functions on the central atom were optimized in all cases. In some cases the exponents of d functions on peripheral atoms were optimized also. Otherwise the standard values $\zeta_d(F) = 0.9$, $\zeta_d(O) = 0.8$, $\zeta_d(N) = 0.7$, $\zeta_d(C) = 0.6$ were used, with $\zeta_p = 1.1$ for the added p function on hydrogen atoms.[4] Very little additional energy lowering is obtained by using the optimum exponent for the peripheral atom d function rather than the standard value. Thus, for SO_2 the (2D/1D) energy obtained by using the standard value ($\zeta_d = 0.8$) for the oxygen d function is −547.23271 hartree; it is lowered only 0.0011 hartree further by using the optimum exponent ($\zeta_d = 0.67$). The level of d function supplementation is indicated as follows: (2D/1D) means supplementation of the central atom in the molecule by two sets of d functions and supplementation of peripheral atoms by one set.

The possibility of basis set superposition error (spurious contributions to the wave function around one atom from diffuse d functions on a neighboring atom) was checked by calculating the energies of O and F atoms with a single set of d functions centered at distances of 143.08 and 155.0 pm, respectively, representing the effect of a single d function set in SO_2 and SF_6. The d function set lowered the O and F atom energies by only 0.00009 and 0.00005 hartree, respectively, and no further notice was taken of errors from this source. Rather larger superposition errors associated with d functions are found in calculations that use s and p basis sets of lower quality.[21]

Magnusson and Schaeffer reported that some 80% of the energy contribution obtained by adding up to five sets of d functions (exponents as chosen by Stromberg et al.[22]) can be obtained from a single set of functions on each center and about 95% from two sets.[4] The more extensive results reported here do not alter this conclusion, which holds from hydrides like H_2S to large hypercoordinate molecules like SF_6. However, it is important to be sure that results from a single set of optimized d functions of Gaussian form do not misrepresent the conclusions that would be obtained from d functions with improved radial dependence. This possibility was tested by optimizing the exponents of Slater-type functions (STFs) added to the basis sets of sulfur, fluorine, oxygen, and hydrogen atoms in the H_2S, SO_2, SF_2, and SF_4 molecules (see Table II). (The STFs were represented by a least-squares fit to exponential form ($r^n e^{-kr}$) of three Gaussian functions.[23]) The absence of significant change in sulfur d function exponent between the four compounds is closely parallel to that obtained by adding one set of Gaussian d functions to basis sets. The STFs produced energy depressions larger by 7–11% (24% for H_2S) than those obtained with the single-Gaussian d functions. The sulfur STF exponents for the four molecules were 2.17 ± 0.05, the maxima of the added STFs being located in substantially the same position in the bonds as those of Gaussian functions optimized for the same compounds (actually 5–7% further away from sulfur).

Results

The bare results of the calculations are presented in the following sections, comment being reserved for the section where the hypotheses are tested (see Discussion). The results are based on all-electron calculations within the molecular orbital model of electronic structure with Gaussian basis sets of moderate size and with no allowance for electron correlation.[9] Hehre, Radom, Schleyer, and Pople have examined the performance of the model at the RHF level of calculation for compounds of second-row elements in both categories considered in this paper.[3] They note the general adequacy of the model to reproduce experimental geometries by gradient methods to a level of accuracy close to that of experiment, provided that d functions are included in the basis sets. There is a small, systematic underestimation of bond length. d functions are also necessary if the MO model is to reproduce other types of experimental results that depend on a good description of the valence shell electron distribution, such as force constants or reaction energies.[2,3]

Table I. Energy Lowerings (ΔE_d, hartrees) and Optimum Exponents (ζ_d) Calculated for the Addition of d Functions to First- and Second-Row Element Basis Sets[a,b]

	ΔE_d	ζ_d		ΔE_d	ζ_d
H_2	0.005	0			
CH_4	0.046 (0.008)	0.84	SiH_4	0.052 (0.041)	0.48
C_2H_2	0.121	0.30			
CO	0.077	0.72			
CO_2	0.124 (0.077)	0.76	SiO_2	0.154 (0.108)	0.50
CF_4	0.187 (0.133)	0.69	SiF_4	0.237 (0.165)	0.59
HCN	0.053	0.83			
HCP	0.052	0.48			
NH_3	0.037 (0.021)	0.83	PH_3	0.051 (0.043)	0.56
NF_3	0.113 (0.071)	0.81	PF_3	0.185 (0.132)	0.64
NOH_3	0.059 (0.028)	0.82	POH_3	0.167 (0.133)	0.58
NO_2F	0.152 (0.094)	0.83	PO_2F	0.297 (0.226)	0.62
NOF_3	0.150 (0.113)	0.82	POF_3	0.345 (0.258)	0.63
			PSF_3	0.306	0.62
HNO_3	0.166 (0.091)	0.83	HPO_3	0.301 (0.219)	0.61
N_2O	0.123	1.03	PF_5	0.375 (0.258)	0.65
H_2O	0.041 (0.025)	0.98	H_2S	0.043 (0.023)	0.69
OCH_2	0.066		SCH_2	0.054	0.65
			$SH_2{\cdot}CH_2$	0.110	0.64
OF_2	0.057 (0.033)	0.90	SF_2	0.115 (0.074)	0.72
			$SO{\cdot}CH_2$	0.170	0.68
O_3	0.102	0.92	SO_2	0.260 (0.209)	0.76
			SOF_2	0.270 (0.200)	0.71
			SNF	0.161 (0.112)	0.66
			SF_4	0.287 (0.203)	0.71
			SNF_3	0.380 (0.279)	0.70
			SF_6	0.544 (0.383)	0.69
			SO_3	0.405 (0.304)	0.71
HF	0.028	1.14	HCl	0.030	0.82
F_2	0.026	0.90	ClF	0.046	0.76
			ClF_3	0.169 (0.111)	0.75
			ClO_2F	0.354	0.78
			ClO_3F	0.541	0.81
			ClF_5	0.356 (0.234)	0.72

[a] ΔE_d values refer to calculations with Dunning–Hay (11s7p/6s4p) and (9s5p/4s2p) basis sets supplemented on all atoms (1D/1D) relative to the unsupplemented basis calculations (0D/0D). The values in parentheses refer to supplementation on the central atom only, i.e. (1D/0D) values relative to the (0D/0D) values. The optimized d function exponent was calculated with basis sets supplemented with d functions on all centers.

1. Molecular Energies. As the summary data in Table I indicate, the energy improvement (ΔE_d) obtained by adding a single set of five d functions to Dunning–Hay basis sets for molecules of second-row elements ranges from about 0.05 hartree for hydrides like H_2S to more than 0.5 hartree for hypercoordinate species like SF_6. Much larger energy depressions are found when the d functions are added to lower quality basis sets because of the way in which d functions are able to compensate for deficiencies in the sp basis in such cases.[21] Omitting d functions is catastrophic for some species, the molecular energies being higher than the sum of the energies of the component atoms.

Tables II and III contain detailed energies and exponents for molecules of first- and second-row main group compounds; d function energy depressions are given on a "per bond" basis in Table IV.

Energy data for three sets of isomeric pairs included in entries of Table II indicate how new bonding arrangements formed after electron transfer greatly increase the d function utilization. The ΔE_d values are 0.167 and 0.098 hartree for H_3PO and H_2POH,

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Table II. Total Molecular Energies Calculated with and without d Function Supplementation for Molecules AB_n Containing Second-Row Elements[a]

molecule AB_n	supplementary basis (A/B)		supplementary function exponents[b]		total energy, hartrees	molecule AB_n	supplementary basis (A/B)		supplementary function exponents[b]		total energy, hartrees
			A	B = O, F etc.					A	B = O, F etc.	
SiH_4	0D	0P			-291.18260	SF_2	0D	0D			-596.26081
	1D	0P	0.55		-291.22322		0D	1D		0.55*	-596.33109
	1D	1P	0.48	1.1 (H)	-291.23195		1D	0D	0.55		-596.33754
SiH_5^{-c}	0D	0D			-291.67187		1D	1D	0.72	0.62*	-596.37568
	1D	1D	0.46	1.1 (H)	-291.73764		1D (STO)	1D (STO)	2.21	2.03	-596.38414
SiO_2	0D	0D			-438.51598	CH_2SO	0D	0D			-511.03883
	1D	0D	0.55		-438.62422		0D	1D		0.28 (C)*, 0.8 (O)	-511.14512
	1D	1D	0.50	0.8	-438.66993		1D	1D	0.68	0.17 (C)*, 0.8 (O)	-511.23494
SiF_4	0D	0D			-686.84661	SOF_2	0D	0D, 0D			-670.99342
	1D	0D	0.55		-687.01202		1D	1D, 1D	0.71	0.8 (O), 0.9 (F)	-671.26348
	1D	1D	0.59	0.64*	-687.08327	SO_2	0D	0D			-546.95504
PH_3	0D	0P			-342.40109		0D	1D		0.52*	-547.09416
	1D	0P	0.6		-342.44363		1D	0D	0.62		-547.16416
	1D	1P	0.56	1.1 (H)	-342.45252		1D	1D	0.71	0.8	-547.21102
PH_5^c	0D	0D			-343.39931		1D	1D	0.76	0.57*	-547.21481
	1D	1D	0.57	1.1 (H)	-343.50969		1D (STO)	1D (STO)	2.20	2.14	-547.24345
P_2	0D				-681.35227		2D	1D	0.55, 2.3	0.57	-547.23277
	1D		0.43		-681.42573	SSF_2	0D	0D			-993.64443
HCP	0D	0D, 0P			-379.06031		1D	1D	0.59	0.9	-993.86671
	1D	1D, 1P	0.63 (P)	0.6 (C), 1.1 (H)	-379.11245	SO_3	0D	0D			-621.63934
POH_3	0D	0D			-417.16934		0D	1D		0.8	-621.82710
	1D	0D, 0P	0.6		-417.30205		1D	0D	0.7		-621.94322
	1D	1D	0.58	0.64 (O)*, 1.1 (H)	-417.33605		1D	1D	0.71	0.8	-622.04418
H_2POH	0D	0D			-417.24701		2D	1D	0.55, 2.32	0.8	-622.07788
	1D	1D	0.60	0.56 (O)*, 1.1 (H)	-417.34476		5D	1D	SWPS	0.8	-622.09217
PF_3	0D	0D			-639.04007	SF_4	0D	0D			-794.96458
	1D	0D	0.54		-639.17221		0D	1D		0.53*	-795.13798
	1D	1D	0.64	0.62*	-639.22851		1D	0D	0.57		-795.16952
HPO_3	0D	0D			-565.69423		1D	1D	0.71	0.57*	-795.25169
	0D	1D		0.8 (O), 1.1 (H)	-565.84642		1D (STO)	1D (STO)	2.14	2.00	-795.27272
	1D	0D	0.6		-565.91292		2D	1D	0.52, 2.00	0.9	-795.26470
	1D	1D	0.61	0.8 (O), 1.1 (H)	-565.99545		5D	1D	SWPS	0.9	-795.27271
	2D	1D	0.50, 2.3	0.8 (O), 1.1 (H)	-566.01501	H_2SO_4	0D	0D			-697.66783
FPO_2	0D	0D, 0D			-589.69459		1D	1D	0.72	0.8 (O), 1.1 (H)	-698.12541
	1D	1D, 1D	0.62	0.8 (O), 0.9 (F)	-589.99205		1D	1D	0.72	0.63 (O)*, 1.1 (H)	-698.12889
POF_3	0D	0D			-713.79913	NSF	0D	0D			-551.17895
	0D	1D		0.8 (O), 0.9 (F)	-713.97551		0D	1D		0.8 (N), 0.9 (F)	-551.25160
	1D	1D	0.63	0.8 (O), 0.9 (F)	-714.14370		1D	1D	0.66	0.56 (N)*, 0.9 (F)	-551.33985
	2D	1D	0.55, 2.42	0.8 (O), 0.9 (F)	-714.16314		2D	1D	0.50, 2.00	0.8 (N), 0.9 (F)	-551.35091
PSF_3	0D	0D			-1036.44529	NSF_3	0D	0D			-749.79732
	0D	1D		0.7 (S), 0.9 (F)	-1036.55439		1D	1D	0.70	0.8 (N), 0.9 (F)	-750.17747
	1D	1D	0.62	0.36 (S)*, 0.9 (F)	-1036.75178		1D	1D	0.70	0.57 (N)*, 0.9 (F)	-570.18018
PH_4F	0D	0D, 0P			-442.33626		2D	1D	0.50, 2.3	0.8 (N), 0.9 (F)	-750.20630
	1D	1D, 1P	0.6	0.9 (F), 1.1 (H)	-442.47228	SF_6	0D	0D			-993.64798
PH_3F_2	0D	0D, 0P			-541.25862		0D	1D		0.42*	-993.97131
	1D	1D, 1P	0.6	0.9 (F), 1.1 (H)	-541.42444		1D	0D	0.59		-994.03147
PH_2F_3	0D	0D, 0P			-640.12078		1D	1D	0.69	0.61*	-994.16617
	1D	1D, 1P	0.6	0.9 (F), 1.1 (H)	-640.35097		2D	1D	0.55, 2.45	0.61*	-994.19549
PHF_4	0D	0D, 0P			-738.98433	HCl	0D	0P			-460.03029
	1D	1D, 1P	0.6	0.9 (F), 1.1 (H)	-739.28216		1D	1P	0.82	0.61*	-460.06014
PF_5	0D	0D			-837.84402	Cl_2	0D				-918.84557
	0D	1D		0.9	-838.02942		1D		0.55		-918.89973
	1D	0D	0.6		-838.10333	ClF	0D	0D			-558.79608
	1D	1D	0.65	0.68*	-838.20773		0D	1D		0.9	-558.82045
	2D	1D	0.64, 2.45	0.9	-838.21875		1D	1D	0.76	0.9	-558.84246
H_2S	0D	0P			-398.63672		2D	1D	0.6, 2.3	0.9	-558.84524
	0D	1P		1.1 (H)	-398.64653	ClF_3	0D	0D			-757.39440
	1D	0P	0.7		-398.65977		0D	1D		0.8	-757.47845
	1D	1P	0.69	1.1 (H)	-398.67011		1D	0D	0.75		-757.50514
	1D (STO)	1P (STO)	2.12	1.54	-398.67740		1D	1D	0.71	0.9	-757.56373
SH_5^{+c}	0D	0D			-399.76947	ClO_2F	0D	0D			-707.85672
	1D	1D	0.68	1.1 (H)	-399.92805		1D	1D	0.78	0.8 (O), 0.9 (F)	-708.21027
$SH_2{\cdot}CH_2$	0D	0D, 0P			-437.46709	ClO_3F	0D	0D			-782.58311
	1D	1D, 1P	0.64 (S)	0.38 (C)*, 1.1 (H)	-437.57644		0D	1D		0.8 (O), 0.9 (F)	-782.81990
							1D	1D	0.81	0.8 (O), 0.9 (F)	-783.12444
							2D	1D	0.5, 2.3	0.9 (O), 0.9 (F)	-783.16991
						ClF_5	0D	0D			-955.91722
							0D	1D		0.9	-956.06793
							1D	0D	0.75		-956.15128
							1D	1D	0.72	0.60*	-956.27289
							2D	1D	0.5, 2.3	0.9	-956.28929

[a] Calculations performed at experimental geometries[47] with Dunning–Hay (11s7p/6s4p) basis sets (see text) supplemented with 0, 1, or 2 sets of d functions (p functions on hydrogens) as indicated. [b] Exponents of d functions on the central atom were optimized; d function exponents on peripheral atoms took standard values except where separately optimized (indicated with an asterisk). SWPS refers to the five sets of d functions on sulfur used by Stromberg et al.[22] [c] For the hypothetical SiH_5^-, PH_5, SH_5^+ molecules see Reed and Schleyer.[8]

0.111 and 0.085 hartree for CH_2PH_3 and CH_3PH_2, and 0.109 and 0.055 hartree for CH_2SH_2 and CH_3SH.

2. Energy Depressions: Compounds of First- and Second-Row Elements. Energy depressions for compounds of first- and second-row elements are readily compared in Table I, the entries being derived from the separate listing in tables II and III. Several compounds of first-row elements included in the entries in Tables I–III are hypercoordinate; nitrogen is the first-row element in every case except O_3.

3. The d Function Component of the Molecular Wave Function. Inspection of the d function components introduced into the MOs of a molecule by supplementation has been carried out to enable

Table III. The Effect of Supplementary Basis Functions on Calculated Total Energies of Molecules AB_n Containing First-Row Elements[a]

molecule AB_n	supplementary basis (A/B)		supplementary function exponents[b] A	B	total energy, hartrees
H_2	0P	0P			-1.12476
	1P		1.1		-1.12927
CH_4	0D	0P			-40.17639
	1D	0P	0.5		-40.18482
	1D	1P	0.84	1.1	-40.20051
C_2H_2	0D	0P			-76.56251
	1D	1P	0.30	1.1	-76.68363
CO_2	0D	0D			-187.55296
	1D	0D	0.75		-187.63013
	1D	1D	0.76	1.06*	-187.67679
CF_4	0D	0D			-435.57789
	1D	0D	0.7		-435.71049
	1D	1D	0.69	0.9	-435.76504
HCN	0D	0D, 0P			-92.83545
	1D	1D, 1P	0.28 (C)	0.91 (N)*, 1.1 (H)	-92.88821
NH_3	0D	0P			-56.16583
	1D	0P	0.9		-56.18718
	1D	1P	0.83	1.1	-56.20190
NF_3	0D	0D			-352.52422
	1D	0D	0.8		-352.59521
	1D	1D	0.84	0.87*	-352.63728
N_2	0D	0D			-108.87802
	1D		0.89		-108.95933
N_2O	0D	0D			-183.59030
	1D	1D	1.03	0.88*	-183.71347
NOH_3	0D	0D, 0P			-130.91363
	1D	0D, 0P	0.55		-130.94130
	1D	1D, 1P	0.82	0.8 (O), 1.1 (H)	-130.97240
NOH_3	0D	0D, 0P			-279.34367
	1D	0D, 0P	0.8		-279.43489
	1D	1D, 1P	0.83	0.8 (O), 1.1 (H)	-279.50942
NO_2F	0D	0D, 0D			-303.32901
	1D	1D, 1D	0.80	0.8 (O), 0.9 (F)	-303.48121
NOF_3	0D	0D, 0D			-427.25238
	1D	0D, 0D	0.62		-427.36495
	1D	1D, 1D	0.82	0.8 (O), 0.9 (F)	-427.40283
	2D	1D, 1D	0.50, 1.3	0.8 (O), 0.9 (F)	-427.40651
H_2O	0D	0P			-76.00065
	1D	0P	0.9		-76.02535
	1D	1P	0.98	1.1	-76.04028
OF_2	0D	0D			-273.46883
	1D	0D	0.9		-273.50204
	1D	1D	0.90	0.9	-273.52553
O_3	0D				-224.07023
	1D		0.92		-224.14636
	2D		0.45, 1.35		-224.15157
HF	0D	0P			-100.01674
	1D	1P	1.14	1.1	-100.04398
F_2	0D				-198.70782
	1D		0.90		-198.73466

[a] Calculations performed at experimental geometries[47] with Dunning–Hay (9s5p/4s2p) basis sets (see text) supplemented with 0, 1, or 2 sets of d functions (p functions on hydrogens) as indicated. [b] Exponents of d functions on the central atom were optimized; d function exponents on peripheral atoms took standard values except where separately optimized (indicated with an asterisk).

Table IV. d Function Contributions per Bond to Electron Populations and Molecular Energy in Sulfur, Phosphorus, and Chlorine Components[a]

	atomic population	overlap population	molecular energy, hartree
SF_2	0.03	0.13	0.06
SF_4	0.05	0.20	0.08
SF_6	0.06	0.22	0.09
SO_2	0.09	0.33	0.13
SO_3	0.09	0.35	0.14
PF_3	0.03	0.18	0.06
PF_5	0.04	0.19	0.07
ClF	0.01	0.07	0.05
ClF_3	0.02	0.09	0.06
ClF_5	0.03	0.12	0.07

[a] (1D/1D) calculations.

Table V. Total Energies and Energy Components (hartrees) from Dunning–Hay Basis Set Calculations with and without d Function Supplementation[a]

	basis set	E_{total}	$2\sum\epsilon_i$	$\sum H_{ii}$	$\sum 2J - K$
NF_3	0D/0P	-352.52422	216.44242	-488.60602	136.08180
	1D/1D	-352.63595	215.87792	-489.39398	136.75803
	Δ	-0.112	0.565	0.676	-0.788
O_3	0D	-224.07023	-141.12408	-307.01638	82.94615
	1D	-224.14636	-140.84696	83.29940	-307.44576
	Δ	-0.076	0.277	0.353	-0.429
SO_2	(0D/0D)	-546.95504	-342.07904	-751.83104	204.87600
	(2D/1D)	-547.23271	-340.98438	-753.48104	206.24833
	Δ	-0.27767	1.09466	-1.65000	1.37233
	(0D/1D)	-547.07247	-341.58964	-752.55530	205.48283
	Δ	-0.11743	0.48940	-0.72426	0.60683
SF_6	(0D/0D)	-993.64798	-615.99332	-1371.30264	377.65466
	(2D/1D)	-994.19507	-611.88760	-1376.50254	382.30747
	Δ	-0.54709	4.10572	-5.19990	4.65281

[a] For meanings of symbols, see text.

the d function role in the molecular wave function to be inspected. Some results appear in Tables V–VII. In general, adding d functions to the basis set (a) raises the sum of the orbital energies, $\sum\epsilon_i$, (b) raises the energies of core orbitals, although no significant d function contributions occur in these parts of the molecule, and (c) distributes the d function contributions more or less uniformly across the higher lying orbitals of the valence shell. In a highly symmetrical molecule the added functions interact with functions centered on other atoms in only a few MOs. SF_6, for example, displays one kind of interaction in the e_g MOs and one in the t_{2g} MOs. In less symmetrical molecules like SO_2 (see Table VI) many types of interaction are dispersed across MOs of several different symmetry types; no one type of interaction predominates.

The effect of supplementary d functions on higher lying MOs is also to raise energies, often by quite large amounts, and the overall effect is that the sum of the occupied orbital energies is substantially raised (see Table V). Within the sample of molecules studied here there are just two exceptions. In SO_2 the second highest MO (a_2 symmetry) is lowered by 0.02 hartree and in H_2S the second highest MO (a_1 symmetry) is also lowered in energy (0.007 hartree). Since the orbital energies exaggerate the repulsive contributions to total molecular energy, interelectron repulsion energies being counted twice, any favorable effect on the attractive energy terms that result from adding d functions to the basis is likely to be obscured by the effect on the repulsion energy term. However, in cases where the contribution of the d function to bonding is especially large, the effect on the attractive energy component may become big enough to exhibit itself by lowering of the eigenvalue. This occurs in the upper a_1 MO of H_2S because the d_{z^2} and $d_{x^2-y^2}$ orbitals provide a small σ-type bonding interaction that augments the bonding between sulfur s and p orbitals and the s orbitals of the hydrogens.

In SO_2 the a_2 orbital, which is composed of oxygen p orbitals perpendicular to the plane of the molecule, gains enough dπ–pπ bonding character when d functions are used on sulfur to lower the eigenvalue of this MO. As a result, the a_2 MO acquires some bonding character and provides a small amount of charge transfer back to the sulfur atom. (See also Reed and Schleyer.[11b])

Comparison of SO_2 and O_3. A comparison of sulfur dioxide with its first-row analogue, ozone, is possible from the energy data in Tables III and V and the electron distribution data in Table VII. Supplementary functions in the SO_2 wave function produce more than three times the energy lowering found for O_3, and d function contributions to the atomic and overlap populations are an order of magnitude greater. Improving the quality of the supplementary basis has, relatively, the same effect in ozone as it has in sulfur dioxide, and when the d function exponents are varied the shape of the energy surface around the minimum is very similar for the two molecules.

Table VI. The Effect of d Supplementation of the Basis Set on the MO Energies of SO_2[a]

MO	(2D/1D)	(0D/1D)	(0D/0D)	role
a_1	-0.496	-0.487	-0.493	sulfur lp; dσ-pσ bonding
a_2	-0.520	-0.501	-0.503	oxygen π lp; dπ-pπ bonding
b_2	-0.541	-0.545	-0.550	in plane oxygen 2p lp; dπ-pπ bonding
b_1	-0.665	-0.680	-0.694	π-bonding; dπ-pπ bonding
a_1	-0.695	-0.702	-0.718	in-plane; σ-bonding and lp character
b_2	-0.699	-0.707	-0.695	in-plane; σ-bonding and lp character
a_1	-0.868	-0.888	-0.898	nonbonding; mainly sulfur 3s
b_2	-1.404	-1.412	-1.444	σ-bonding
a_1	-1.509	-1.533	-1.573	σ-bonding
a_1	-6.838	-6.892	-6.913	sulfur 2p
b_1	-6.839	-6.893	-6.913	sulfur 2p
b_2	-6.841	-6.896	-6.920	sulfur 2p
a_1	-9.160	-9.217	-9.239	sulfur 2s
a_1	-20.618	-20.610	-20.629	oxygen 1s
b_1	-20.618	-20.610	-20.629	oxygen 1s
a_1	-92.180	-92.221	-92.234	sulfur 1s
E_{total}	-547.23271	-547.07247	-546.95504	

[a] Energies in hartrees. At eigenvalues near ϵ = 0.7 hartree note the change in the order of the a_1 and b_2 MOs in the (0D/0D) calculation relative to the (2D/1D) results. "lp" = "lone pair".

Table VII. Atomic and Overlap Populations for s, p, and d Functions in O_3 and SO_2 Calculated with and without d Function Supplementation of the Basis Set[a]

basis set	central atom	terminal atoms
SO_2		
(2D/1D)	$s^{6.10(-0.72)}p^{7.78(1.49)}d^{0.17(0.67)}$	$s^{3.90(-0.08)}p^{4.30(0.76)}d^{0.01(0.05)}$
(0D/0D)	$s^{6.43(-1.21)}p^{8.10(1.39)}$	$s^{4.19(-0.23)}p^{4.53(0.20)}$
O_3		
(2D)	$s^{3.80(-0.07)}p^{3.77(0.24)}d^{0.01(0.10)}$	$s^{4.00(-0.11)}p^{4.06(0.08)}d^{0.01(0.04)}$
(0D)	$s^{3.07(0.74)}p^{4.09(0.05)}$	$s^{3.24(0.72)}p^{4.01(0.06)}$

[a] The data listed represent the total atomic populations and, in parentheses, the total overlap populations for each type of function in inner as well as valence shells.

Introduction of d functions into the calculation has unexpectedly large effects on the distribution of electrons in these molecules. In Tables VII the overall populations have been subdivided into atomic and overlap populations. In SO_2, electronic charge is distributed in favor of the more electronegative oxygen atoms, leaving sulfur with a (Mulliken) charge of +1.5. This figure is reduced by 0.25 when d functions are included in the calculation. Without d functions, the valence s orbital of sulfur is heavily occupied, the advantage of its low energy being captured even at the expense of a substantial negative overlap population (-1.21). The inclusion of d functions sees this figure whittled to -0.72. Further, the valence shell p orbitals of sulfur, which are responsible for the S-O binding, increase their contribution to binding. The overlap population contributed from $3p_S$ rises from 1.39 to 1.49 when the d functions are included in the basis.

The electron distribution for ozone is generally similar to that for sulfur dioxide. (Caution: the near-degeneracy of two configurations in O_3 makes single-determinant wave functions unreliable for many conclusions.) The same dependence on p orbitals for bonding is found for O_3 as for SO_2. Further, the inclusion of d functions in the calculation produces changes in the occupations and the role of s and p orbitals well beyond what would be expected from the degree of involvement of the d functions themselves. As in SO_2, the supplemented basis calculation displays increased p orbital overlap density. One notable feature is that the addition of d functions alters the role of the 2s AO from bonding to nonbonding. The magnitude is surprisingly large for so low a total d function population (Mulliken gross atomic population = 0.11). It is possible that the extreme sensitivity of s and p function bonding to introduction of d functions is due to the fact that d functions are not affected by the orthogonality requirement, contributing to the wave function in a part of the internuclear region where the s and p amplitude changes rapidly.

HNO_3 and HPO_3. In these molecules the contributions from d functions to the wave function are greatest in the highest lying orbitals, as is usual. However, there are contributions to all the valence shell MOs, the d function coefficients in the HOMO being no more than about twice as big as those in the tenth MO from the top. The d function contributions on the oxygen atoms are spread across the valence shell MOs in a similar manner. The d function coefficients in the MOs of HNO_3 are generally about half as big as those in similar orbitals in HPO_3, which correlates with the size of the energy depressions (ΔE_d is 0.166 hartree for HNO_3 and 0.301 hartree for HPO_3).

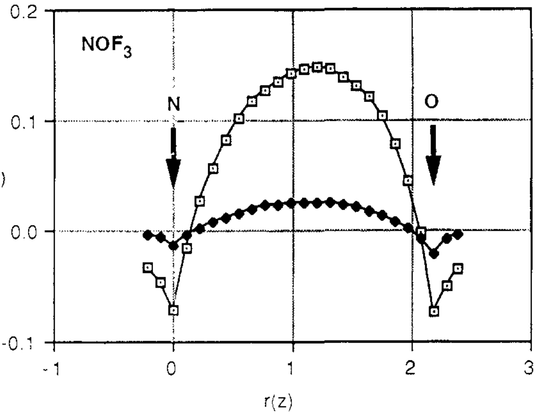

Figure 1. Overlap density of the N-O bond in NOF_3 plotted along the N-O bond axis (open squares); data from a calculation in which the sp basis on each center is supplemented by one set of d functions. The contribution from the d functions on nitrogen is shown separately (filled symbols).

The existence of d functions with symmetry properties not shared by p or s functions is responsible for a small amount of dπ-pπ bonding in the highest π-type MO in both molecules, but this is only a small part of the overall d function role in these molecules. The direction of electron transfer in bonds is an important factor in determining the role of the added functions: d functions in HNO_3 tend to increase the importance of electron transfer from N to O; they provide for the opposite in HPO_3 where charge transfer from the less electronegative phosphorus atom is already extreme.

NOF_3 and POF_3. The main features of the comparison between HNO_3 and HPO_3 recur when NOF_3 and POF_3 are compared: the d function populations are larger and the energy depressions bigger in the molecule with the second-row element. The d function contributions occur in most of the valence shell MOs but, as usual, they are greatest in the highest lying orbitals.

4. Identifying the Site of d Function Involvement. Information about the location of density differences due to d function supplementation of the basis set has been obtained in two ways: direct inspection of the electron density distribution in calculations made with and without supplementation and comparisons of the effect on molecular energy of supplementation of the basis set by s and p functions as well as d functions.

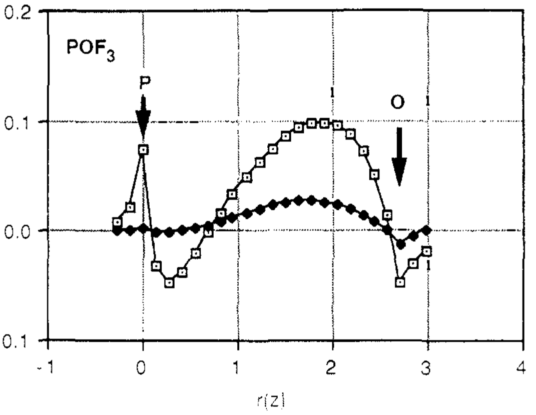

Figure 2. Overlap density of the P–O bond in POF$_3$ plotted along the P–O bond axis (open squares); data are from a calculation in which the sp basis on each center is supplemented by one set of d functions. The contribution from the d functions on phosphorus is shown separately (filled symbols).

N–O and P–O Overlap Density in NOF$_3$ and POF$_3$. Figures 1 and 2 contain plots of the N–O and P–O σ-bond overlap density, $p(r)$, as measured along the N–O and P–O bonds of these compounds in (1D/1D/1D) calculations. [The overlap density is the sum of the two-center terms in the electron density expression; the atomic density is the sum of the one-center terms.] In both figures the upper curve (open squares) indicates the total overlap density and the lower curve (filled symbols) indicates the d function contribution.

Three features of the overlap component of the electron density need to be pointed out. The first is the position of the d function contribution, which peaks very close to the peak of $p(r)$, the overall overlap density. Second, the d function contribution in POF$_3$ is polarized in the direction of the more electronegative atom, compared with a more evenly balanced contribution in the nitrogen compound where the electronegativity difference is so much smaller. Third, the most striking feature of the plot is the large density trough near phosphorus in the POF$_3$ plot. This trough, like the smaller examples in the vicinity of the first-row atoms, is a consequence of the orthogonality constraints on 2s, 3s, and 3p atomic orbitals, all of which are involved in the N–O and P–O overlap density in these compounds.

S–O Overlap Density in SO$_2$. Figure 3 contains a plot of the sulfur–oxygen overlap density [$p(r)$] as computed at points along the S–O axis. The sulfur atom is at the origin and the position of the O nucleus is shown, distances being given in atomic units (a_H = 52.9 pm). The effect of orthogonality on the s and p AOs of sulfur is apparent in the sharp drop in $p(r)$ between $r = 0$ and $r = 0.5a_H$. A similar feature occurs near the O nucleus where it is the 2s AO of oxygen that is responsible. Figure 3a shows $p(r)$ as calculated in the 2D/1D case ($\zeta_d' = 2.3$, $\zeta_d'' = 0.55$) together with the contribution to $p(r)$ made by the d functions on sulfur. Figure 3b shows a comparison between the contribution to $p(r)$ from d functions on both atoms and that from those on sulfur only.

The overlap part of the S atom d function contribution to the wave function, for optimum exponents, produces a maximum at a point roughly two-thirds of the distance from the sulfur to the oxygen nuclei. The d function contribution is almost totally contained between the S and O nuclei and reduces somewhat the negative contribution to overlap density produced by the node in the 3p orbital of sulfur. At the position between the nuclei where the S–O overlap density is maximum, about 35% of it is due to the d function contributions.

P–F Overlap Density in PF$_3$ and PF$_5$. Figure 4 contains overlap density plots, similar to those in the other figures, in this case computed along the P–F axis of PF$_3$ and PF$_5$ to facilitate comparison of the d function bonding contribution in the two categories of compound.

5. Orbital Exponents of Supplementary d Functions. Optimization of the central atom d function exponent was carried out for all compounds listed in Tables II and III, and the optimum values are included there for the (1D/1D) case. The results conform to the tolerances reported by Magnusson and Schaeffer.[4]

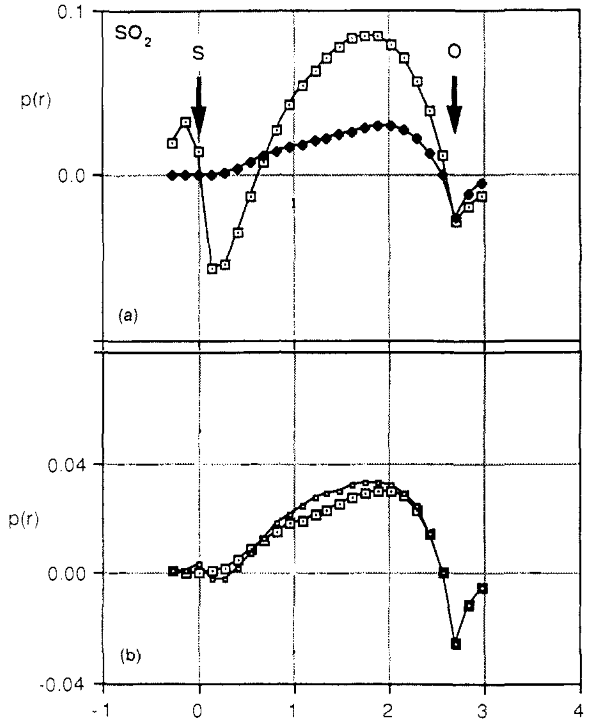

Figure 3. (a) Overlap density of the S–O bond in SO$_2$ plotted along the S–O bond axis (open squares). The contribution to overlap density from the supplementary d functions on sulfur is shown separately (filled symbols). In part b this same contribution (large squares) is shown in relation to the total d function contribution from both atoms (small squares), the difference being the small additional contribution from the d functions on oxygen. The data are from a calculation in which the sp basis on each center is supplemented by one set of d functions.

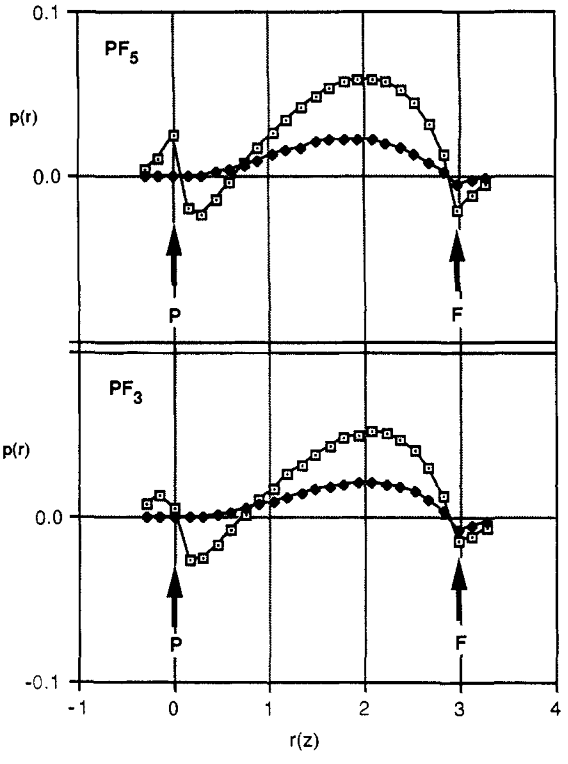

Figure 4. Overlap density of the P–F bond (open squares) in PF$_3$ and PF$_5$ (axial bond). The contributions from the supplementary d functions are shown separately (filled symbols) in both cases.

For d functions added to Dunning–Hay basis sets of Si, P, S, or Cl the exponents $\zeta(d)$ = 0.55, 0.60, 0.70, 0.75, respectively, yield molecular energies within 0.001 hartree of those obtained by detailed optimization of the d function exponent of the second-row atom. With basis sets of the level of the Dunning–Hay double-ζ set used here there is no interaction between the sp and d functions. For example, in calculations of anions containing second-row elements, the energy depressions gained by adding diffuse functions[24] and d functions are quite independent of one another.

For oxo and fluoro compounds the optimum value of the central atom d function exponent is almost unchanged from one compound to another (Tables I–III), but different values are sometimes required in calculations of compounds containing elements such as carbon (HCP, $SH \cdot CH_3$, $SH_2 \cdot CH_2$, etc.). The optimum values are particularly prone to change when bond lengths are short, as in the case of P_2 for which the optimum exponent moves from the value characteristic of the phosphorus oxides and fluorides (ζ_d = 0.60) to 0.43. Nevertheless, the energy difference between calculations at ζ_d = 0.43 and 0.60 is still only 0.007 H, only 10% of the total energy depression due to supplementation. Exponent values for d functions on first-row atoms show little variation between different nitrogen compounds and different oxygen compounds, but the variance in optimum exponent values between different carbon compounds is greater.

The effect of changing the d function exponent on the overlap part of the electron distribution in SO_2 can be appreciated from the following data for SO_2. ΔE_d, p, and p_{max}, as calculated for the three separate values of the supplementary function exponent, are

ζ_d	ΔE_d	$p_{max}(r)$	p
0.4	0.223	0.089	0.453
0.7	0.258	0.083	0.302
1.0	0.247	0.068	0.168

p is the S–O bond order and p_{max} is the height of the overlap density maximum along the S–O axis. It is clear that the shape of the electron density profile between the two atoms is important, not merely the size of the maximum value to which it rises. As already mentioned, the introduction of an orthogonality effect at oxygen is probably why the size of ΔE_d is so sensitive to lowering the d function exponent. Increasing the exponent has not nearly so great an effect.

Interdependence of Exponents of d Functions on Different Centers. In SO_2, the optimum value of the d function exponent on sulfur depends on the d function exponent used for the oxygen centers. When $\zeta_d(O)$ = 0.57, the value obtained by separately optimizing it, the optimum sulfur d exponent is 0.76. When the oxygen d function exponent is fixed at the "standard" value [$\zeta_d(O)$ = 0.9] the optimum sulfur d exponent is 0.71. When no functions on oxygen are used at all, the optimum sulfur d exponent is 0.62. This behavior is quite typical.

Radial Dependence of s, p, and d Functions. Atomic orbitals of all types (s, p, and d) respond to bond formation by changes in the radial profile, and this process, together with transfer of charge from the less to the more electronegative atom in the bond, is commonly referred to as "electronegativity equalization". Radial dependence changes cannot be modeled by the use of "minimal" basis sets and, in consequence, the calculation of optimum geometries and other molecular properties related to bonding often produces distorted results.[25]

In bonds to highly electronegative elements, the valence shell orbitals of elements of low electronegativity are contracted. The AOs of the more electronegative elements are expanded, the outer components of the valence shell functions appearing with greater weight than in the unbound atom. This phenomenon, viz. the effect of the field of fluorine atoms on sulfur 3s and 3p orbitals in SF_2, SF_4, and SF_6, has been monitored by determining the mean radii ($\langle r_s \rangle$,$\langle r_p \rangle$) of the functions that represent these AOs in the molecular wave functions. The results (Table VIII) show the range of $\langle r_s \rangle$ and $\langle r_p \rangle$ values calculated for sulfur 3s and 3p AOs contributing to the various valence shell MOs of these compounds. The more compact sulfur orbital contributions occur in the lower energy MOs (such as MOs describing the 3s electrons) and the more diffuse contributions in the higher lying MOs. Comparison of these values with mean radii for the S atom and the S^+ ion shows the effect of the potential field of the fluorines on electrons in the sulfur valence shell.

Table VIII. Mean Radii (pm) of the Valence Shell s and p Functions of Sulfur in SF_2, SF_4, SF_6, S, and S^+

	$\langle r_s \rangle$	$\langle r_p \rangle$	$\langle r_d \rangle$
S atom (^3P)	80–81	106–110	
S^+ ion (^4S)	76–78	99	
SF_2	74–90	84–107	82–85
SF_4	69–80	84–102	80–84
SF_6	65–66	79–101	84–85

Table IX. Variation of Sulfur, Oxygen, and Fluorine Optimum d Function Exponents with Change of S–O Bond Length and OSO Angle in SO_2 and SF_6

bond length, pm	bond angle	optimum exponent $\zeta_d(S)$	optimum exponent $\zeta_d(O)$	total energy, hartree (1D/1D) basis	total energy, hartree (0D/0D) basis	ΔE_d, hartree
SO_2						
133	119.3	0.82	0.65	−547.191 64	−546.844 71	0.347
138	119.3	0.79	0.63	−547.212 86	−546.918 99	0.294
143.1	119.3	0.76	0.57	−547.214 81	−546.955 04	0.260
148	119.3	0.73	0.55	−547.203 10	−546.973 13	0.230
153	119.3	0.64	0.54	−547.180 52	−546.962 64	0.218
143.1	110.0	0.69	0.58	−547.207 77	−546.954 91	0.253
143.1	130.0	0.75	0.60	−547.206 60	−546.947 09	0.266

	bond angle	optimum exponent $\zeta_d(S)$	total energy, hartree (1D/1D) basis	total energy, hartree (0D/0D) basis	ΔE_d, hartree
SF_6					
145	90.0	0.75	−994.092 80	−993.431 88	0.661
155	90.0	0.69	−994.158 15	−993.647 98	0.510
165	90.0	0.64	−994.109 86	−993.717 09	0.393

6. Dependence of d Function Exponents on Molecular Geometry. The data in Table IX represent the results of optimization of the exponents of d functions on sulfur and phosphorus in SO_2 and SF_6 as the S–O and S–F bond lengths are changed in both directions from the experimental values (142 and 155 pm, respectively). No other feature of the geometry or of the (1D/1D) basis set on sulfur, oxygen, or fluorine atoms was changed.

Calculations on SO_2 with bond angle arbitrarily set at 110° and 130° (see Table IX) show hardly any change in the optimum exponent values from those calculated for the experimental equilibrium value 119.3°; d functions are clearly much less sensitive to bond angle variation than to compression or elongation of a bond.

7. Geometry Optimization with and without d Functions. Geometries obtained by the gradient method are reported in Table X for three normal valency fluorides calculated with and without d functions; they may be compared with results of the same procedures applied to hypercoordinate molecules.[2,3]

Discussion: Tests of the d Function Hypotheses

The two proposals for characterizing d functions in molecules formed by second-row elements are now tested against the evidence presented in the preceding sections.[26] The primary evidence is

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(24) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609–5612. Spitznagel, G. W.; Clark, T.; Schleyer, P. v. R.; Hehre, W. J. *J. Computational Chem.* **1987**, *8*, 1109–1116.

(25) Magnusson, E. *Aust. J. Chem.* **1988**, *41*, 827–837.

(26) Valence expansion by means of d orbitals in oxygen and fluorine compounds should not be confused with d orbital explanations for other phenomena. Thus, although they consider the sulfur d orbitals to make important contributions to the "semi-polar" S–O bonds of dimethyl sulfone and related compounds, Streitwieser and co-workers find no d orbital induced stabilization of carbanions adjacent to the sulfone or the sulfide groups (Bors, D. A.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 1397–1404. Streitwieser, A., Jr.; Williams, J. E., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 191–192). Also, valence d orbitals should not be confused with Rydberg d states needed to describe excited states of SF_6 (Hay, P. J. *J. Am. Chem. Soc.* **1977**, *99*, 1003–1012).

Table X. Geometry Optimization Results Calculated with and without d Function Supplementation[a]

		3-21G	3-21G(d)	(0D/0D)	(1D/1D)	exptl
BF_3	E_{total}	−321.465 84	−321.566 84	−232.158 98	−323.276 12	
	r(B–F), pm	132.8	129.8	133.6	130.6	130.7
SiF_4	E_{total}	−683.272 08	−683.487 34	−686.861 61	−687.083 48	
	r(Si–F), pm	158.4	152.8	162.2	155.0	155.4
PF_3	E_{total}	−635.775 05	−635.955 69	−639.056 54	−639.229 01	
	r(P–F), pm	161.0	153.8	165.7	156.0	156.3
	∠(FPF), deg	96.2	97.4	95.9	97.1	96.9

[a] Energies in hartrees. For experimental values see ref 46.

the effect on calculated molecular energy of including d functions in the basis set, the magnitude of which is large and clearly not "chemically irrelevant".[27] On the other hand, the experimental evidence suggests that d orbital occupancies must be very low.[13,28] However, for the purpose of argument this evidence will be ignored.

(i) Energy Depressions—Normal Valency and Hypercoordinate Species. The results from this study show large ΔE_d values for many other types of molecule than the allegedly hypervalent species and provide no clear demarcation between them and normal valency compounds. ΔE_d increases smoothly from first-row hydrides (ca. 0.03 hartree), through second-row hydrides (ca. 0.05 hartree), other first-row species like O_3 and NF_3 (ca. 0.1 hartree), first-row hypercoordinate compounds like NOF_3 (ca. 0.2 hartree), second-row normal valency compounds like PF_3 (ca. 0.2 hartree), to second-row hypercoordinate species (0.15 to 0.55 hartree). Although the second-row hypercoordinate compounds exhibit the largest ΔE_d values, the large energy depressions in other categories frustrate the use of the energy criterion to argue that d orbitals play a role in so-called hypervalent molecules but not in the other kinds of molecule.

Provided the basis set level is the same, ΔE_d values may be decomposed into values appropriate to different kinds of bond. These "per bond" values show only limited variation from one molecule to another. This is true for the binary molecules examined in Table IV, for the $PH_{5-n}F_n$ series, and also for more complex compounds. (See also Baird and Taylor.[29]) This observation is most easily explained if the involvement of d functions is characteristic of the bond, rather than the kind of molecule that contains it. The data suggest that the extra involvement of d functions in hypercoordinate compounds (like NOF_3 and POF_3) over normal valency compounds (like NF_3 or PF_3) is mainly due to the fact that they have more bonds; the "per bond" ΔE_d values are roughly the same for both categories. On the assumption that d orbitals are responsible for expanding the octet, very different "per bond" values of the energy depression would have been expected for the pairs: SO_2 and SO_3, SF_4 and SF_6, and PF_3 and PF_5. In fact, "per bond" ΔE_d values increase very little on going from normal valency compounds to hypervalent species.

If d functions enter the wave function of hypercoordinate molecules as polarization functions, not as valence orbitals, an explanation is required for the anomalously large size of their participation. Two features of second-row elements, one quantitative and one qualitative, provide it. The first is related to the size of an element and the number of bonds it can accommodate and the second to the degree of charge transfer that occurs when it is bound to oxygen or fluorine, the ligands which are pre-eminent in inducing hypervalent behavior. The results here show that d function participation is greatly enhanced by charge transfer whatever the provenance of the supplemented atom. (Energy data for the hypothetical molecules[8] SiH_5^-, PH_5, and SH_5^+ are of value here; although the molecules are isoelectronic the ΔE_d values rise from 0.066 to 0.159 hartree, an increase paralleled by the trend in charge transfer from the hydrogens.) When large size, the existence of orthogonality constraints, and relatively low electronegativity come together, as in the case of the second-row elements, no further explanation for the contrast in d function participation between first- and second-row examples is necessary.

The influence of electron withdrawal from the central atoms on d function involvement is clear in the data on the effects of substituting a peripheral sulfur for an oxygen atom. Thus, ΔE_d is greater for PF_3O (0.345 hartree) than it is for PF_3S (0.306 hartree). The same kind of contrast applies to SOF_2 (0.270 hartree) and SSF_2 (0.222 hartree), and ΔE_d values for CO, CO_2, and CH_2O (0.075, 0.120, and 0.064 hartree) are all 10–20% greater than the values for the corresponding sulfur compounds CS, CS_2, and CH_2S (0.068, 0.095, and 0.054 hartree). This behavior is accommodated by the suggestion that d functions take the role of facilitating π-type charge transfer back to the central atom from which electronic charge has been removed by more electronegative groups on the periphery. The data here suggest that heavy removal of charge by an electronegative first-row atom invites a bigger contribution from d functions than the presence of a less electronegative second-row atom, in spite of the expected greater complexity of the potential field surrounding the atom with the extra electrons.

(ii) Energy Depressions—Peripheral Atoms. As the data in Tables I–III show, molecular energies are lowered by adding d functions to the basis sets of peripheral atoms as well as to those of the central atom. The energy increment per added function is much greater for the central atom, but when the energy depressions are calculated on a "per bond" basis the distinction disappears, d functions on the outer atoms being only slightly less important than those in the middle. In SF_6, for example, ΔE_d is 0.323 hartree when d functions are added to fluorine atoms only. Adding d functions to sulfur as well provides a further 0.195 hartree. (There is redundancy between the d functions on the different atoms; supplementing sulfur only yields ΔE_d = 0.383 hartree.)

(iii) Energy Depression—Compounds of First-Row Elements. When energy depression results are obtained at the same basis set level the contrast between second shell and third shell behavior is less spectacular than usually reported. Corresponding pairs of first- and second-row hydrides, such as NH_3/PH_3 and H_2O/H_2S, show only slightly more d function involvement in the wave function and only slightly greater energy depressions for the compounds of the heavier element. When oxygen or fluorine is substituted for hydrogen (OF_2/SF_2, NF_3/PF_3, etc.) the differences are greater. ΔE_d values (hartrees) for the hydrides and fluorides of elements in groups 14–17 reveal a progression that is easier to explain as the result of several different causes (the degree of electron withdrawal from the central atom, the nature of the surrounding atoms, and the number of bonds) than as due to a sudden change in the nature of the participating orbitals when the octet is exceeded.

group 14	CH_4	SiH_4	CF_4	SiF_4		
ΔE_d	0.046	0.052	0.187	0.237		
group 15	NH_3	PH_3	NF_3	PF_3	PF_5	
ΔE_d	0.037	0.051	0.113	0.185	0.375	
group 16	H_2O	H_2S	OF_2	SF_2	SF_4	SF_6
ΔE_d	0.041	0.043	0.057	0.112	0.287	0.544
group 17	HF	HCl	ClF	ClF_3	ClF_5	
ΔE_d	0.028	0.030	0.046	0.169	0.343	

If the hydrides are excluded, the energy depressions per bond range

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(27) Coulson, C. A. *Proc. Robert A. Welch Found. Conf. Chem. Res.* **1972**, *62*, 61–98.

(28) A recent example is: Gassman, P. G.; Callstrom, M. R.; Martin, J. C.; Rongione, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 8724–8725. See also experimental work cited by Reed and Weinhold (ref 12).

(29) Baird, N. C.; Taylor, K. F. *J. Computational Chem.* **1981**, *2*, 225–230.

from 0.029 hartree for OF_2 to 0.085 hartree for SF_6. However, when electron withdrawal by fluorine from elements of either row is taken into account and comparison made between compounds with bonds between elements of similar electronegativity, the contrast between compounds of first- and second-row elements is much less marked.

(iv) Energy Depressions—First-Row Hypercoordinate Compounds. Some ΔE_d values in hartrees for nitrogen and phosphorus compounds follow; they refer to calculations carried out with a single set of d functions on each center (1D/1D/1D) compared with the unsupplemented case (0D/0D/0D).

	NH_3	NOH_3	NF_3	FNO_2	HNO_3	NOF_3
ΔE_d	0.037	0.059	0.113	0.152	0.166	0.173
	PH_3	POH_3	PF_3	FPO_2	HPO_3	POF_3
ΔE_d	0.051	0.167	0.185	0.297	0.301	0.345

ΔE_d is bigger in molecules containing a second-row atom but, once allowance is made for the very much greater ionic character in the bonds around phosphorus, d functions respond to the rising complexity of the internuclear potential represented by the series of compounds in a similar way.

(v) Attractive and Repulsive Energies. Comparison of eigenvalues and total electronic energies obtained with and without d function supplementation of basis sets shows that d functions facilitate the transfer of electronic charge into the internuclear, bonding region at the expense of the outer parts of the valence wave function. This results in increased repulsion energies between core electrons and the valence shell and accounts for the rise in core orbital energy levels. This effect of adding d functions is easily explained. Inner shell d functions do not exist, and since the supplementary functions are orthogonal to all s and p functions by virtue of their angular dependence they may contribute to the inner parts of the valence shell without inhibition. The conclusion is similar to that of Cruickshank, who concludes, on different grounds, that the effects of d functions are due to "penetration".[30]

The results of a comparative energy analysis are readily explained by d function polarization of the wave function, an effect of which s and p functions are not capable, for orthogonality reasons. However, they do not invalidate the idea of a valence role for d functions, since these effects would also be observed if the d functions represented valence orbitals.

(vi) The Type of d Function Involvement in the Molecular Wave Function. Very few attempts have been made to use shape indications to identify d function contributions to molecular wave functions. Stromberg et al.[22] do so, claiming that the bond length of SO_3^{2-} cannot be correctly calculated without using sets of d functions with a high-exponent component, and they make the point that the result is similar in shape to the d orbital optimized for the $s^2p^2d^1$ ^4F state of S^+. However, by itself this is insufficient evidence for positive identification of the d function as a d orbital. Cruickshank and Eistenstein[30] argue from their calculations of deformation density maps that it is the absence of radial nodes in the d functions that enables them to make strong contributions close to sulfur in compounds with S–O bonds. They reinforce the argument with radial distribution data obtained from atomic calculations of sulfur atoms and ions (and nitrogen atoms and ions) building on earlier work of particular importance in the history of this subject.[31] These "penetration effects" explain the importance of the d functions of sulfur compared to those of nitrogen in NO_2 where the orthogonality that results from the radial distribution of the d function offers no advantage. Elsewhere Cruickshank and co-workers show how the close similarity between features of the experimental and theoretical deformation density maps depends on the presence of d functions in the sulfur basis set. While attributing the importance of d functions in SO_2, SO_3, etc. to the penetration/orthogonality mechanism, Cruickshank still takes the "polarization function" view.[32]

The evidence obtained from this study about d function contributions to molecular wave functions provides persuasive evidence for a polarization role for d functions. Results gathered in this study are in harmony with the conclusions drawn from difference density maps by Cruickshank[30-33] as well as with other work showing higher angular momentum functions facilitating "bond shortening" and a removal of electron density from the remote side of bonded atoms.[34] Patterson and Messmer have used valence bond calculations to show that d functions introduce angular correlation which becomes important when the number of electron pairs around sulfur increases, hence the much greater energy lowering in SO_2 than in H_2S.[35] The evidence here about the effect of adding d functions seems to point entirely at the improvement in the bonding part of the wave function. The absence of evidence for angular effects is probably due to the absence of correlation in the method.

SO_2 is a useful test case for the question of role, illustrating how the transfer of charge from O to S facilitated in the second highest MO (a_2 symmetry) by the d_{xy} function on sulfur, a role precluded for s and p functions. However, even though the unique d function contribution to the a_2 MO of SO_2 is enough to lower the a_2 eigenvalue below the value calculated for the unsupplemented case, its small magnitude militates against a valence orbital explanation; it is still of the same order of magnitude as the interactions involving d functions in the other MOs where they are not unique. In general then, the contributions of the d functions to bonding are not dominated by one or two valence interactions but are distributed over many of the higher lying MOs. In this respect, there is no difference between hypercoordinate compounds and normal valency molecules.

Angyan et al.[7,36] have argued for a valence role for d orbitals in sulfuranes and other allegedly hypervalent molecules from the fact that an MO which is non-bonding in an sp basis (contributions only from the oxygen AOs in an OSO fragment) becomes formally bonding in a spd basis. (The case is similar to that of SO_2, just considered.) Although this interaction is stronger than any other made by the sulfur d functions, it is too small to sustain the weight of a valence d orbital hypothesis. The character of the MO is unchanged, even though it now includes a bonding interaction. Yadav et al. concede that energy, geometry, and bond order contributions from d functions would be individually inadequate as criteria for determining role but opt for the "true valence orbital" description in hypervalent sulfur compounds from a consideration of all three.[6] In the process they note that the optimum size of the d "orbitals" varies from one criterion to another. However, this analysis is inadequate. First, the only physically meaningful method of optimizing the size of d functions is that which leads to minimum energy and, second, neither energy nor any other criterion of size permits any choice to be made about roles. Sizable d function involvement is a necessary condition for a d orbital role, but it is not sufficient. (Note that the use of Mulliken bond orders to measure d function contributions to the electron density has been criticized.[37])

A final comment in this section concerns the fact that functions of low order centered away from nuclei ("bond functions") are able to provide the same energy and geometry optimization advantages as nuclear-centered d functions.[38] This is evidence

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(30) Cruickshank, D. W. J.; Eisenstein, M. *J. Mol. Struct.* **1985**, *130*, 143–156; *J. Computational Chem.* **1987**, *8*, 6–27.

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against a unique valence role for the latter. Both types of supplementation provide the necessary degree of deformation to the wave function between the nuclei, but the bond functions do so with an unacceptable level of overlap with basis functions on other centers and, in consequence, with large basis set superposition erros.[39]

(vii) Exponent Optimization. As clearly displayed in Table I, optimizing the d function exponents for any particular element produces values that are almost entirely independent of whether the molecule is a normal compound or hypercoordinate. The fact that d functions appears in molecular wave functions with such uniform size is the single item of evidence most destructive of the "valence role" idea for d functions: the effects of the molecular field, postulated to contract loosely bound d orbitals to the point where bonding is possible,[18] seem to be completely absent.

The radial dependence calculations of d functions in normal valency and hypercoordinate molecules confirm this evidence and, in addition, show how different is the role of d functions from that of s and p functions. For SF_2, SF_4, and SF_6, for example, the mean radii of d functions incorporated in MOs lies within a range of 80–85 pm. This is quite remarkable because it is so narrow (much more so than the ranges found for s and p functions in the same molecules) and because it is so low (lying well inside the mean radii found for d functions in states of the atom derived from one or two d electrons).[30,40] Adding additional fluorine atoms in the SF_2, SF_4, SF_6, sequence produces an easily observed effect: the effect of the two fluorine atoms in SF_2 on the mean sulfur s and p radii is as great as that of removing an electron from the sulfur atom; in SF_4 and SF_6 it exceeds it. d functions, however, show no such response! There is also no sign of any progressive contraction of the d functions across the SF_2, SF_4, SF_6 sequence.

In this category there is a new item of information from this study—the strong response in the optimum exponent and d function energy increment to lengthening or shortening of the bond length (see Table IX). Note that the optimum d function exponent on the peripheral atom also changes, but less so than the sulfur d function exponent. Over the 20-pm increase in S–O bond length from 133 to 155 pm the optimum exponent drops from 0.82 to 0.64. This change far exceeds the variation in optimum sulfur d exponent between all the sulfur compounds with SH, SO, and SF linkages examined in this study ($\zeta_d = 0.71 \pm 0.02$) which, using experimental geometries, cover a range of bond distances to the sulfur atoms of 133–159 pm. Such constancy in the optimum size of d functions across this range of compounds, which includes changes in the bond order to sulfur as well as bond length differences in compounds where the formal bond order does not change, is unexpected.

A final item of evidence in this category is the way in which the optimum d function exponent of one element in a molecule changes when d functions are left out of the basis sets of the others (compare the optimum d function exponents for (0D/1D) and (1D/0D) wave functions with those for (1D/1D) cases in Tables II and III). The most obvious explanation for this is that the distortions in the wave function which d functions ameliorate are to be found around every atom, not merely near second-row atoms; supplementary functions in the basis set of one atom can then compensate for their omission from another, provided that the exponent of the remaining function is appropriately reduced. Such behavior would be unexpected if second-low atoms were utilizing valence d orbitals.

(viii) Geometry Optimization. d function supplementation of sp basis sets immediately removes the large discrepancies from experiment obtained when the geometries of hypercoordinate molecules are optimized by the ab initio gradient procedure.[2] So far as the two roles are concerned, this evidence is equivocal, since discrepancies would be expected in either case. The same applies to calculations of other bond-dependent properties, such as harmonic vibrational frequencies.[41] Note, however, that although d functions are necessary for quantitative accuracy in geometry determinations, they are not required to reproduce qualitative features, such as different lengths for axial and equatorial bonds in PF_5, ClF_3, etc. (see the compilation in Hehre et al.[3])

The second result of the new calculations is that supplementary d functions are just as important in gradient optimization calculations of first- and second-row normal valency compounds as they are for hypercoordinate compounds if compounds with similar bonding characteristics are chosen. This observation clearly eliminates the use of the "geometry optimization" criterion to confer valence orbital status on d functions in hypercoordinate molecules when it is unacceptable in molecules in other categories.

(ix) The d Function Contribution to the Bond Electron Density. In contrast to s and p functions, d functions are shown by population analysis to make large contributions to the shared electron density and small contributions to one-center density terms (see Tables IV and VII). Actual plots of overlap density along the bond axis in the molecules considered in this report confirm the heavy involvement of the d functions in the two-center part of the distribution. So, it is not because of any deficiency in valence that the "valence d orbital" role is not sustained. The crucial point is that the functions are not "orbitals". In bonds between the same pair of elements, there are no significant differences in the d function contribution to overlap density between normal valency and hypercoordinate compounds. Just as bond energy data (e.g. Sanderson's compilation[42]) and "per bond" ΔE_d values indicate, so the shared electron density profiles confirm (Figure 4) that the roles of d functions in the two categories are indistinguishable.

A second use of overlap density profiles arises in the comparison of first- and second-row hypercoordinate molecules where it coorborates the evidence from analysis of the wave functions. Some differences are expected because of the effects of orthogonality on second- and third-shell s and p functions (see subsection 4), and because of differences in the magnitude and direction of charge transfer. But after allowing for these explainable differences, it is clear that d function participation in the overlap density is still much the same in the two categories. If d functions are not valence orbitals in the nitrogen and oxygen hypercoordintae molecules, there is nothing in the electron density data to invoke them in the phosphorus and sulfur hypercoordinate compounds.

Mayer has recently proposed that the role of d functions be regarded as a true valence role because their use obviates the "unrealistically large positive gross charges" on the central atom that are obtained when sp basis functions only are used.[43] The argument is not persuasive. Large positive charges on second-row atoms may be better taken as an indication that there is a heavy ionic contribution to the bonding and that the idea of expansion of the octet is unnecessary.[10–13,41,44]

Discussion. Notwithstanding the theoretical objections to the "orbital concept", the s and p orbitals of dominant configurations of the component atoms are readily identifiable in the MOs of normal valency compounds. This is not true of d orbitals, which are inaccessible in first-row atoms and only occupied in the excited states of second-row atoms. The d functions required in basis sets in molecules like H_2O, NF_3, H_2S, PF_3, etc. act as entities for which there is no parallel in spherically symmetrical atoms, enabling the wave function to conform to the complex molecular potential

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[40] From considerations of valence bond theory, Harcourt proposes that d orbitals be considered for a hybridization role when the central second-row atom appears in important structures with a charge of +2 or more. Harcourt, R. D. *Qualitative Valence-Bond Descriptions of Electron-Rich Molecules: Pauling 3-Electron Bonds and Increased Valence Theory*; Lecture Notes in Chemistry 30; Springer: Berlin, 1982. In actual detailed applications of valence bond theory to compounds of second-row elements, Maclagan and Hay found charge-transfer structures to be more important than structures involving valence d orbitals: Maclagan, R. G. A. R. *Aust. J. Chem.* **1988**, *41*, 527–533. Hay, P. J. *J. Am. Chem. Soc.* **1977**, *99*, 1003–1012.

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in a way that is not possible with sp basis functions only. The main conclusion of this investigation is that the role of d functions in hypercoordintae molecules like PF_5 or SF_6 is simply an extension of the role of d functions in normal valency molecules. In no single feature of the supplemented wave functions investigated here was there any qualitative difference between the two categories.

None of the evidence uncovered here overturns the explanation given by Kutzelnigg, Musher, Pimentel, and others[10-12] for apparently "hypervalent" compounds: major ionic contributions and a large central atom accommodating the extra bonds without any need to exceed the octet. The data here which show the similarity of the bonding in the first- and second-row hypercoordinate compounds are in complete accord with the descriptions of "semipolar" N–O and P–O bonds in H_3NO, H_3PO, etc. provided by Wallmeier and Kutzelnigg[11a] and, more recently, Reed and Schleyer.[11b] In view of this, the non-existence of first-row analogues of SF_6, PF_5, etc. is a consequence of the small size of the first-row atoms, not inaccessible d orbitals.[10]

It is now possible to make proper distinctions between the polarizing role, the valence orbital role, and the "intermediate role" for d functions. The new results open the major categories of main group compounds to fair comparison for the first time and make it impossible to regard the two roles as alternatives, one or the other being chosen according as some index of bonding is large or small. The size of the d function populations is not at issue; they occur in several important classes of molecules as a consequence of the electronic structure models currently used and are associated with strong ionic contributions to bonding irrespective of whether valence d orbitals of a second-row atom are available to contribute to the wave function. The criterion for the valence orbital role, not satisfied in any of the wave functions surveyed here, is the appearance of unique bonding interactions as distinctively different in different bonding environments (e.g. in SF_2, SF_4, and SF_6) as those that involve s and p orbitals.

The two roles proposed for d functions belong to different genres. The valence orbital concept belongs to the kind of chemical explanation that draws an analogies between atoms and the molecules built out of them. Theoretical evidence for it will be uninterpretable unless the calculations use atom-centered basis sets with easily identifiable "orbitals" and "shells".[45] The polarization role for d functions, by contrast, is not "chemical" at all; it evolves from a mathematical apparatus chosen for its utility in modelling electronic structure in molecules.

An "intermediate role" for d functions has frequently been proposed. Schmidt et al.[15] do so in a study of phosphine oxide, but their use of the d function population as the criterion of the d function role is unsatisfactory. They categorize the d function role as polarization when the population is near zero and as a true valence when the population is ≥ 1. The results here show this to be false dichotomy, since either condition is feasible from d functions in either role. In the same way, the distinction made by Ball et al.[45] between "symmetry-deficient" sp bases (as in SO_2) and sp bases that are not symmetry deficient (as in H_2S) is not sustained by the results of this study; qualitative differences in d function utilization in such molecules have not been discovered.

Summary. Just as p functions are customarily added to hydrogen atom s functions[2] and f functions to transition-metal d functions,[46] so the supplementation of s and p functions by d functions in calculations involving main group elements greatly improves the quality of the resulting molecular wave function. d functions seem to make the greatest contribution in responding to the rapidly varying electrical potential close to the nuclei of second-row atoms, where orthogonality to inner functions relieves d functions of the constraints that hinder s and p functions.

The major concluisons established by this study are, on the one hand, the high level of d function involvement in wave functions of all compounds with major ionic contributions to bonding and, on the other, the absence of the dependence of d function behavior on molecular environment which would be expected if the diffuse d orbitals of excited-state second-row atoms were modified by the molecular field to overlap strongly with orbitals on other centers. The utilization of d functions is greatest when the connectivity of a central atom is high, a feature that is better explained by the obvious increase in d function contribution when the number of bonds increases than by any major change in their character from "normal" to "hypervalent". There are no special properties of d functions in hypercoordinate molecules that cannot be accommodated by these concepts.

The evidence shows that the resemblance between valence d orbitals and d functions in the hypercoordinate wave functions is an artifact of the method used for modelling the electronic structures of molecules. The "valence d orbital" role is rejected because d functions are not "orbitals", not because of any incompetence in bonding. Their important role in the wave function in hypercoordinate molecules formed by second-row elements is indistinguishable from that of d functions in normal valency molecules and in first-row species, and the term "d orbitals" is not warranted.

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