(r) O(2)–H···O(3). (Lower case letters refer to data key[22].)
(14) J. E. Del Bene, *J. Chem. Phys.*, **55**, 4633 (1971).
(15) (a) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971). Standard molecular scaling factors were employed. (b) The calculations were carried out on a version of the GAUSSIAN 76 program (J. S. Binkley, R. Whiteside, P. C. Hariharan, R. Seeger, W. J. Hehre, W. A. Lathan, M. D. Newton, R. Ditchfield, and J. A. Pople (submitted to QCPE)).
(16) M. D. Newton and G. A. Jeffrey, *J. Am. Chem. Soc.*, **99**, 2413 (1977).
(17) (a) Somewhat larger force constants have been obtained previously (in units of kcal/(mol deg^2)): $\sim 2.8 \times 10^{-3}$ (CNDO[6]); $\sim 3.5 \times 10^{-3}$ (minimal-basis ab initio[10]); ~ 6–7×10^{-3} (analysis of variance in X-ray data[10]). The present value of $\sim 2 \times 10^{-3}$ cannot be directly compared with the previous ones, however, since its definition is in terms of $r_{H \cdots O}$ instead of $r_{O \cdots O}$. Furthermore, some averaging and other approximations were employed in extracting the θ_1 force constant from the raw theoretical data.[10] The precise meaning (i.e., definition in terms of internal coordinates) of the experimentally defined[10] force constants is not clear. (b) The quadratic least-squares fit (eq 5) reproduces the relative energies (i.e., $-KT \ln \bar{g}$) at the four angles employed in the fit to within 2×10^{-3} kcal/mol (or better than 5%), and the root mean square deviation is 2.9×10^{-3} kcal/mol.
(18) Minimized with respect to φ_1 and φ_2 (i.e., 180 and 0°, respectively), with the other parameters assigned as discussed in section II ($\chi = 90°$, $\theta = 132°$, and $r_{H \cdots O} = 1.94$ Å).
(19) K. Kuchitsu and Y. Morino, *Bull. Chem. Soc. Jpn.*, **38**, 814 (1965).
(20) Based on optimal φ values ($\varphi_1 = 180°$, $\varphi_2 = 0°$, $\varphi_3 = 180°$; Table III). Note that the term "symmetric" refers only to the oxygen framework, since in general ($\varphi_1 \neq \pm 90°$, $\varphi_2 \neq \pm\varphi_3$) the monomer conformations destroy the symmetry plane which bisects the $O_2H_1O_3$ angle.
(21) Distance-dependent basis set artifacts (e.g., see discussion in section I of ref 4c) may cause the stability of the bifurcated structure (relative to that of the dimer) to be slightly exaggerated (by $\lesssim 1$ kcal/mol).
(22) Key to experimental data follows. (a) β-L-Arabinose: S. Takagi and G. A. Jeffrey, *Acta Crystallogr., Sect. B*, **B33**, 3033 (1977). (b) β-DL-Arabinose: S. Takagi and G. A. Jeffrey, *Acta Crystallogr.*, submitted. (c) β-D-Lyxose: S. Takagi and G. A. Jeffrey, *ibid.*, submitted. (d) α-L-Xylose: S. Takagi and G. A. Jeffrey, *ibid.*, submitted. (e) α-D-Glucose: G. M. Brown and H. A. Levy, *Science*, **147**, 1038 (1965). (f) β-D-Fructose: S. Takagi and G. A. Jeffrey, *Acta Crystallogr., Sect. B*, **33**, 3510 (1977). (g) α-L-Rhamnose: S. Takagi and G. A. Jeffrey, *ibid.*, in press. (h) α-L-Sorbose: S. Nordenson, S. Takagi, and G. A. Jeffrey, *Acta Crystallogr.*, submitted. (i) D-Glucitol: Young Ja Park, G. A. Jeffrey, and W. C. Hamilton, *Acta Crystallogr., Sect. B*, **27**, 2393 (1971). (j) Methyl α-D-altroside: B. J. Poppleton, G. A. Jeffrey, and G. J. B. Williams, *ibid.*, **31**, 2400 (1975). (k) Methyl α-D-galactoside: S. Takagi and G. A. Jeffrey, *Acta Crystallogr.*, submitted. (l) Methyl β-D-galactoside: S. Takagi and G. A. Jeffrey, *ibid.*, submitted. (m) Methyl α-D-glucoside: G. A. Jeffrey, R.K. McMullan, and S. Takagi, *Acta Crystallogr., Sect. B*, **33**, 728 (1977). (n) Methyl α-D-mannoside: G. A. Jeffrey, R. K. McMullan, and S. Takagi, *ibid.*, **33**, 728 (1977). (o) Methyl β-D-riboside: V. J. James, J. D. Stevens, and F. H. Moore, *ibid.*, **34**, 188 (1978). (p) Methyl β-D-xyloside: S. Takagi and G. A. Jeffrey, *ibid.*, **33**, 3033 (1977). (q) Sucrose: G. M. Brown and H. A. Levy, *ibid.*, **29**, 790 (1973). (r) β-Maltose hydrate: M. E. Gress and G. A. Jeffrey, *ibid.*, **33**, 2490 (1977).
(23) In spite of the large scatter in the data of Figure 5, a linear least-squares analysis of the 67 data points revealed a small negative slope ($\sim -20°$/Å). A similar scatter and small negative slope are apparent from Figure 8.7 of ref 7. We note that the root mean square deviation of the present fit (±6°) is slightly larger than the change in angle ($\sim 5°$) predicted within the region of interest ($r_{H \cdots O} \sim 1.7$–2.0 Å), thus underscoring the weakness of the coupling of angle and distance. It is also worth noting that inclusion of the eight data points which are associated with asymmetrical bifurcated interactions leads to a slope of greater magnitude ($\sim -30°$/Å); the shorter H···O member in each bifurcated set was used (see Table III). As discussed in the text, these bifurcated bonds represent special cases which accordingly were excluded from the data displayed in Figures 3, 5, and 6.
(24) M. D. Newton, *J. Chem. Phys.*, **67**, 5535 (1977), and data cited therein.
(25) W. Klyne and V. Prelog, *Experientia*, **16**, 521 (1960).

Investigation of the Basis of the Valence Shell Electron Pair Repulsion Model by ab Initio Calculation of Geometry Variations in a Series of Tetrahedral and Related Molecules

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Abstract: Energy-optimized geometries were calculated ab initio for NH_3, NF_3, OH_2, OF_2, PH_3, PF_3, SH_2, SF_2, SO_2, SOF_2, SOH_2, SO_2H_2, HSF, SH_3^+, NH_2^-, NF_2^-, and NH_4^+ using consistent basis sets and optimization criteria. An understanding of the predictions of the valence shell electron pair repulsion (VSEPR) model was sought by a comparison of the calculated geometries and various properties of the localized bonding and lone-pair orbitals. The calculated relative sizes of bonds and lone pairs agreed very well with the VSEPR assumptions. Some apparent failures of the VSEPR model can be explained by examining the total angular space requirements of the bond and lone-pair orbitals, rather than restricting attention only to the angles formed between bonds. An extensive investigation was made of the effect of polarization functions in the basis set both on calculated geometries and on the properties of the resulting localized orbitals.

Introduction

The simple valence shell electron pair repulsion (VSEPR) model[2] is successfully used in explaining variations of molecular geometries in extensive classes of inorganic compounds. The model assumes that the geometry around a central atom is determined by the number of electron pairs in the valence shell of that atom. Finer details of the structure are predicted by considering that nonbonding electron pairs require more angular space than single bonds, with double bonds requiring nearly as much space as lone pairs. When this model was tested against recent experimental data on some tetrahedral and related molecules, it was found[3] that most, but not all, of the geometrical variations in these systems follow readily the original predictions of the VSEPR model. Gillespie noted in his book[2a] that ". . . in the series CH_4, NH_3, and H_2O the bond angle decreases from 109.5° to 107.3° and to 104.5° as the number of non-bonding pairs increases." As is demonstrated in Figure 1 by recent experimental data,[3-17] most analogous compound series do not entirely follow this trend.

Substitution of one of the ligands by a lone electron pair in the AX_4 molecules is accompanied indeed by a decrease in the X–A–X angle and this is well understood in terms of the VSEPR model. As a second ligand of AX_3E is replaced by another lone pair, a further decrease of the XAX bond angle would be expected to occur according to Gillespie's original statement. This is observed, however, for NH_3 and H_2O, and PH_3 and SH_2 only. For other molecule pairs with chlorine or fluorine ligands the opposite trend is realized.

For systems with double bonds to oxygen, the VSEPR model does not make predictions concerning the changes in the bond

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angle by substitution of a double bond by a lone pair. The experimental data indicate curious variations in Cl and F bond angles; the X-S-X angles are smallest for the OSX_2 sulfoxide molecules.

It should be stressed that those structural changes discussed above which are at variance with or unaccounted for by the VSEPR model are subtle variations. The general shapes of the molecules are in good agreement with the VSEPR model. An attempt to interpret these subtle variations by a simple point charges on a sphere model[3b] showed that the application of different repulsion exponents could bring the results in agreement with the experimental data.

In order to gain more insight into the bonding properties of these simple molecules and to find an explanation for the observed geometrical variations, ab initio calculations were performed. Needless to say, there have been numerous calculations at various levels of sophistication on many of the molecules studied here.[18] Certain limited comparisons have been made, for example, in the study of the series SH_2, SOH_2, SO_2H_2 by Van Wazer and Absar,[19] but there has been no systematic comparison of these molecules with the same basis sets so that wave-function properties could be directly compared with all bond lengths and bond angles optimized to the lowest energy structure. The relevant molecules previously studied have therefore been recalculated along with some newer ones to produce a body of comparable data among which relationships may be sought.

From comparisons of the wave functions the angular positions of the localized lone pairs are found to be particularly important. These show a need for reinterpretation of the VSEPR model in which emphasis is given to the total angular space required by a bond pair or a lone pair rather than only to the angles formed between bond pairs.

Method

Ab initio wave functions for NH_3, NF_3, OH_2, OF_2, PH_3, PF_3, SH_2, SF_2 SO_2, SOF_2, SOH_2, SO_2H_2, HSF, SH_3^+, NH_2^-, NF_2^-, and NH_4^+ have been calculated within the MO-LCAO-SCF approximation using the program MOLPRO written by Meyer and Pulay. Except as otherwise noted, the calculations used a (7,3,1) basis set of Gaussian lobe functions contracted to ⟨5,3,1⟩ on N and O, a (10,6,1) set contracted to ⟨7,4,1⟩ on P and S, and a set of 3s functions on H. All calculations were repeated with the d functions omitted, and three molecules (NF_3, PF_3, and SOF_2) were done only without the d functions. All orbital exponent coefficients were taken from Roos and Siegbahn.[20,21] Unfortunately the misprint in their fifth coefficient for S was not noted until the calculations were completed. A check showed that the correct coefficient lowered the total energy of SH_2 by 0.34 hartree, but the forces affecting the geometry were altered by only 0.003 mdyn for the bond length and 0.0003 mdyn Å/rad for the angle, amounts which would have negligible effect on the calculated structure. This is reasonable, since the erroneous coefficient belongs to an s orbital describing the inner shell of the sulfur atom.

The geometries of all molecules were optimized using the force or gradient method[22] in which the forces on all atoms are calculated analytically. The criteria for convergence of the geometries were that residual forces be less than 0.015 mdyn for bond stretching and less than 0.0075 mdyn Å/rad for bond bending. Certain exceptions to this are noted in the appropriate tables. As a general rule, the residual forces imply that the calculated structures should be within 0.002 Å and 0.45° of their true theoretical geometries, assuming that the force constants used are within ±50% of their true values.

To assist in correlation of the computed wave functions with the language of VSEPR theory, the canonical orbitals were converted to localized orbitals according to the criterion of Boys,[23] which in effect maximizes the sum of the squares of the distances between the centroids of charge of the orbitals.

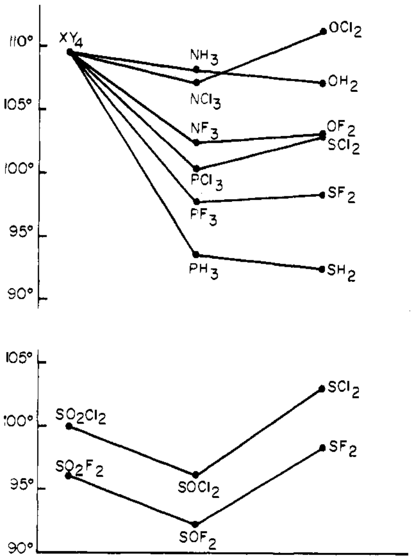

Figure 1. Experimental bond angles of some series of tetrahedral and related molecules. Data from ref 3–17.

Results and Discussion

A. Geometries. All of the calculated energy-optimized geometries are shown in Table I together with the corresponding parameters derived from experiment in the cases where they are available. The total energies of the optimized structures are also given.

Where experimental information is available, it can be seen that the calculations reproduce very well all of the bond angles involving fluorine or oxygen as ligands. Indeed, even omission of polarization functions from the basis set does not produce serious error in these angles. Agreement with experiment in the calculated hydrogen bond angles is slightly poorer, and here the polarization functions are necessary to produce acceptable results. This of course, has been previously noted.[24]

Bond lengths are also well reproduced with use of the complete basis set, the worst case being SF_2, where the disagreement is 0.028 Å. Omission of polarization functions on the central atoms yields excessively long calculated bond lengths to fluorine and oxygen ligands while the effect on bonds to hydrogen atoms is quite small. It should be noted that the calculated and experimental bond lengths are not strictly comparable. The computation yields r_e values while the experimental results (r_s, r_o, etc) refer to averages over intermolecular motion. The differences are very small for the present purpose.

Several points should be noted from the theoretical geometries. Only in the comparison of NF_3 with NF_2^- or of NH_3 with NH_2^- does there seem to be any significant correlation of bond length with bond angle. In these substances, the bond lengths increase with the substitution of a lone pair and the bond angles decrease, a behavior which could be described in terms of more participation of p atomic orbitals in NF_2^- and NH_2^-.

The inference from the VSEPR model that bond angles should progressively decrease as lone pairs are substituted for bonded atoms appears to be valid only for comparisons in which the central atom remains the same. The sets SH_3^+ and SH_2, NF_3 and NF_2^-, and NH_4^+, NH_3, and NH_2^- clearly show the predicted effect as AEX_3-type molecules are changed to AE_2X_2. On the other hand, when only neutral molecules are compared by changing the central atom, as in PF_3 and SF_2, the bond angle actually becomes larger, as previously noted.[3] The

Table I. Calculated Energies and Calculated and Experimental Geometries

	total energy[a]			bond length[b]				bond angle[c]		
	spd	(sp)		spd	(sp)	exptl		spd	(sp)	exptl
OF_2	−273.1004	(−273.0830)	O-F	1.407	(1.492)	1.4053 ± 0.0004^{d}	∠FOF	102.0	(101.7)	103.07 ± 0.05^{d}
SF_2	−595.6154	(−595.5601)	S-F	1.615	(1.669)	1.5874 ± 0.0002^{e}	∠FSF	98.3	(98.1)	97.95 ± 0.017^{e}
SOF_2		(−670.2183)	S-F		(1.647)	1.583 ± 0.003^{f}	∠FSF		(91.7)	92.2 ± 0.3^{f}
			S-O		(1.492)	1.420 ± 0.003^{f}	∠FSO		(107.6)	106.2 ± 0.2^{f}
SH_2	−398.2489	(−398.2091)	S-H	1.335	(1.353)	1.335^{g}	∠HSH	93.6	(95.6)	92.2^{g}
SH_3^+	−398.5223	(−398.4573)	S-H	1.345	(1.358)		∠HSH	95.5	(99.6)	
SOH_2	−472.9042	(−472.8147)	S-H	1.361	(1.360)		∠HSH	89.2	$(92.8)^{h}$	
	-472.9242^{i}			1.363^{i}				$89.7^{i,j}$		
			S-O	1.510	$(1.690)^{k}$		∠HSO	109.1	$(107.7)^{l}$	
				$1.493^{i,m}$				$109.9^{h,i}$		
SO_2H_2	−547.6258	(−547.4326)	S-H	1.346	$(1.357)^{n}$		∠HSH	97.7	(98.1)	
			S-O	1.444	(1.590)					
							∠HSO	108.3	(107.7)	
SO_2	−546.5275	(−546.3777)	S-O	1.434	(1.526)	1.431 ± 0.000^{o}	∠OSO	118.2	(114.6)	119.32 ± 0.012^{o}
HSF	−496.9222	(−496.8766)	S-H	1.336	(1.355)		∠HSF	96.3	(95.6)	
			S-F	1.647	(1.698)					
PH_3	−342.3764	(−342.3259)	P-H	1.414	(1.425)	1.4115 ± 0.0005^{p}	∠HPH	94.0	(95.4)	93.36 ± 0.08^{p}
NH_4^+	−56.4765	(−56.4624)	N-H	1.016	(1.015)		∠HNH	109.5	(109.5)	
NH_3	−56.1235	(−56.1032)	N-H	1.008	(0.999)	1.0128^{q}	∠HNH	105.4	(111.4)	107.03^{q}
NH_2^-	−55.3929	(−55.3762)	N-H	1.046	(1.061)		∠HNH	96.7	(97.7)	
NF_3		(−352.0162)	N-F		(1.405)	1.364 ± 0.002^{r}	∠FNF		(102.4)	102.37 ± 0.03^{r}
NF_2^-	−252.8006	(−252.7892)	N-F	1.495	$(1.525)^{s}$		∠FNF	99.4	(99.1)	
PF_3		(−638.5478)	P-F		$(1.624)^{t}$	1.563 ± 0.002^{u}	∠FPF		(96.9)	96.88 ± 0.68^{u}
OH_2	−75.9112	(−75.8908)	O-H	0.950	(0.961)	0.962^{v}	∠HOH	104.9	(107.9)	104.6^{v}

[a] Energy in hartrees. [b] Bond lengths in ångstroms. [c] Bond angles in degrees. [d] Y. Morino and S. Saito, *J. Mol. Spectrosc.*, **19,** 435 (1966). [e] T. Chikaraishi and E. Hirota, private communication. [f] I. Hargittai and F. C. Mijlhoff, *J. Mol. Struct.*, **16,** 69 (1973). [g] T. H. Edwards, N. K. Moncour, and L. E. Snyder, *J. Chem. Phys.*, **46,** 2139 (1967). [h] ±1.6°. [i] spd^2 basis. [j] ±1.1°. [k] ±0.016 Å. [l] ±1.1°. [m] ±0.005 Å. [n] ±0.014 Å. [o] J. K. G. Watson, *J. Mol. Spectrosc.*, **48,** 479 (1973); S. Saito, *ibid.*, **30,** 1 (1969). [p] F. Y. Chu and T. Oka, *J. Chem. Phys.*, **60,** 4612 (1974). [q] P. Helminger, F. C. deLucia, and W. Gordy, *Phys. Rev. A*, **9,** 12 (1974). [r] M. Otake, C. Matsumura, and Y. Morino, *J. Mol. Spectrosc.*, **28,** 316 (1968). [s] ±0.15 Å. [t] ±0.008 Å. [u] E. Hirota and Y. Morino, *J. Mol. Spectrosc.*, **33,** 460 (1970). [v] F. C. deLucia, P. Helminger, and W. Gordy, *Phys. Rev. A*, **8,** 2785 (1973).

calculated bond angle in NF_3 has a very slightly larger value than that of OF_2, in contrast with the very small opposite effect reported from experiment, but in either case the alteration is too small to be in significant agreement with the VSEPR model.

In the set of sulfur compounds SO_2F_2, SOF_2, and SF_2, the central atom is not changed in the series, the only change being the substitution of a lone pair for an S=O bond. Again, the calculated geometries agree with the experimental ones in showing that the F-S-F bond angle increases rather than decreases in going from SOF_2 to SF_2. We have done calculations on the analogous series SO_2H_2, SOH_2, and SH_2 and obtained a similar result, showing that the effect is not unique to fluorine as a ligand. There are no pronounced changes in bond lengths that would indicate any significant difference in hydridization of the bonds as the lone pairs are substituted.

Disagreement with another possible inference from the VSEPR model may also be found in comparing the bond angles

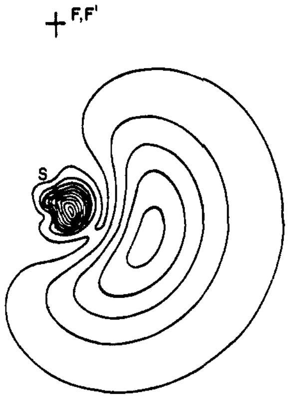

Figure 2. Electron density in sulfur lone pair orbital in SF_2 (sp basis) in plane perpendicular to the molecular plane.

Table II. Computed Angles (deg) Involving Localized Lone Pairs[a]

	∠HX(lp)	∠FX(lp)	∠OX(lp)	∠(lp)X(lp)
OF_2		104.3 (104.0)		133.8 (135.0)
SF_2		104.4 (104.3)		135.2 (135.7)
SOF_2		(109.5)	(125.8)	
SH_2	107.8 (108.2)			126.9 (124.5)
SH_3^+	121.3 (118.1)			
SOH_2	110.9 (111.0)		122.5 (122.5)	
HSF	107.6 (108.5)	105.1 (104.8)		130.0 (129.2)
NH_3	113.3 (107.5)			
NH_2^-	107.3 (107.4)			126.8 (125.8)
NF_3		(115.9)		
NF_2^-		103.3 (102.9)		138.3 (139.7)
OH_2	108.2 (10.2)			118.5 (115.9)

[a] spd basis (sp basis results shown in parentheses).

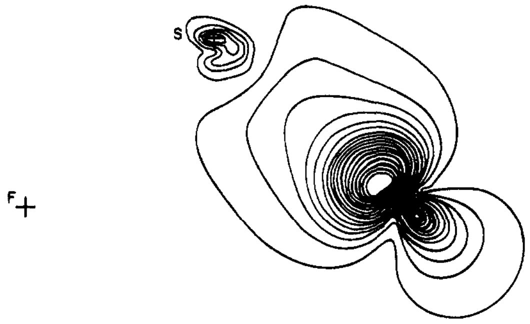

Figure 3. S-F bonding orbital in SF_2 (sp basis) in the molecular plane.

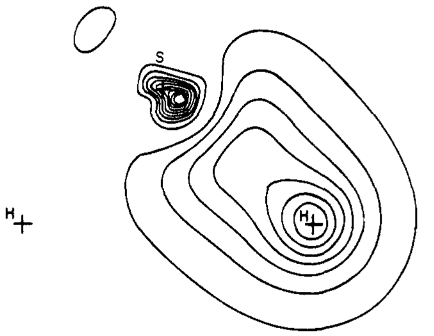

Figure 4. S-H bonding orbital in SH_2 (sp basis) in the molecular plane.

of SF_2 and SH_2, NF_2^- and NH_2^-, and PF_3 and PH_3. Since fluorine is more electronegative than hydrogen, its bond to the central atom should occupy less space, and the F-X-F bond angle would be predicated to be smaller than the corresponding angle in the compounds containing hydrogen. Although this prediction is correct for OF_2 and OH_2 and for NF_3 and NH_3, it is wrong for the other three sets of substances listed above. However, Gillespie[2b] remarks that "bond angles in hydrides are generally smaller than would be expected from the electronegativity of hydrogen . . ." because of hydrogen's lack of core electrons.

B. Localized Orbitals and Lone Pairs. Angular Space Requirements. The plots of localized orbitals (Figures 2-4) corresponding to bonds and lone pairs show clear confirmation of the basic assumptions of the VSEPR model, i.e., lone pairs occupy more space than bonding pairs, and bonds to more electronegative atoms such as fluorine occupy less space than ones to atoms such as hydrogen. The apparent angular range of electron density contours from our wave functions is in all cases in excellent agreement with these qualitative ideas, the difference between lone pairs and bonding pairs being particularly striking.

In an attempt to analyze the structure of the molecules within the framework of the contribution of lone pairs, the centroid of charge of the lone pair has been taken as a measure of its position. The angles between bonds and lone pairs have been calculated and are shown in Table II. Comparison with Table I makes it obvious that the angle between the lone pairs in the AE_2X_2 molecules is greater than either the bond angles or the bond-lone pair angles. This is further borne out by comparison of the electron density plots of the localized orbitals in Figure 2 with Figures 3 and 4. In Figure 2, the larger angular extension of the lone pairs in the region close to the central atom is clearly visible.

Several comparisons among the data in Table II are of interest. In the pair SOF_2, SF_2 it appears that the S=O bond and the lone pair have less mutual repulsion than the two lone pairs since the angle increases 10° when the lone pair is substituted for an S=O bond. Comparing NF_2^- and NH_2^- or SF_2 and SH_2 one can see that not only is the bond angle larger for fluorine ligands but the lone pair angle, too, is larger by approximately 10°, the difference in the lone pair angles being far greater than the difference in the bond angles. The angles involving lone pairs are thus in agreement with the VSEPR theory.

A more general regularity can also be found among these angles if the average of the angles to the other three ligands around the central atom is computed. This triple angle average, much used in discussions of tetrahedral oxide structures,[27,28] gives a measure of the solid angle required by each pair. The results are shown in Table III. The remarkable constancy of the angular requirements of a given bonding or lone pair orbital in a variety of molecules and ions suggests that the angular geometries can be considered as being determined only by orbital interaction. Note that the average angular space required by S-F, O-F, and N-F bonds is slightly smaller than for S-H, O-H, and N-H bonds. The requirement of an S=O bond is nearly as large as that of a lone pair on sulfur. Note also that N and O lone pair requirements are near that of sulfur.

Table III shows very clearly that the average angular space required by a lone pair (or by a double bond to oxygen) is considerably greater than that required by a single bond. Further, for any particular molecule (apart from NH_3 in the sp basis) the lp-X-lp angle > lp-X-b angle > b-X-b angle,

Table III. Angular Requirements for Bonds and Lone Pairs (Average of the Three Angles Involving Each Bond or Lone Pair) (deg)

orbital	molecule	spd	(sp)	orbital	molecule	spd	(sp)
S–F	HSF	102.2	(101.7)	O–F	OF_2	103.5	(103.2)
	SF_2	102.4	(102.2)	O–(lp)	OF_2	114.1	(114.3)
	SOF_2		(102.9)		OH_2	111.6	(110.8)
S–H	HSF	103.8	(104.2)	N–F	NF_3		(106.9)
	SH_2	103.1	(104.0)		NF_2^-	102.0	101.6)
	SOH_2	103.1	(103.8)	N–H	NH_3	108.0	(110.1)
	SO_2H_2	104.7	(104.5)		NH_2^-	103.8	(104.2)
	SH_3^+	104.1	(105.8)	N–(lp)	NF_3		(115.9)
S=O	SOH_2	113.6	(112.6)		NH_3	113.3	(107.5)
	SO_2H_2	113.3	(113.3)		NF_2^-	115.0	(115.2)
	SOF_2		(113.7)		NH_2^-	113.8	(113.5)
S–(lp)	SH_2	114.2	(113.6)	P–F	PF_3		(104.7)
	HSF	114.2	(114.2)	P–H	PH_3	103.5	(104.0)
	SOH_2	114.8	(114.8)	P–(lp)	PF_3		(120.2)
	SF_2	114.7	(114.8)		PH_3	122.4	(121.3)
	SOF_2		(114.9)				
	SH_3^+	121.3	(118.1)				
O–H	OH_2	107.1	(108.2)				

where lp denotes a lone pair and b a bond pair. Hence, for these molecules, we see the justification of Gillespie's generalization[2c] that electron pair repulsions decrease in the order lp:lp > lp:b > b:b.

The dilemma posed by Figure 1 thus arises from an overextended inference from the VSEPR model. For example, though the F–S–F angle in SF_2 is greater than the F–P–F angle in PF_3 (by both experiment and calculation), the angular space taken by the S–F bond is less than that taken by the P–F bond. Note also that the phosphorus lone pair is larger than each sulfur lone pair. Similar remarks apply to OF_2 and NF_3. It is only when the lone pair positions are revealed by calculation that one can understand the overall competition for angular space around the central atom. When we compare an AE_2X_2 molecule having two bulky lone pairs with a related $A'E'X_3$ molecule, we may expect normally that the lone pair E′ will occupy more angular space than one of the lone pairs E, and that an A′X bond pair will occupy more space than an AX bond pair.

Another aspect of spatial requirements is illustrated by the molecules SH_2, SF_2, and HSF. As already noted, the average angular space required for S–H is a little greater than for S–F. In the molecule HSF, lp–S–H angle = 107.6° > lp–S–F angle = 105.1°, which suggests that the lp:(S–H) repulsion is a little greater than the lp:(S–F) repulsion. Consequently if SH_2 is formed by replacing F in HSF by H, the two lp–S–H angles will increase and the H–S–H angle will then decrease to preserve the typical triple-angle average for a sulfur–hydrogen bond. Conversely on replacing H in HSF by F, the decrease in the two lp–S–F angles will allow the F–S–F angle to increase. The fact that there are two lp–S–X repulsions tends to make these repulsions more important than the bond–bond repulsions. It does not follow because the F–S–F angle in SF_2 is greater than the H–S–H angle in SH_2 that S–F needs more angular space than S–H.

Our calculations suggest some revision to Gillespie's remark[2b] that "bond angles in hydrides are generally smaller than would be expected from the electronegativity of hydrogen." At the first sight the bond angles of 93.6° in SH_2 and 98.3° in SF_2 fit Gillespie's suggestion, but the density plots for the bonds (Figures 3 and 4) and the triple-angle averages agree in requiring more angular space for SH than SF. Similarly for the ions NH_2^-, NF_2^- more angular space is required for NH than for NF, despite H–N–H angle < F–N–F angle. On the other hand, the pair PH_3 and PF_3 matches Gillespie's statement both from calculation and experiment. Consideration of these and other molecular structures suggest that the comparisons should be made of the angular space required by X–H bonds instead of simply the hydride bond angles.

The results shown in Table III for SH_2, SOH_2 and SO_2H_2, and SF_2 and SOF_2 are also consistent with VSEPR theory in terms of average angular space requirements. In each of the first three molecules the triple-angle averages for S–H are very similar, as are the averages for S–F in the other two molecules. This constancy is of course linked to the space requirement of S=O being nearly as large as for a sulfur lone pair. The problem of why the X–S–X angle is smaller in the SOX_2 molecule than in SX_2 or SO_2X_2 is discussed in section F.

C. Radial Distances to Pair Centroids. Figure 5 shows a graph of the distances of the centroid of charge of the lone pair from the position of the central atom. This distance is seen to depend quite strongly on the electronegativity of the central atom, the more electronegative elements holding the lone pair charge density at a shorter average distance. The trend follows that for the atomic covalent radii. Calculated gross atomic charge excesses on the central atoms are shown in Figure 6.

Electronegativities of ligands are important in the VSEPR model, since the greater the difference in electronegativity, the more the charge in the bond should be drawn to or away from the central atom. The average angular space required by a bond should be smaller in cases where the charge density is lower around the central atom. However, it is not sufficient simply to examine the radial distances of the bond centroids from the central nucleus, since these distances will depend strongly on the size of the atoms. In VSEPR terms, a more pertinent measure will be the ratio of the distances to the bond centroid and to the lone pair centroid (since the latter distance is also influenced by the size of the atom).

The angular space requirement for a given bond pair is compared with its distance ratio in Figure 7. The angular space requirement for any pair is taken as the triple-angle average defined in the previous section. The angular space requirements for lone pairs are not shown in Figure 7, as they are directly related to the bond-pair requirements, though with an important difference between AE_2X_2 and AEX_3 type molecules. For AE_2X_2 molecules geometrical considerations show that $(l - a) = (a - b)$, while for AEX_3 molecules $(l - a) = 3(a - b)$, where l is the angular requirement for a lone pair, b is that for a bond pair, and a is the actual average of all four triple-angle averages in the molecule. The values of a in the present molecules are slightly less than the tetrahedral value of 109.5° (they would be equal to this if the deviations of the individual angles from 109.5° were of the first order of smallness).

In Figure 7 one would expect to see a trend, with the further

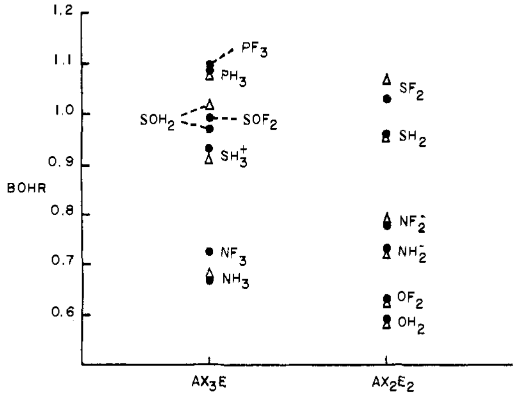

Figure 5. Distance of the centroid of charge of the localized orbital corresponding to the central atom lone pair from its nucleus. Points indicated by Δ were obtained with the complete basis set and those by • were with the d functions omitted.

Table IV. Central Atom to Bond Centroid and Central Atom to Lone Pair Centroid[a]

	distance to bond centroid	distance to lone pair centroid
PF_3	(1.20)	(0.574)
PH_3	1.04 (1.03)	0.570 (0.574)
NF_3	(0.852)	(0.383)
NH_3	0.619 (0.607)	0.359 (0.354)
SF_2	1.14 (1.15)	0.566 (0.546)
SH_2	0.903 (0.891)	0.509 (0.510)
OF_2	0.778 (0.791)	0.331 (0.332)
OH_2	0.531 (0.530)	0.307 (0.312)
NF_2^-	1.01 (1.03)	0.412 (0.410)
NH_2^-	0.727 (0.734)	0.380 (0.386)
SH_3^+	0.85 (0.820)	0.48 (0.49)

[a] Distances in ångstroms. Values in parentheses obtained with sp basis.

out the scaled bond centroid, the less the angular requirement of the bond pair (and hence the greater the lone-pair requirement). In general, this is the trend for a given central atom with a fixed number of ligands. For example, in NF_2^- and NH_2^- the greater radial distance to the N–F bond centroid as compared with that to the N–H bond centroid does correlate with its slightly smaller space requirement. Indeed the line from the spd point for NF_2^- to the reference point for a regular tetrahedron (109.5°, distance ratio 1.0) passes close to the NH_2^- point. Equally the lone-pair space requirements in these two ions correlate with the distance ratios; in particular the large individual angle of 139° for lp-N-lp in NF_2^- can be correlated with the small space requirement of N–F.

Roughly similar trends are found for the series SF_2 and SH_2, and the series OF_2 and OH_2. If the sp calculation for NH_3 with its poor estimate of the H–N–H bond angle is excluded, the points for NH_3 and NF_3 form a further series. On the other hand, the results for PF_3 and PH_3 are exceptional; not only is this the only series where the XH bond pair requires less angular space than the XF bond pair, but the lone pairs in these two molecules, and in SH_3^+, are by far the most bulky of any. One is reminded of Gillespie's remarks[2d] about Si, P, and S being able to accommodate six electron pairs in their valence shells, and that, when there are only four pairs, angles are easily distorted. He cites PH_3 as having a nonbonding pair which spreads out to take as much space as possible around the central core. This description is consistent with our results. For PF_3 the repulsion between the larger fluorine atoms must be taken into account. In SH_2 the space competition between the two lone pairs seems to prevent either of them being as large as the pair in SH_3^+.

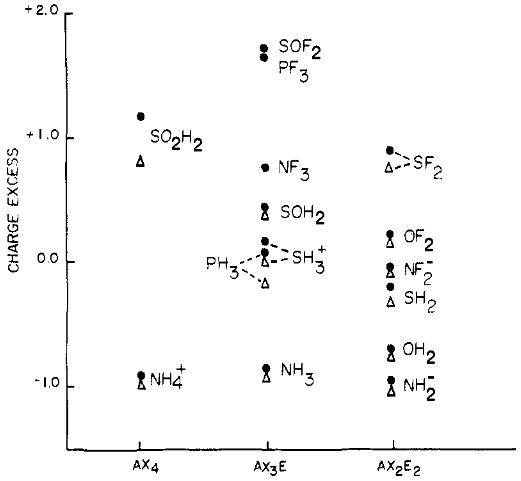

Figure 6. Gross atomic charge excess on the central atom. Points indicated by Δ were obtained with the complete basis set and those by • were with the d functions omitted.

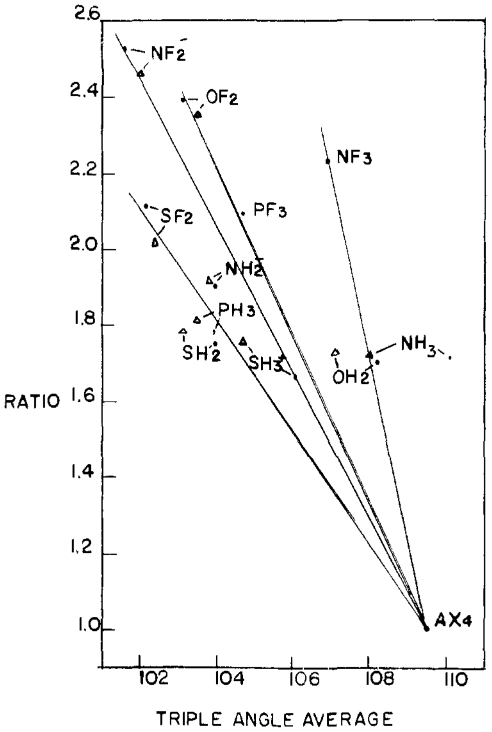

Figure 7. Bond-pair distance to lone-pair distance ratio vs. triple angle average for the bond pair.

The actual distances to the bond-pair and lone-pair centroids are given in Table IV. It will be noticed that, when H is replaced by F as a ligand, the lone-pair centroid moves out by about 0.03 Å, while the bond-pair centroid moves out by about 0.25 Å. When a first-row central atom is replaced by a second-row central atom, the lone-pair centroid moves out by about 0.21 Å and the bond-pair centroid by about 0.37 Å.

D. Geometry and sp Hydridization. Some of the differences in geometry may be viewed according to the traditional theories of sp hybridization. The ratio of the sum of the squares of the 2s (or 3s) coefficients to the sum of the squares of the 2p (or 3p) coefficients is a measure of the s/p ratio. This quantity is listed in Table V for the localized orbitals corresponding to bonds to fluorine and to hydrogen. The decrease in average angular space and the increase in bond distance in the pairs NF_3, NF_2^- and NH_3, NH_2^- both correlate with the greater usage of p atomic orbitals in the AE_2X_2 case, since p orbital participation produces longer bonds.

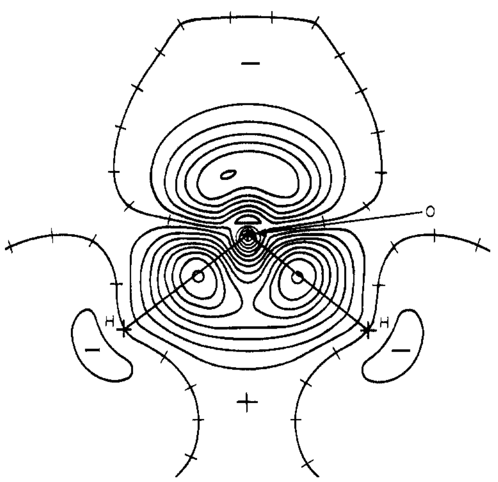

Figure 8. Total charge density in the plane of the H_2O molecule at the experimental geometry calculated with the spd basis minus that calculated with the sp basis. The zero line is hashed and the contour interval is 0.05 electrons Bohr^{-3}.

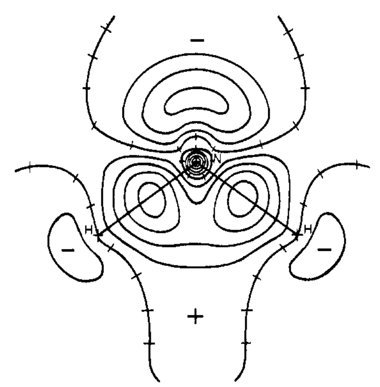

Figure 9. Total charge density in the plane of the NH_2^- ion calculated with the spd basis minus that calculated with the sp basis. The zero lines are hashed and the contour interval is 0.05 electrons Bohr^{-3}.

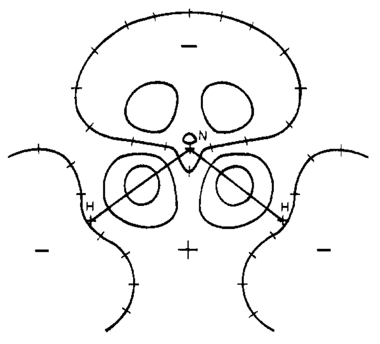

Figure 10. Total charge density in one of the H-N-H planes of the NH_3 molecule calculated with the spd basis minus that calculated with the sp basis. The zero line is hashed and the contour interval is 0.05 electrons Bohr^{-3}.

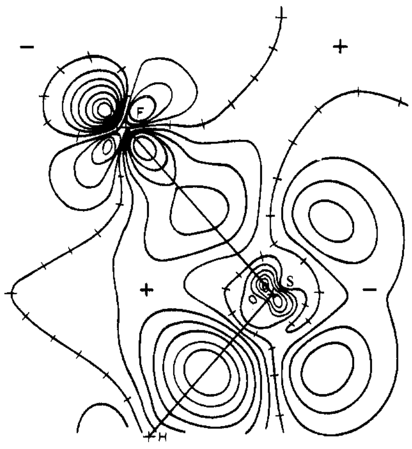

Figure 11. Total charge density in the plane of the HSF molecule calculated with the spd basis minus that calculated with the sp basis. The zero line is hashed and the contour interval is 0.05 electrons Bohr^{-3}.

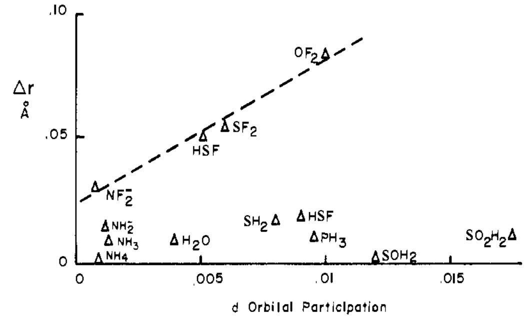

Figure 12. Decrease in bond length vs. d orbital participation in the localized bond (sum of the squares of the coefficients of the d atomic orbitals). The dotted line connects the points for bonds to fluorine; the scattered points at the bottom are for bonds to hydrogen.

The effect of using polarization functions in the basis set may also be seen in the relative amount of s and p character. Addition of the polarization functions slightly increases the s character of bonds to fluorine in SF_2, OF_2, and NH_2^- and very slightly increases the F-X-F bond angles. On the other hand, bonds to hydrogen in every molecule except SO_2H_2 have less s character when polarization functions are used, which correlates with the smaller spd H-X-H bond angles.

E. Effect of Polarization Functions. As reported above, exclusion of d atomic orbitals from the basis set does not appreciably affect bond lengths to hydrogen, but the bond angles involving hydrogen become too large. This agrees with the fact that there is more s character in the bonds in calculations without the polarization functions. In order to visualize the effect of the d functions, the total charge densities of H_2O with the sp and the spd basis sets were calculated in the plane of the molecule at the experimental geometry. Figure 8 shows a plot of the difference between the two density distributions. Additional electron density in the spd basis is a positive quantity in this and subsequent plots. It can be seen that charge is taken from the region of the lone pair and transferred to the region of the bonds and to the hydrogen atoms when d functions are used. There is considerably less d orbital participation in NH_2^- as shown in Figure 9. The maximum contour values of the charge density difference in the plane of the molecule are only about half the value found in H_2O. It is interesting to note from Figure 10 that in NH_3, for which the use of polarization functions makes a large difference in the H-N-H bond angle (the sp basis giving an optimized value of 111.4° compared with 105.4° for the spd), there is very little change in the charge density in the region of the bonds or in the region between the bonds.

The molecules with fluorine ligands show somewhat different effects from the inclusion of polarization functions. The main geometry change is the decreased X-F bond lengths, which has been shown to be consistent with the increased s character of the bonds. The difference produced by the addition of d functions in the total electron density in the plane of the molecule for HSF is shown in Figure 11. The bond to fluorine differs from the bond to hydrogen in that the spd basis set allows a greater concentration of charge to be nearer the fluorine atom. This concentration of charge density is characteristic of electronegative atoms since a similar increase occurs near the oxygen atom in SOH_2.

Table V. s/p Ratio of Fluorine and Hydrogen Bonds

	bond	spd	(sp)		bond	spd	(sp)
OF_2	O–F	0.20	(0.19)	PH_3	P–H	0.46	(0.56)
SF_2	S–F	0.49	(0.47)	NH_4^+	N–H	0.48	(0.50)
SOF_2	S–F		(0.58)	NH_3	N–H	0.40	(0.49)
SH_2	S–H	0.35	(0.37)	NH_2^-	N–H	0.19	(0.20)
SH_3^+	S–H	0.49	(0.57)	NF_3	N–F		(0.42)
SOH_2	S–H	0.40	(0.44)	NF_2^-	N–F	0.16	(0.15)
HSF	S–H	0.36	(0.28)	OH_2	O–H	0.28	(0.31)
	S–F	0.42	(0.42)				

Table VI. Angles from Sulfur Nucleus to Pair Centroids and Corresponding Angular Requirements (Triple-Angle Averages)[a] (deg)

	SH_2		SOH_2		SO_2H_2		SF_2		SOF_2
				Angles to Pair Centroids					
∠XSX	94.3	(96.1)	90.7	(94.7)	98.0	(99.8)	96.8	(97.6)	(91.6)
∠(lp)S(lp)	126.9	(124.5)					135.2	(135.8)	
∠(lp)SO			126.2	(123.3)					(128.8)
∠OSO					116.8	(121.6)			
∠(lp)SX	107.7	(108.1)	111.1	(111.2)			104.5	(104.4)	(110.4)
∠OSX			105.7	(106.2)	110.2	(108.2)			(104.5)
				Triple-Angle Averages					
S–X(p)	103.2	(104.1)	102.5	(104.0)	106.1	(105.4)	101.9	(102.1)	(102.2)
S–(lp)	114.1	(113.5)	116.1	(115.2)			114.7	(114.9)	(116.5)
S–O(p)			112.5	(111.9)	112.4	(112.7)			(112.6)

[a] Values in parentheses calculated with sp basis.

Figure 12 shows a plot of the amount of d orbital participation in a localized bond (the sum of the squares of the coefficients of the d atomic orbitals) against the amount of decrease in bond length. The relationship is nearly linear for the bonds to fluorine. Some of the X–H bond lengths are plotted on the same diagram, and it is obvious that there is no apparent correlation between bond lengths and d orbital participation. The same conclusion holds for changes in the H–S–H angle. Although these angles are smaller with the spd basis set, the decrease in the bond angle is not simply related to the amount of d orbital participation. The increase in charge density in the region of the bonds explains the shortening of the fluorine bond lengths, and the concentration of charge near the fluorine atom makes the consistent but slight decrease in bond angle reasonable on the basis of the VSEPR model. The angle may decrease since charge is pulled further from the central atom. However, these views of the charge density differences do not seem to explain the larger decrease in hydrogen bond angles. Sabin[25] discusses the problem of d orbital participation in SH_2 with the conclusion that, although d polarization functions give a better quality wave function, they do not change the bonding significantly. In fact, Roos and Siegbahn[21] have reported that there is more charge redistribution in H_2O than in H_2S when d functions are added to the outer shells in the basis sets.

A particularly interesting result appears from analysis of the calculations on SOH_2. The use of d orbitals on sulfur which permit back-bonding, as has also been noted by Roos and Siegbahn,[26] significantly decreases the S=O bond length in all cases. In addition to the other calculations, we have also geometry-optimized SOH_2 with a basis including a set of d orbitals on oxygen as well as on sulfur, obtaining an additional small decrease in the S=O bond length. Examination of plots of the localized orbital corresponding to the S–O bonding orbital from the sp basis set shows a typical polarized single bond. In this basis set there are three localized orbitals corresponding to apparently normal lone pairs on oxygen. When d orbitals centered on sulfur are added, giving the spd basis set, plots show a stronger S–O bond with more charge density concentrated between the atoms. The three lone pairs on oxygen have become slightly distorted in the direction which permits some small participation in the bond. When d functions centered on the oxygen atom are also added, producing the spd^2 basis set, localized orbital plots from the optimized geometry indicate two true bonding orbitals. One of the lone pairs on oxygen has become part of a double bond with the two remaining lone pairs distorted so that they also participate in it to some extent. Though the results clearly indicate the importance of having a wave function of high quality at the proper geometry, the apparently dramatic switchover from a single bond to a double bond may arise only from a slight variation in the relative heights of the two maxima of a double maximum in the Boys' function. In this molecule one can transform one polarized bond and three lone pairs around oxygen to two bonds and two (somewhat distorted) lone pairs.

F. The X–S–X Angle in SX_2, SOX_2, and SO_2X_2. We remarked in section **B** that the angular space requirement for a sulfur–oxygen bond is nearly as great as for a sulfur lone pair. The distance from the sulfur nucleus to the centroid of a polarized S–O single-bond pair is typically about 0.9 Å. This is similar to that for an S–H bond pair. In an spd calculation on SO_2, the Boys localization criterion yielded two S=O double bonds; in each double bond the two bond pair centroids were 1.04 Å from S and 0.26 Å above and below the molecular plane. Considering that a sulfur lone pair centroid is typically 0.53 Å from the nucleus, it is thus a little surprising that the angular space requirement for a sulfur–oxygen bond (whether regarded as single or double) should be nearly as great as for a lone pair.

These considerations and comparisons of the orbital plots in Figures 2–4 suggested a closer look at the positions of bond-pair centroids in relation to the internuclear directions. It was found that, whereas the directions to the bond-pair centroids of A–H and A–F bonds are usually within 1° of the internuclear direction, the bond-pair centroids of polarized S–O single bond pairs are up to 4° off axis. The deviations are in a sense such as to decrease slightly the triple-angle averages for oxygens. The values of the individual angles involving pair centroids and the corresponding triple-angle averages are given in Table VI for the spd calculations for SH_2, SOH_2, SO_2H_2, and SF_2 and for the sp calculations for SOF_2. In SOH_2 the oxygen pair centroid is displaced from the S–O line toward the hydrogens. The triple-angle average for the oxygen pair of

112.5°, though remaining above 109.5°, is now distinctly less than the average of 116.1° for the single lone pair in SOH_2. The optimum geometry spd[2] calculation for SOH_2 yields similar results, as does the sp calculation for SOF_2. To some extent the single lone pair in the sulfoxides can be regarded as analogous to the very large lone pair in SH_3^+. As compared with the sulfides, the X atoms in the sulfoxides move further away from the lone pair and in compensation the X-S-X angle decreases so as to keep the triple-angle average for X roughly constant.

In SO_2H_2 the oxygen pair centroids are slightly inside the O-S-O internuclear angle. The second oxygen requires less space than the removed lone pair, so the hydrogens have more available space and the H-S-H angle increases. Hopefully the same explanation will apply to SO_2F_2 when the calculations can be done. Its experimental geometry is consistent.

The large size of a single lone pair on a second-row atom appears also to be confirmed by the comparison[3c] of the experimental geometries of PX_3 and POX_3 molecules; in Hargittai's table for four sets of corresponding molecules the mean of the triple-angle averages for P-(lp) is 117.1° whereas the mean of the triple-angle averages for P=O is 114.4°

Conclusions

Ab initio calculations have been done on many of the small molecules noted by Hargittai[3] as being in disagreement with the VSEPR model. The basic assumptions of the VSEPR theory concerning relative sizes of various orbitals were clearly confirmed. With both the sp and spd basis sets, the bond angle trends were reproduced well.

The differences produced by the use of polarization functions in the basis set were extensively explored since every calculation, where the time required was not unreasonable, was done with both basis sets. It has been shown that d atomic orbitals on the central atom introduce significantly more charge density into the region of the bonds and take charge from the central atom, especially from the lone pairs. The effects are observed as shorter fluorine bond lengths and smaller hydrogen bond angles.

The present work was undertaken because many of the bond angle series shown in Figure 1 do not follow trends thought to be expected from the VSEPR model. By providing positions for lone pairs, the ab initio calculations have made available a new range of data. The results completely support the VSEPR postulate that lone pairs require more angular space than the electron pairs of single bonds, while double bonds require nearly as much space as lone pairs. For the molecules studied, all the ab initio calculations show distortions from regular tetrahedral geometry which are consistent with Gillespie's statement that electron-pair repulsions decrease in magnitude in the order (lone-pair-lone-pair) > (lone-pair-bond-pair) > (bond-pair-bond-pair). But, now that information on lone-pair positions is available, it can be seen that this relation does not require that the X-A-X angle in AX_3E should be greater than the X-A-X angle in AX_2E_2, and VSEPR predictions should be restricted accordingly.

The fact that X-S-X angles decrease from the sulfides to the sulfoxides, and then increase again in the sulfones, appears to be due to (1) the lone pair in a sulfoxide being significantly larger than either lone pair in the corresponding sulfide, and (2) sulfur-oxygen bonds being less space filling than lone pairs with the result that hydrogens or fluorines in a sulfone have more angular space than in the corresponding sulfoxide.

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References and Notes

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