

less response to alteration of geometry.

(d) A relationship also exists between bond angle and s- and p-orbital participation in bonding. Antibonding contributions to the electron distribution from the central-atom s orbital occur over a substantial section of the (lower) bond-angle range, the transition to bonding sp hybrids occurring at different points (generally between 100 and 130°) for different molecules. p-Orbital contributions to bonding change much less, dropping by only about one-third over the bond-angle range.

(e) s-Orbital populations increase, and s-orbital participation in bonding decreases, in parallel with the central atom s-p energy separation. sp hybridization is thus much more in evidence in bonds formed by elements to the left of the periodic table.

(f) For main-group hydrides, spⁿ ratios calculated from Mulliken atomic populations (for AOs participating in σ bonds only) fall into four almost nonoverlapping ranges from sp^{1.8}-sp^{2.2} for the tetrahedral hydrides to sp^{0.5}-sp^{0.8} for the diatomic hydride group. Large nonbonding densities by the s orbital disqualify the use of this ratio as a valid measure of the relative s,p contributions to bonding, but the alternative, calculating spⁿ ratios from s- and

p-overlap densities, is usually not feasible because of the prevalence of very small or negative s-orbital overlap densities.

The utilization of s and p orbitals in bonding, as estimated from gross atomic population data and overlap density data, varies so far from the familiar spⁿ stereotypes that there is no justification for retaining the sp-ratio/bond-angle rule in its usual form. The extra stability of s over p orbitals in main-group elements introduces a factor which the maximum overlapping principle ignores and makes the attainment of a high s-orbital density, not overlap, the main driving force toward optimum s- and p-orbital participation in the electronic structure of the molecule.

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Registry No. CH₄, 74-82-8; SiH₄, 7803-62-5; NH₄⁺, 14798-03-9; PH₄⁺, 16749-13-6; BH₃, 13283-31-3; AlH₃, 7784-21-6; CH₃⁺, 14531-53-4; SiH₃⁺, 41753-67-7; NH₃, 7664-41-7; PH₃, 7803-51-2; H₃O⁺, 13968-08-6; H₃S⁺, 18155-21-0; PH₂⁺, 13937-34-3; H₂O, 7732-18-5; H₂S, 7783-06-4; NH₂⁻, 17655-31-1; HF, 7664-39-3; HCl, 7647-01-0; OH⁻, 14280-30-9; SH⁻, 15035-72-0; BH₄⁻, 16971-29-2; AlH₄⁻, 19469-81-9.

sp Hybridization Reconsidered: Effect of Substitution on the Utilization of s and p Orbitals

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Abstract: The effect of substitution on the way in which s and p orbitals are utilized in bonding by first- and second-row main-group elements is surveyed by ab initio MO methods. The Walsh-Bent hypothesis, that the attachment of electronegative groups favors the use of p rather than s orbitals in bonding by a central atom, is not supported. Charge distributions around the central atom in the AX₄, AX₃, AX₂, and AX series (X = CH₃, F) conform to the same overall patterns in the use of s and p orbitals as those adopted by the corresponding hydrides and reported in the preceding paper, but s orbitals generally make much lower contributions to A-X bonding than to A-H bonding. s orbitals are still used to some extent in bonding in high-symmetry AX_n molecules (tetrahedral AX₄ compounds and the planar and linear conformations, respectively, of AX₃ and AX₂ compounds), but in lower symmetry AX_n compounds and the partly substituted AH₃X, AH₂X, and AHX groups bonding is provided almost entirely by the p orbitals, with s orbital densities tending toward the s² nonbonding configuration. Segregation of s and p orbitals to nonbonding and bonding parts of the electron distribution is an important feature of the lower symmetry molecules especially when the s-p energy separation is large. As in the hydrides, the occupation of the s orbital is high and its interaction with orbitals of attached atoms antibonding over the lower part of the XAX angle range, the angle of crossover between antibonding and bonding roles for the s orbital, is much higher than it is for the hydrides.

Analysis of s and p orbital contributions to bonding in main-group hydrides has uncovered some characteristic trends in the utilization of central atom orbitals, the major constraint being the very favorable contribution to molecular energy obtained by utilizing the s orbital in a nonbonding role; the results of ab initio calculations of first- and second-row hydrides that lead to this conclusion were discussed in the preceding paper. Strong bonding by the central atom s orbital is found in molecules with maximum symmetry (tetrahedral AH₄ systems, planar AH₃ systems, and linear AH₂ systems), but in the normal ground-state geometries of AH₃ and AH₂ hydrides, the s orbital contributions to bonding (as measured by overlap densities) are meager. The s electron density often approaches the nonbonding s² configuration and bonding is almost entirely due to the p orbitals. Because the s orbital contributions to bonding are so often small or negative, the behavior that the all-electron calculations reveal comes into conflict with traditional concepts about s:p ratios in bonding.¹

(1) Undergraduate level chemistry textbooks often present the notion that spⁿ ratios may be deduced from bond angles. It is stated more cautiously than usual in: Streitwieser, A., Jr.; Heathcock, C. H. "Introduction to Organic Chemistry"; Macmillan: New York, 1976; p 96.

Scrutiny of s and p orbital utilization is now extended to the fully and partly substituted analogues of main-group hydrides. Specifically, the following three hypotheses, which are derived from observations about the nature of bonding in the parent molecules, are tested: (a) Substituted compounds display the same characteristic patterns of s and p orbital utilization that are found for the hydrides of main-group elements. (b) In substituted compounds of main-group elements, the more strongly bound the s orbital of the central atom, the closer the approach of the s orbital to the s² nonbonding configuration. (c) Substituted AX₂ and AX₃ species display the same dependence of s and p orbital utilization on bond angle as is found for the parent hydrides. With this information it should then be possible to test the Walsh-Bent hypothesis.² (d) The electronegativity of substituent groups exercises a determining influence on molecular geometry via its effect on s and p orbital utilization in bonding. Bent's elaboration of arguments presented earlier by Walsh assumes the general validity of the presumed relationship between spⁿ ratio and bond angle,³

(2) (a) Walsh, A. D. *Discuss. Faraday Soc.* 1947, 2, 18. (b) Bent, H. A. *Chem. Rev.* 1961, 61, 275-311.

and this has been called into question by results like those presented in the accompanying paper. However, the reasons given for the sp^n ratios that molecules are said to adopt also deserve scrutiny, because they fail to recognize the possibility that s and p orbital involvement in the molecular wave function may be influenced by factors other than bonding. Like the hybridization rule, the Walsh-Bent rule rests on arguments about s and p orbital utilization in bonding. Bent applies perturbation theory to the utilization of s and p orbitals in particular bonds, which requires attention to all the MOs that contribute to the electron distributions of those particular bonds, and not to individual MOs in the manner of Walsh.⁴ Testing this hypothesis thus requires analysis of the overall electron densities of molecules, as was carried out in the work on main-group hydrides.

Method of Calculation. The calculations were carried out with the GAUSSIAN 80 series of programs³ at the 3-21G basis set level (for first-row elements) and at the 3-21G(*) level (for second-row elements), but for oxygen-containing series (OHX, OH₂X⁻, and OX₂) the basis was the 4-31G set and for sulfur-containing molecules (SHX, SH₂X⁻, and SX₂) the 4-31G(*) set.⁶ Geometry optimization was carried out except where optimum bond lengths and angles were available in the literature; in the case of series of calculations performed against variation of bond angles the same value of the bond length (the value found for the minimum-energy geometry) was used throughout the series, and for the CH₃ group the standard geometry of Pople and Gordon was used.⁷

Population Analysis. As found for AH_n systems, the quantities relied on in the population analysis are of overriding importance. Because the concept of hybridization in molecular wave functions is usually advanced on the basis of arguments about the function of s and p orbitals in strengthening bonds, critical analysis of the concept ought to be on the basis of population data which refer unambiguously to bonding. The immediate question, how to discriminate between bonding and nonbonding electron density in orbitals that contain both, was answered in the previous paper by using Mulliken gross atomic populations in conjunction with overlap populations, the contributions made to each by the central atom s and p orbitals being considered separately.⁸ The same approach is adopted here.

The uncertainty that surrounds the use of overlap density data (bond orders) to indicate bond strengthening is more acute in the kinds of molecule considered here than it was with hydrides. Results from two recent studies are apposite. In a comparison of the Mulliken and Roby procedures for population analysis, Cruickshank and Avramides show that whereas Mulliken overlap populations for series of molecules containing atoms of increasing electronegativity frequently run counter to expectation, the Roby shared populations do not.⁹ The study of first-row diatomic molecules by Hirshfeld and Rzotkiewicz¹⁰ underlined the fact that the buildup of electron density in the internuclear region of the H₂ molecule was not the only adjustment made by atoms

Table I. s and p Orbital Utilization in Main-Group AH₃X Molecules^a

	CH ₃ X
X = H	(2s) ^{1.50(0.17)} (2p) ^{3.30(0.57)}
X = CH ₃	(2s) ^{1.48(0.06)} (2p) ^{3.12(0.42)}
X = NH ₂	(2s) ^{1.41(0.04)} (2p) ^{2.98(0.45)}
X = OH	(2s) ^{1.39(0.02)} (2p) ^{2.88(0.44)}
X = F	(2s) ^{1.38(-0.07)} (2p) ^{2.79(0.41)}
	SiH ₃ X
X = H	(3s) ^{1.22(0.20)} (3p) ^{2.21(0.52)}
X = CH ₃	(3s) ^{1.14(0.07)} (3p) ^{2.03(0.47)}
X = NH ₂	(3s) ^{1.12(0.09)} (3p) ^{1.97(0.53)}
X = OH	(3s) ^{1.10(0.06)} (3p) ^{1.90(0.51)}
X = F	(3s) ^{1.09(0.05)} (3p) ^{1.83(0.45)}
	NH ₃ X ⁺
X = H	(2s) ^{1.71(0.12)} (2p) ^{4.18(0.48)}
X = CH ₃	(2s) ^{1.72(-0.03)} (2p) ^{4.14(0.23)}
X = NH ₂	(2s) ^{1.69(0.00)} (2p) ^{4.00(0.27)}
X = OH	(2s) ^{1.68(-0.02)} (2p) ^{3.88(0.26)}
X = F	(2s) ^{1.68(-0.03)} (2p) ^{3.75(0.26)}
	PH ₃ X ⁺
X = H	(3s) ^{1.57(0.15)} (3p) ^{3.15(0.52)}
X = CH ₃	(3s) ^{1.48(0.06)} (3p) ^{2.86(0.46)}
X = NH ₂	(3s) ^{1.38(0.06)} (3p) ^{2.68(0.60)}
X = OH	(3s) ^{1.35(0.03)} (3p) ^{2.55(0.56)}
X = F	(3s) ^{1.37(0.06)} (3p) ^{2.47(0.46)}

^a Mulliken gross atomic populations and, in parentheses, overlap populations are given separately for the s and p orbitals of the central atom.

constrained to overlap, but the other types of redistribution of electron density were even more important for bonding, particularly in molecules containing atoms of high electronegativity, experimental indications coming from X-ray diffraction deformation density studies.¹¹

The two kinds of results probably relate to a single phenomenon, that of the rising importance of atomic terms in the electron distribution for atoms of effective nuclear charge greater than hydrogen since it is atomic terms that the Roby formula combines with overlap terms when orbitals from one center are projected on to the space of the full set of contributing atomic orbitals. Note the expressions for the Roby shared population, s_{AB} , and the Mulliken overlap population, p_{AB} , for the simple case of a two-center MO populated by one electron:⁹

$$s_{AB} = 2c_a c_b s_{AB} + (c_a^2 + c_b^2) S_{AB}^2$$

$$p_{AB} = 2c_a c_b S_{AB}$$

Consequently, falling trends in overlap densities apparent for the AX_n (X = CH₃, NH₂, OH, F) series considered here should not be taken to imply that bond strengths as a whole are falling; conclusions from overlap densities of particular bonds are restricted to the relative importance of s and p orbitals to that particular part of the electron distribution and to the corresponding part of the molecular energy.

Population analysis results are sensitive to basis set variation. For example, the P-C bond overlap density in PH₂-CH₃ rises by over a half from its value with the 3-21G basis set to the STO-3G* set. In spite of this, the relative s and p orbital contributions to Mulliken populations and the way they vary with substituent and bond angle are relatively stable, and it may be argued that the conclusions based on them in this paper are valid to the Hartree-Fock limit and beyond.¹²

(11) Dunitz, J. D.; Schweizer, W. B.; Seiler, P. *Helv. Chim. Acta* **1983**, *66*, 123-133.

(12) The variation in population data calculated with the basis sets STO-3G, 3-21G, 4-31G, and 6-31G, with and without polarization functions on the phosphorus atom (and, in the 6-31G case, on the carbon and hydrogen atoms as well), may be gauged by the fact that the separate s and p orbital contributions to the gross atomic populations and P-C bond overlap populations (in parentheses) for the PH₂-CH₃ molecule (geometry optimized calculations) all lie within the following limits:

$$3s^{1.691 \pm 0.007(-0.005 \pm 0.057)} 3p^{3.085 \pm 0.129(0.551 \pm 0.020)}$$

(3) The general application of the sp^n hybrid bond angle rule to main-group molecules is more hazardous than to carbon compounds because of the prevalence of low symmetries. Huheey (Huheey, J. E. "Inorganic Chemistry"; Harper and Row: New York, 1978; p 45) introduces both the hybrid angle rule and the Walsh-Bent hypothesis.

(4) For a modern discussion of the Walsh approach to the effect of angle deformation on individual MOs, see: Burdett, J. K. "Molecular Shapes"; Wiley: New York, 1980.

(5) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1980**, *12*, 406.

(6) (a) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654-3665. (b) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939-947. (c) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *Ibid.* **1982**, *104*, 5039-5048.

(7) Pople, J. A.; Gordon, M. J. *Am. Chem. Soc.* **1967**, *89*, 4253-4261.

(8) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833-1840. The appropriateness of using Mulliken overlap and gross atomic populations to assess bonding has been stressed recently by: Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270-274.

(9) Cruickshank, D. W. J.; Avramides, E. J. *Philos. Trans. R. Soc. London, Ser. A* **1982**, *No. 304*, 533-565.

(10) Hirshfeld, F. L.; Rzotkiewicz, S. *Mol. Phys.* **1974**, *27*, 1319-1343.

Table II. s and p Orbital Utilization in Main-Group AH₂X Molecules^a

NH ₂ X	
X = H	(2s) ^{1.67(0.14)} (2p) ^{4.22(0.54)}
X = CH ₃	(2s) ^{1.66(0.05)} (2p) ^{4.13(0.46)}
X = NH ₂	(2s) ^{1.61(0.05)} (2p) ^{4.03(0.32)}
X = OH	(2s) ^{1.72(0.02)} (2p) ^{3.79(0.33)}
X = F	(2s) ^{1.74(-0.04)} (2p) ^{3.64(0.28)}
PH ₂ X	
X = H	(3s) ^{1.77(0.00)} (3p) ^{3.31(0.73)}
X = CH ₃	(3s) ^{1.71(-0.10)} (3p) ^{3.11(0.53)}
X = NH ₂	(3s) ^{1.63(-0.09)} (3p) ^{2.97(0.57)}
X = OH	(3s) ^{1.65(-0.10)} (3p) ^{2.83(0.50)}
X = F	(3s) ^{1.67(-0.08)} (3p) ^{2.74(0.39)}
OH ₂ X ⁺	
X = H	(2s) ^{1.75(0.11)} (2p) ^{4.96(0.39)}
X = CH ₃	(2s) ^{1.82(-0.06)} (2p) ^{4.78(0.05)}
X = NH ₂	(2s) ^{1.81(-0.05)} (2p) ^{4.88(0.06)}
X = OH	(2s) ^{1.83(-0.05)} (2p) ^{4.70(0.09)}
X = F	(2s) ^{1.81(-0.05)} (2p) ^{4.70(0.13)}
SH ₂ X ⁺	
X = H	(3s) ^{1.86(0.02)} (3p) ^{4.04(0.55)}
X = CH ₃	(3s) ^{1.84(-0.03)} (3p) ^{3.94(0.42)}
X = NH ₂	(3s) ^{1.81(-0.13)} (3p) ^{3.63(0.35)}
X = OH	(3s) ^{1.78(-0.15)} (3p) ^{3.53(0.28)}
X = F	(3s) ^{1.79(-0.13)} (3p) ^{3.39(0.25)}

^a Mulliken gross atomic populations and, in parentheses, overlap populations are given separately for the s and p orbitals of the central atom.

Table III. s and p Orbital Utilization in Main-Group AHX Molecules^{a, b}

OHX	
X = H	(2s) ^{1.88(-0.00)} (2p _{x,z}) ^{2.93(0.53)} (2p _y) ^{2.00(0.00)}
X = CH ₃	(2s) ^{1.91(-0.09)} (2p _{x,z}) ^{2.90(0.43)} (2p _y) ^{1.97(-0.02)}
X = NH ₂	(2s) ^{1.92(-0.14)} (2p _{x,z}) ^{2.71(0.35)} (2p _y) ^{1.99(-0.04)}
X = OH	(2s) ^{1.92(-0.14)} (2p _{x,z}) ^{2.53(0.35)} (2p _y) ^{2.00(-0.11)}
X = F	(2s) ^{1.93(-0.13)} (2p _{x,z}) ^{2.33(0.30)} (2p _y) ^{2.00(-0.07)}
SHX	
X = H	(3s) ^{1.86(-0.08)} (3p _{x,z}) ^{2.39(0.64)} (3p _y) ^{2.02(0.00)}
X = CH ₃	(3s) ^{1.86(-0.11)} (3p _{x,z}) ^{2.28(0.59)} (3p _y) ^{2.01(-0.03)}
X = NH ₂	(3s) ^{1.84(-0.23)} (3p _{x,z}) ^{2.03(0.52)} (3p _y) ^{2.01(-0.05)}
X = OH	(3s) ^{1.84(-0.15)} (3p _{x,z}) ^{1.91(0.40)} (3p _y) ^{2.03(-0.10)}
X = F	(3s) ^{1.94(-0.15)} (3p _{x,z}) ^{1.80(0.30)} (3p _y) ^{2.03(-0.10)}
NHX ⁻	
X = H	(2s) ^{1.83(-0.21)} (2p _{x,z}) ^{2.29(0.66)} (2p _y) ^{2.00(0.00)}
X = CH ₃	(2s) ^{1.81(-0.19)} (2p _{x,z}) ^{2.23(0.68)} (2p _y) ^{1.90(0.12)}
X = NH ₂	(2s) ^{1.85(-0.32)} (2p _{x,z}) ^{1.29(0.52)} (2p _y) ^{1.97(0.00)}
X = OH	(2s) ^{1.87(-0.20)} (2p _{x,z}) ^{2.09(0.34)} (2p _y) ^{1.72(-0.08)}
X = F	(2s) ^{1.89(-0.13)} (2p _{x,z}) ^{1.68(0.28)} (2p _y) ^{2.00(-0.06)}
PHX ⁻	
X = H	(3s) ^{1.84(-0.17)} (3p _{x,z}) ^{1.96(0.69)} (3p _y) ^{2.04(0.00)}
X = CH ₃	(3s) ^{1.79(-0.16)} (3p _{x,z}) ^{1.74(0.64)} (3p _y) ^{2.02(0.02)}
X = NH ₂	(3s) ^{1.79(-0.23)} (3p _{x,z}) ^{1.54(0.54)} (3p _y) ^{2.03(-0.02)}
X = OH	(3s) ^{1.80(-0.18)} (3p _{x,z}) ^{1.46(0.39)} (3p _y) ^{2.01(-0.08)}
X = I	(3s) ^{1.81(-0.13)} (3p _{x,z}) ^{1.40(0.22)} (3p _y) ^{2.04(-0.08)}

^a Mulliken gross atomic populations and, in parentheses, overlap populations are given separately for the s and p orbitals of the central atom. ^b The population data are given separately for the p orbitals in the plane of the molecule (p_x, p_z) and the p_π orbital (p_y).

Results

(a) **Substitution Series AH_n (X = CH₃, NH₂, OH, F).** Electron population data (Mulliken gross atomic populations for the s and p orbitals of the central atom with s and p orbital overlap densities in parentheses) are presented for several series of main-group molecules in Tables I–III. The AH₃X group is represented by the neutrals CH₃X and SiH₃X and the cations NH₃X⁺ and PH₃X⁺. Population data for the AH₂X group are presented for NH₂X and PH₂X (neutrals) and OH₂X⁺ and SH₂X⁺ (charged species) and for the AX₂ group the data are given for OHX and SHX (neutrals) and NHX⁻ and PHX⁻ (charged species).

Table IV. Response in s and p Orbital Populations to Bond Angle Change in Pyramidal Molecules^a

90°		120°	
NH ₃	(2s) ^{1.85(0.00)} (2p) ^{3.73(0.62)}	(2s) ^{1.59(0.20)} (2p) ^{4.36(0.50)}	
N(CH ₃) ₃	(2s) ^{1.88(-0.10)} (2p) ^{3.68(0.57)}	(2s) ^{1.61(0.10)} (2p) ^{4.20(0.43)}	
NF ₃	(2s) ^{1.74(-0.16)} (2p) ^{2.50(0.32)}	(2s) ^{1.27(0.08)} (2p) ^{3.30(0.17)}	
PH ₃	(3s) ^{1.78(-0.01)} (3p) ^{3.30(0.65)}	(3s) ^{1.45(0.22)} (3p) ^{3.83(0.49)}	
P(CH ₃) ₃	(3s) ^{1.61(-0.14)} (3p) ^{2.66(0.57)}	(3s) ^{1.29(0.18)} (3p) ^{3.32(0.32)}	
PF ₃	(3s) ^{1.61(-0.08)} (3p) ^{1.94(0.40)}	(3s) ^{2.04(-0.46)} (3p) ^{1.44(0.37)}	

^a Mulliken gross atomic populations and, in parentheses, overlap populations are given separately for the s and p orbitals of the central atom.

Table V. Response in s and p Orbital Populations to Bond Angle Change in Bent AX₂ Molecules^a

90°		180°	
H ₂ O	(2s) ^{1.93(-0.06)} (2p) ^{4.78(0.58)}	(2s) ^{1.73(0.20)} (2p) ^{5.24(0.38)}	
(CH ₃) ₂ O	(2s) ^{1.96(-0.12)} (2p) ^{4.66(0.58)}	(2s) ^{1.77(0.10)} (2p) ^{5.08(0.40)}	
F ₂ O	(2s) ^{1.95(-0.13)} (2p) ^{3.89(0.32)}	(2s) ^{1.68(0.07)} (2p) ^{5.31(0.11)}	
H ₂ S	(3s) ^{1.94(-0.14)} (3p) ^{3.37(0.67)}	(3s) ^{1.65(0.24)} (3p) ^{5.21(0.40)}	
(CH ₃) ₂ S	(3s) ^{1.87(-0.22)} (3p) ^{4.02(0.58)}	(3s) ^{1.60(0.15)} (3p) ^{4.74(0.22)}	
SF ₂	(3s) ^{1.85(-0.11)} (3p) ^{3.36(0.28)}	(3s) ^{1.30(0.10)} (3p) ^{4.61(0.03)}	

^a Mulliken gross atomic populations and, in parentheses, overlap populations are given separately for the s and p orbitals of the central atom.

(b) **Angle Variation Studies.** Bond angle variation studies were carried out on a sample of AX₂ and AX₃ species sufficient to warrant comparison of population data with those previously reported for the AH₂ and AH₃ hydrides. Results are shown in Tables IV and V for OX₂, SX₂, NX₃, and PX₃ (X = CH₃, F).

The bond angle ranges used were 90–180° for the AX₂ group and 90–120° for the AX₃ group, ranges sufficiently wide to permit comparison of electron densities at the maximum-symmetry geometries and minimum-energy geometries.

(c) **Progressive Substitution Studies.** The effect of progressive substitution on electron distribution has been studied for CH_{4-n}X_n, SiH_{4-n}X_n, NH_{4-n}X_n⁺, PH_{4-n}X_n⁺, NH_{3-n}X_n, PH_{3-n}X_n, OHX/OX₂, and SHX/SX₂ (X = CH₃, F). The results are given in Tables VI–VIII.

Discussion

The character of the molecular electron distribution in molecules of the kind considered here may be illustrated by a dissection of the population data for Si(CH₃)₄ and SiF₄ and a comparison with the same data for the lower symmetry molecules SF₂ and S(CH₃)₂. Here, as elsewhere, a general rule may be discerned: the total densities due to particular atomic orbitals in molecules run counter to their contribution to overlap densities. An atomic orbital (AO) involved heavily in bonding must share charge with the orbitals of its partner atom; its contribution to the overlap density may be high but the gross population term will be very much reduced from the value expected for orbitals that are substantially non-bonding (ca. 2.0e).

Si(CH₃)₄. In this molecule, the silicon and carbon gross atomic populations, broken down to s and p orbital contributions and with overlap population figures for the two AOs in parentheses, are

$$\text{Si} \quad (3s)^{0.77(0.14)}(3p)^{1.50(0.41)}$$

$$\text{C} \quad (2s)^{1.56}(2p)^{3.55}$$

The data show substantial involvement in bonding by both s and p orbitals of both silicon and carbon atoms. There is major charge drift from the central atom; charge is concentrated in s orbitals to gain the advantage of extra stability but it is in the s orbitals of the atoms of lower effective nuclear charge, not the s orbital of the central atom. Carbon densities are much the same as ever for the maximum-symmetry situation.

SiF₄. The greater effective charge of the attached atom in SiF₄ induces somewhat greater charge transfer, but the character of the electron distribution around the central atom is virtually

Table VI. Progressive Substitution of AH₄-Type Hydrides: s and p Orbital Atomic Population and Overlap Population Data^a

X = CH ₃	AH ₄	AH ₃ CH ₃	A(CH ₃) ₄
CH ₄ ...CH ₃ X...CX ₄	(2s) ^{1.50(0.17)} (2p) ^{3.30(0.57)}	(2s) ^{1.48(0.06)} (2p) ^{3.12(0.42)}	(2s) ^{1.49(0.11)} (2p) ^{2.51(0.47)}
SiH ₄ ...SiH ₃ X...SiX ₄	(3s) ^{1.22(0.20)} (3p) ^{2.21(0.52)}	(3s) ^{1.14(0.07)} (3p) ^{2.03(0.47)}	(3s) ^{0.77(0.14)} (3p) ^{1.50(0.41)}
NH ₄ ⁺ ...NH ₃ X ⁺ ...NX ₄ ⁺	(2s) ^{1.71(0.11)} (2p) ^{4.18(0.48)}	(2s) ^{1.72(-0.03)} (2p) ^{4.14(0.23)}	(2s) ^{1.75(-0.03)} (2p) ^{4.02(0.32)}
PH ₄ ⁺ ...PH ₃ X ⁺ ...PX ₄ ⁺	(3s) ^{1.57(0.15)} (3p) ^{3.15(0.53)}	(3s) ^{1.48(0.06)} (3p) ^{2.84(0.46)}	(3s) ^{1.12(0.08)} (3p) ^{2.38(0.47)}
X = F	AH ₄	AH ₃ F	AF ₄
CH ₄ ...CHX...CX ₄	(2s) ^{1.50(0.17)} (2p) ^{3.30(0.57)}	(2s) ^{1.38(-0.07)} (2p) ^{2.79(0.41)}	(2s) ^{0.67(0.09)} (2p) ^{1.83(0.36)}
SiH ₄ ...SiH ₃ X...SiX ₄	(3s) ^{1.22(0.20)} (3p) ^{2.21(0.52)}	(3s) ^{1.09(0.05)} (3p) ^{1.83(0.45)}	(3s) ^{0.66(0.12)} (3p) ^{1.43(0.32)}
NH ₄ ⁺ ...NH ₃ X ⁺ ...NH ₄ ⁺	(2s) ^{1.71(0.12)} (2p) ^{4.18(0.48)}	(2s) ^{1.68(-0.03)} (2p) ^{3.75(0.26)}	(2s) ^{1.30(-0.03)} (2p) ^{2.62(0.26)}
PH ₄ ⁺ ...PH ₃ X ⁺ ...PX ₄ ⁺	(3s) ^{1.57(0.15)} (3p) ^{3.15(0.53)}	(3s) ^{1.37(0.06)} (3p) ^{2.47(0.46)}	(3s) ^{0.90(0.11)} (3p) ^{1.98(0.34)}

^a Mulliken gross atomic populations and, in parentheses, A-X bond overlap populations are given separately for the s and p orbitals of the central atom.

Table VII. Progressive Substitution of AH₃-Type Hydrides: s and p Orbital Atomic Population and Overlap Population Data^a

X = CH ₃	AH ₃	AH ₂ CH ₂	A(CH ₃) ₃
NH ₃ ...NH ₂ X...NX ₃	(2s) ^{1.67(0.14)} (2p) ^{4.22(0.54)}	(2s) ^{1.66(0.05)} (2p) ^{4.13(0.46)}	(2s) ^{1.69(0.05)} (2p) ^{4.00(0.49)}
PH ₃ ...PH ₂ X...PX ₃	(3s) ^{1.77(0.00)} (3p) ^{3.31(0.63)}	(3s) ^{1.71(-0.10)} (3p) ^{3.11(0.53)}	(3s) ^{1.53(-0.13)} (3p) ^{2.70(0.55)}
X = F	AH ₃	AH ₂ F	AF ₃
NH ₃ ...NH ₂ X...NX ₃	(2s) ^{1.67(0.14)} (2p) ^{4.22(0.54)}	(2s) ^{1.74(-0.04)} (2p) ^{3.64(0.28)}	(2s) ^{1.65(-0.14)} (2p) ^{2.66(0.34)}
PH ₃ ...PH ₂ X...PH ₃	(3s) ^{1.77(0.00)} (3p) ^{3.31(0.63)}	(3s) ^{1.67(-0.08)} (3p) ^{2.74(0.39)}	(3s) ^{1.61(-0.11)} (3p) ^{1.97(0.40)}

^a Mulliken gross atomic populations and, in parentheses, A-X bond overlap populations are given separately for the s and p orbitals of the central atom.

Table VIII. Progressive Substitution of AH₂-Type Hydrides: s and p Orbital Atomic Population and Overlap Population Data^a

X = CH ₃	AH ₂	AHCH ₃	A(CH ₃) ₂
H ₂ O...HOX...OX ₂	(2s) ^{1.88(0.00)} (2p) ^{4.93(0.53)}	(2s) ^{1.91(-0.09)} (2p) ^{4.85(0.41)}	(2s) ^{1.90(-0.11)} (2p) ^{4.77(0.43)}
H ₂ S...HSX...SX ₂	(3s) ^{1.87(-0.08)} (3p) ^{4.41(0.64)}	(3s) ^{1.86(-0.11)} (3p) ^{4.29(0.56)}	(3s) ^{1.85(-0.15)} (3p) ^{4.14(0.60)}
X = F	AH ₂	AHF	AF ₂
H ₂ O...HOX...OX ₂	(2s) ^{1.88(0.00)} (2p) ^{4.93(0.53)}	(2s) ^{1.93(-0.13)} (2p) ^{4.33(0.23)}	(2s) ^{1.93(-0.19)} (2p) ^{3.83(0.26)}
H ₂ S...HSX...SX ₂	(3s) ^{1.87(-0.08)} (3p) ^{4.41(0.64)}	(3s) ^{1.84(-0.15)} (3p) ^{3.83(0.21)}	(3s) ^{1.82(-0.20)} (3p) ^{3.25(0.25)}

^a Mulliken gross atomic populations and, in parentheses, A-X bond overlap populations are given separately for the s and p orbitals of the central atom.

unchanged. Apart from this, the main difference from the methyl compound is the lone-pair status of the 2s_F orbital.

$$\text{Si} \quad (3s)^{0.66(0.12)}(3p)^{1.43(0.32)}$$

$$\text{F} \quad (2s)^{1.98}(2p)^{5.55}$$

S(CH₃)₂. The sulfur and carbon s and p orbital population data are

$$\text{S} \quad (3s)^{1.85(-0.15)}(3p)^{2.16(0.61)}(3p)^{1.98(-0.01)}$$

$$\text{C} \quad (2s)^{1.38}(2p)^{3.16}$$

The sulfur 3s population is near maximum, much greater than that of the 2s orbital of carbon in the same molecule or of silicon in the molecule detailed above. The energy advantage of such a high population for the very stable 3s_S orbital cannot be gained without some concession to the fact that 3s/2s overlap is quite high and, as in low-symmetry hydrides, it is achieved at the expense of an antibonding interaction with the orbitals of carbon.

Although the carbon 2s orbital ($E(2s_C) = 19.2$ eV) is only slightly less strongly bound than the 3s_S AO ($E(3s_S) = 23.9$ eV), its population is much lower. This is explained by the fact that carbon is in a close-to-maximum symmetry situation in this molecule, and as is usual in such cases, the utilization of the s orbital in bonding is obligatory; the energy advantage of a nonbonding role for the 2s orbital cannot be had. The figures for carbon in methane, obtained from a calculation with the same basis set (4-31G), are very little different:

$$\text{C} \quad (2s)^{1.37}(2p)^{3.25}$$

The negative s orbital overlap density for the 3s_S orbital occurs because s character appears in several MOs (four of the 17 MOs in the valence shell) have the requisite a₁ symmetry, and the negative interactions in some exceed the positive interactions in

the others). s character is found mainly in low-lying MOs as is usual in molecules with lone pairs, but there is a strong contribution to the a₁-type lone pair near the top of the eigenvalue spectrum and in it the 3s_S-2s_C interaction is antibonding; its sign is decisive because the net overlap density from the lower a₁ m.o.s. is zero. Bonding between carbon and sulfur is almost homopolar and is provided entirely by the sulfur p orbitals, the 3p_S densities being, appropriately, about 1.0 e per contributing p orbital.

SF₂. The 3s_S orbital still performs in a nonbonding role in this molecule, the gross population showing only the merest response to substitution of F for CH₃. Bonding is still provided by the sulfur p orbitals, the density in the p orbitals showing the expected effect on bond polarity of the high effective charge of the fluorine. The 3p population, slightly reduced by the π-acceptor role of CH₃ in the thioether, responds to the π-donor, fluorine, by moving in the opposite direction:

$$\text{S} \quad (3s)^{1.81(-0.20)}(3p)^{1.22(0.35)}(3p)^{2.03(-0.11)}$$

$$\text{F} \quad (2s)^{1.99}(2p)^{5.44}$$

A net negative p(s) value (the s orbital contribution to the S-F overlap density) again comes about as a result of the fact that, of the contributions from individual MOs, some are bonding and some antibonding in character. The utilization of 2s and 2p AOs by fluorine resembles that of other fluorine-containing molecules: large nonbonding densities for both s and p orbitals, the 2s density being near maximum. Bonding from fluorine is entirely due to the p orbitals. s orbital populations of both S and F atoms are near the s² maximum and the s character from both is concentrated in the two lowest MOs of appropriate symmetry (a₁), appearing there in the same way as inner-shell AOs appear, i.e., as an orbital sum in the lower MO and an orbital difference in the upper MO. Likewise, contributions from the p orbitals of both S and F atoms are confined to higher lying MOs. For this reason, interaction

between the s orbital of one atom and the p orbitals of the other is minimal.

Effects of Substitution. The data in Tables VI–VIII show the same overall patterns of s and p orbital utilization in the substituted AX_4 , AX_3 , AX_2 , and AX series as are found in the corresponding hydrides. As in the hydrides, s orbital utilization in bonding is strongest in the tetrahedral AX_4 compounds, the gross s orbital populations being much lower and the overlap populations higher than in comparable lower symmetry molecules. The trends across the AX_4 , AX_3 , AX_2 , AX series are the same as they are across the analogous hydrides, s orbital overlap densities dropping to negative values and s orbital populations rising to approach the s^2 nonbonding configuration. p orbitals continue to predominate in bonding, providing an even greater share of the overlap density than in the hydrides.

The increasing effective charge of the substituents atoms (X = CH_3 , NH_2 , OH, F) has the expected effect on the polarity of the AX bond in all series. Consequently p orbital populations and p orbital overlap densities uniformly fall in the X = CH_3 ...F direction. When this charge transfer is taken into account, the effectiveness of the p orbitals in bonding shows a smaller fall across the CH_3 , NH_2 , OH, F sequences than the raw p orbital overlap densities, but it remains a fall, rationalized, it would seem, on the basis of the increasing disparity between the energies of the central atom p orbital and the orbitals of X toward the right of the CH_3 , NH_2 , OH, F sequence.

s orbital utilization in bonding seems to vary less smoothly than do the p orbital contributions, and no easy generally trend can be described, a result to be expected when there are four variable parameters (energies of s and p orbitals of atoms A and X and overlap integrals between the s and p orbitals of each) not to mention nonbonding interactions associated with the variation in the number of bonding and lone-pair electrons in the CH_3 ...F sequence.

Successive Substitution. In general, the effect of successive replacement of hydrogen by the methyl is to drain small amounts of charge away from both the s and p orbitals of the central atom; p orbital overlap densities, already small, take part in a reorganization of the electron density in which a much greater fraction of the s electron population is nonbonding.

AH_n molecules possess only four valence-shell MOs, and in the high-symmetry cases only one of these can accommodate the central-atom s orbital. Segregation of the s and p contributions to nonbonding and bonding orbitals, respectively, is precluded. In contrast, the additional valence-shell MOs of the AX_n species do permit segregation, even in high-symmetry cases, although it is less marked than in low-symmetry situations. Thus, the CH_4 ... $C(CH_3)_4$ substitution produces a drop in s orbital overlap density from 0.17 to 0.11 compared with 0.06 for ethane (the lower symmetry, singly substituted molecule). Other examples are apparent in Table VI.

The effects of successive fluorine substitution have the expected effect on central-atom charge densities; the s orbital populations suffer much less depletion of charge than do those of the p orbitals.

AH_3X , AH_2X , and AHX Groups. In comparison with the hydrides, the most obvious effect of substitution is the drop in s orbital bonding. Tables I–III show the effects of the reduction in symmetry that occurs when single substitution occurs. The s orbital contribution to the A–X overlap density is much reduced from its value in the parent hydride irrespective of the electronegativity of the substituent. As Table IX indicates, the effect does not extend to the A–H bonds, which retain the characteristics they possess in the unsubstituted hydrides.

Figure 1 uses the SiH_4 , SiH_3F , SiF_4 series to indicate the way in which central-atom s orbital contributions are distributed in several MOs in a high-symmetry AX_n type molecule compared with the single a_1 MO in the hydride. Bonding/antibonding interactions then lead to an energetically favorable high occupation of the s orbital but with a minimum contribution from the overlap density term. Lowering the symmetry to the partly substituted compound then produces even more orbitals to which the s orbital may contribute and an even greater nonbonding population.

Table IX. Comparison of s and p Orbital Contributions to A–X and A–H Overlap Density in AH_3X -Type Series (X = CH_3 , NH_2 , OH, F)

CH_3X	C–X overlap density		C–H overlap density	
	p(s)	p(p)	p(s)	p(p)
X = H	0.17	0.57	0.17	0.57
X = CH_3	0.06	0.42	0.17	0.58
X = NH_2	0.04	0.45	0.17	0.55
X = OH	0.02	0.44	0.17	0.54
X = F	–0.01	0.41	0.18	0.52

SiH_3X	Si–X overlap density		Si–H overlap density	
	p(s)	p(p)	p(s)	p(p)
X = H	0.20	0.52	0.20	0.52
X = CH_2	0.07	0.47	0.23	0.57
X = NH_2	0.09	0.53	0.22	0.40
X = OH	0.06	0.51	0.23	0.40
X = F	0.05	0.45	0.23	0.40

NH_3X^+	N–X overlap density		N–H overlap density	
	p(s)	p(p)	p(s)	p(p)
X = H	0.12	0.48	0.12	0.48
X = CH_3	–0.03	0.23	0.11	0.51
X = NH_2	0.00	0.27	0.12	0.48
X = OH	–0.02	0.26	0.11	0.47
X = F	–0.03	0.26	0.10	0.45

PH_3X^+	P–X overlap density		P–H overlap density	
	p(s)	p(p)	p(s)	p(p)
X = H	0.15	0.53	0.15	0.53
X = CH_3	0.06	0.46	0.16	0.53
X = NH_2	0.06	0.60	0.18	0.43
X = OH	0.03	0.56	0.20	0.45
X = F	0.02	0.45	0.19	0.44

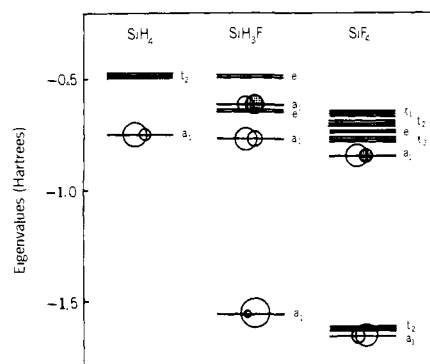


Figure 1. Eigenvalue spectra of valence-shell molecular orbitals of SiH_4 , SiH_3F , and SiF_4 . Shown schematically are the contributions to the a_1 MOs from the silicon s orbital (left circle) and the orbitals of the attached groups (right circle): hydrogen 1s orbitals (SiH_4), fluorine 2s and 2p orbitals (SiH_3F , SiF_4); negative coefficients are indicated by hatching, from which the bonding and antibonding contributions from different MOs can be identified.

The effects of conformational change on the electron distribution around the central atom also show up in s and p orbital population data, but the effects are small. Data for methylamine are given as an example:

	p(s)	p(p)
$CH_3 \cdot NH_2$ staggered	0.059	0.454
$CH_3 \cdot NH_2$ eclipsed	0.053	0.445

The Effect of Bond Angle Change. The response in s and p orbital utilization in AX_3 and AX_2 systems to a change in the bond angle is qualitatively the same as that encountered in the hydrides. In maximum-symmetry conformations the s and p orbitals are confined by symmetry to different MOs. Each MO has a dominant central-atom orbital, and its contribution alters surprisingly little over the bond angle range, the biggest change occurring in

the loss of s character in the nonbonding a_1 MO. However, in the overall electron density figures the changes are more noticeable. At the 90° end of the bond angle range, bonding from the central atom is almost exclusively provided by the p orbitals and the s orbital is nonbonding. As in the hydrides, the effect of bonding s orbital contributions to the overlap density in some MOs and anti-bonding contributions in others is a net s orbital overlap density that is very small or, more often, negative. At the upper end of the bond angle range the high symmetry partly prevents this situation, and considerable s orbital contributions to bonding are found, as in the hydrides.

Because bond angle alteration usually has a greater effect on s orbital than p orbital bonding, the increase in the former with bond angle more than compensates for the decrease in the latter. Thus bond strengths are expected to be smaller for the ground-state conformations of AX_3 and AX_2 group molecules than they are for their planar and linear conformations. This is further evidence for the proposal that bond energy is not the major component in the angle dependence of total energy, i.e., that AH_n geometry is not simply the result of a process of minimization of bond energy against bond angle but that other factors are involved, with s orbital occupation chief among them.

Tests of the Hypotheses

An examination of the data for s and p orbital utilization as a whole shows that substitution introduces no new feature to the pattern of behavior observed in the hydrides. However, although there are overall similarities between substituted and unsubstituted compounds, some of the clear distinctions between different groups of hydrides are obscured by substitution.

Hypothesis a: Data relating to s and p orbital utilization (overlap and atomic populations and sp^n ratios calculated from them) show that the fully substituted compounds (AX_n) follow the same trends as the parent hydrides but that the distinctions are blurred. For example, AX_3 and AX_2 groups no longer fall into separate categories. The attachment of peripheral groups that contribute p as well as s orbitals has the effect of allowing drift of charge from the central atom and compressing the s orbital populations for different groups of AX_n compounds into ranges that are no longer distinct.

Although hybridization in bonding is most in evidence in high-symmetry molecules (T_d , D_{3h} , and $D_{\infty h}$ for AX_4 , AX_3 , and AX_2 species, respectively), s orbital mixing is at a lower level than in the hydrides, and there are exceptional cases where it is absent, e.g., NX_4^+ . This is explained as due to the fact that when there is more than one orbital with symmetry to contain the s orbital the "segregation mechanism" can operate to maximize s occupations even in cases of high symmetry.

Partly substituted compounds (AH_3X , AH_2X , AHX groups) uniformly show very low levels of s orbital involvement in bonding, since the reduction in symmetry allows a ready opportunity for maximizing the nonbonding occupation of the s orbital. The effect is largely independent of the electronegativity of the substituent.

In sum, s and p orbital utilization in substituted compounds is the result of the same factors as operate in hydrides, but as the factors involved in the attachment of the substituents are more numerous than they are with hydrogen atoms, so the patterns of behavior are more complex.

Hypothesis b: Attached groups have major effects on central atom s and p orbital populations. Atomic populations, particularly, show the effects of charge drift toward orbitals of higher effective nuclear charge on other atoms; this is the major difference in the appearance of the population data between the substituted compounds and the hydrides. s orbital overlap populations tend to remain at low values in substituted compounds, particularly the partly substituted AH_nX molecules, but the size of the overlap is dependent on the magnitude of the s-p energy separation. As argued by Hall for hydrides,¹³ the s-p energy separation remains the chief stereochemical constraint in the substituted compounds.

Hypothesis c: As detailed in the paragraphs above, s orbital utilization in bonding is lower in substituted compounds than it is in the parent hydrides, and therefore, the range of its variation in response to bond angle change is smaller; apart from this, the response of substituted AX_n compounds is the same as it is in the hydrides. Gross s orbital populations in AX_2 and AX_3 group molecules decline as the XAX angle rises from 90° and the s orbital, which negative overlap populations show to take no part in bonding over much of the lower part of the bond angle range, only begins to make significant contributions to bonding toward the top of the range. The actual crossover from antibonding to bonding and the degree of sp mixing varies from molecule to molecule as s-p separation and the nature of the substituent vary, but it is much higher in substituted compounds than in hydrides, probably always higher than the bond angle of the molecule in its ground state.

Electronegativity and sp Orbital Preference

One of the major generalizations to flow from Bent's major survey of hybridization is the following rule: "atomic p character concentrates in orbitals directed toward electronegative substituents".^{2b} The rule restates in general terms what Walsh had earlier suggested for carbon.^{2a}

For the hypothetical XAY system with electronegativities $\chi_Y > \chi_A > \chi_X$ Bent cites perturbation theory to support the idea that s orbital character from atom A is concentrated in the AX bond and p character in the AY bond. This modification tends to minimize the energy by placing charge in those parts of the molecule where the potential is lowest, tightly bound s-character near A in the AX bond and less tightly bound p-character near Y in the AY bond. The s:p ratios that result from this then determine bond angles, it is suggested, via the bond angle/hybridization relationship.

Support for the rule is claimed from bond angle data on group 5 and 6 compounds in which the lone-pair electrons are regarded as if they bound very electropositive atoms; the observed progressive reduction of bond lengths for several series of methyl compounds, hydrides, and fluorides of the elements N, O, P, S, and As is taken to indicate increased s character in the lone pairs and increased p character in the bonding pairs, steric factors being presumed absent.¹⁴

A direct test of the predicted effect of the electronegativity of attached groups on s and p orbital utilization is possible by using overlap density data for different bonds in the same molecule broken down into s and p orbital contributions. The relevant data are collected in Table IX. A direct comparison is possible because A-X and A-H overlap density data in AH_nX type molecules are obtained separately from population analysis of MO results.

The four AH_3X group series (CH_3X , SiH_3X , NH_3X^+ , and PH_3X^+ for X = H, CH_3 , NH_2 , OH, and F) show generally similar behavior. A-H bonds show relatively little alteration from the AH_4 model, s and p contributions both remaining strong, as is usual for the maximum-symmetry model. However, the contributions to A-X bonding are quite different. Although the sharp drop in s orbital participation is in apparent conformity to the Walsh-Bent hypothesis, a different explanation is required because the response to substitution is unrelated to the electronegativity of the substituent. Population data differences between molecules with different substituents are irregular, and all are much smaller than the difference from the parent hydride. Analysis of the MO data shows that the sharp drop in s orbital bonding is due to the mechanism of segregation that operates when symmetry is lowered and when a substituent X has both s and p orbitals to overlap with the s orbital of A: bonding between the central-atom s orbital and one of these is offset by an antibonding interaction with the other. The total central-atom s occupation remains high, as is important if maximum advantage is to be taken of the low energy of the s orbital, but the overlap density part of it is low. As data in Tables VI-VIII make clear, this occurs in all partly substituted

(13) Hall, M. B. *Inorg. Chem.* **1978**, *17*, 2261-2269; *J. Am. Chem. Soc.* **1978**, *100*, 6333-6338.

(14) A careful account of the factors that determine molecular geometry and of the conditions under which some become dominant is given in ref 4, Chapters 6 and 7.

compounds, but in the fully substituted compounds AX_4 etc., where the segregation mechanism is somewhat restrained by symmetry, the s orbital contributions are again higher, though not so high as in the hydrides themselves. The inability of the perturbation model to deal with features of molecular structure such as the tendency for s orbital density to be heavily utilized in a nonbonding role stands out clearly, there being no tendency for the s and p orbital contributions to bonding in A-X and A-H bonds to vary at all with change of substituent once H has been replaced by X.

Results of A-H and A-X overlap population comparisons in AH_2X and AHX group molecules are not given. At the optimum geometries of the molecules in these series the bond angles are close enough to 90° to ensure that the central-atom s orbital is almost fully occupied, the contribution to the overlap populations of both A-X and A-H bonds being small and usually negative. The possibility of negative involvement in bonding cannot be accommodated in the perturbation theory model, and the results do not conform to the Walsh-Bent rule.

Comparisons on an intermolecular basis are now considered. Most may be made from entries in Tables I-III. Data in apparent conformity with the hypothesis are encountered in a few cases, but most are like those described in the previous paragraph for intramolecular comparisons. Similarly, it is hard to discern any trends in the data for the fully substituted AX_3 and AX_2 series compounds that could be construed in favor of the hypothesis. (The relevant results appear in Tables VII and VIII.)

The infrequency of comparisons that conform to the Bent-Walsh rule is easily predicted from the earlier results. The inability of the perturbation theory treatment to accommodate the important nonbonding role of the central-atom s orbital has already

been noted. In addition, there is the difficulty that overlap integrals of both the s and p orbitals together with the orbital energies must all enter the reckoning when relative s and p orbital usage is being estimated; the difficulty of accounting for this with a single parameter, electronegativity, is obvious. Although there is a relationship between bond angle and s and p orbital utilization, the nature of the relationship invalidates any argument that uses geometrical data to estimate participation of s and p orbitals in bonding.

Registry No. CH_4 , 74-82-8; CH_3CH_3 , 74-84-0; CH_3NH_2 , 74-89-5; CH_3OH , 67-56-1; CH_3F , 593-53-3; SiH_4 , 7803-62-5; SiH_3CH_3 , 992-94-9; SiH_3NH_2 , 13598-78-2; SiH_3OH , 14475-38-8; SiH_3F , 13537-33-2; NH_4^+ , 14798-03-9; $NH_3CH_3^+$, 17000-00-9; $NH_3NH_2^+$, 18500-32-8; NH_3OH^+ , 43332-84-9; NH_3F^+ , 53768-39-1; PH_4^+ , 16749-13-6; $PH_3CH_3^+$, 28602-10-0; $PH_3NH_2^+$, 88392-38-5; PH_3OH^+ , 88392-39-6; PH_3F^+ , 64306-13-4; NH_3 , 7664-41-7; NH_2NH_2 , 302-01-2; NH_2OH , 7803-49-8; NH_2F , 15861-05-9; PH_3 , 7803-51-2; PH_2CH_3 , 593-54-4; PH_2NH_2 , 13598-67-9; PH_2OH , 25756-87-0; PH_2F , 14500-81-3; OH_3^+ , 13968-08-6; $OH_2CH_3^+$, 17836-08-7; $OH_2NH_2^+$, 20712-83-8; OH_2OH^+ , 63949-01-9; OH_2F^+ , 81128-65-6; SH_3^+ , 18155-21-0; $SH_2CH_3^+$, 18683-23-3; $SH_2NH_2^+$, 88392-40-9; SH_2OH^+ , 76261-93-3; SH_2F^+ , 88392-42-1; OH_2 , 7732-18-5; $HOCH_3$, 67-56-1; $HOOH$, 7722-84-1; HO_2F , 14034-79-8; SH_2 , 7783-06-4; $SHCH_3$, 74-93-1; $SHNH_2$, 14097-00-8; $HSOH$, 62607-44-7; SHF , 62064-82-8; NH_2^- , 17655-31-1; $NHCH_3^-$, 54448-39-4; $NHNH_2^-$, 25415-88-7; $NHOH^-$, 88392-43-2; NHF^- , 67131-46-8; PH_2^- , 13937-34-3; $PHCH_3^-$, 31386-69-3; $PHNH_2^-$, 88392-44-3; $PHOH^-$, 88392-45-4; PHF^- , 88392-46-5; $N(CH_3)_3$, 75-50-3; NF_3 , 7783-54-2; $P(CH_3)_3$, 594-09-2; PF_3 , 7783-55-3; $(CH_3)_2O$, 115-10-6; F_2O , 7783-41-7; $(CH_3)_2S$, 75-18-3; SF_2 , 13814-25-0; $C(CH_3)_4$, 463-82-1; $Si(CH_3)_4$, 75-76-3; $N(CH_3)_4^+$, 51-92-3; $P(CH_3)_4^+$, 32589-80-3; CF_4 , 75-73-0; SiF_4 , 7783-61-1; NF_4^+ , 30494-78-1; PF_4^+ , 29075-80-7.

Dye-Loaded Polymer Electrodes. 2. Photoelectrochemical Sensitization of Croconate Violet in Polymer Films

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Abstract: Enhanced sensitized photoelectrochemical effects are observed upon dispersal of croconate violet (1), an anionic pseudooxocarbon dye, in an adherent polymer coating (poly(4-vinylpyridine)) on a highly doped tin oxide electrode. Benzoquinone, functioning as a supersensitizer, enhanced cathodic photocurrent generation by an order of magnitude. Characteristics of a photoelectrochemical cell employing such a dye-loaded polymer electrode have been investigated. Evidence is presented that the dye-loaded polymer coating can mediate electron transfer between the electrode surface and a dissolved redox couple.

Introduction

Exploration of novel photoelectrochemical systems for solar energy conversion has been a subject of great interest. Marked improvements in photostability and efficiency of solar energy conversions have been made with light-responsive inorganic semiconductors¹ and with chemically modified electrodes.²

An attractive technique for the extension of the absorptive range of such materials involves the attachment of organic dyes of high extinction coefficients to the irradiated electrode surface, and

several studies seeking to examine the performance of photovoltaic systems involving organic dyes have been reported.³⁻⁶ When the dyes are reversibly adsorbed onto the electrode, however, energy losses from the excited state and photoinduced instability often limit practical applications of these systems. Structural modifications of the absorptive dye or environmental changes at the interface could, in principle, obviate some of these problems.⁷ For

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