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sp Hybridization Reconsidered: The Composition of Orbitals in Main-Group Hydrides

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Abstract: The utilization of s and p orbitals in first- and second-row hydrides has been investigated in an ab initio molecular-orbital study. The results provide no justification for retaining the familiar model of a strict relationship between bond angle and the participation of s and p orbitals in bonding. Instead the calculations underline the highly variable nature of A–H bond structure, with maximum nonbonding occupation of the s orbital, not bonding, dominant among the many factors contributing to the bond-angle dependence of s and p orbital bonding. Calculations over the 90–120° bond-angle range (for AH_3 hydrides) and 90–180° (for AH_2 hydrides) reveal the expected decline in total s-orbital occupation but not the expected gradual increase in s-orbital participation in bonding from zero at 90° to full trigonal or linear hybridization (at 120 or 180°). Instead, the s orbital is antibonding over a substantial section of the lower range, the transition to a bonding contribution occurring at different points (generally between 100 and 130°) for different molecules. In consequence, the ground-state conformations of many molecules, particularly second-row hydrides, are configured with central-atom s-orbital populations close to s^2 and with bonding provided exclusively by p orbitals. When overlap density data rather than atomic populations are used to gauge the involvement of s and p orbitals in covalent bonding, the whole idea of a "bonding s:p ratio" breaks down; it appears to retain meaning only in the special case of molecules in maximum symmetry conformations (T_d for AH_4 hydrides, D_{3h} for AH_3, $D_{\infty h}$ for AH_2) where the presence of only one totally symmetric valence-shell MO precludes a high s-orbital occupation. In lower symmetry hydrides there are too MOs which the s orbital can enter and, when s–p energy separation is high, s-orbital occupation is high. Very small or negative bond orders occur because the s orbital is bonding in one MO and antibonding in the other, with the result that central-atom s and p character is segregated into the nonbonding and bonding parts of the electron distribution, respectively. Analysis of overlap density data reveals characteristic patterns of s- and p-orbital involvement for the AH_4, AH_3, AH_2, and AH groups of hydrides; sp ratios, where they can be determined, fall into nonoverlapping ranges which are generally far from the familiar sp^n stereotypes. Even when bond angles are the same, the utilization of s and p orbitals in bonding in hydrides belonging to different groups contrasts sharply.

One of the contributions of simple valence-bond (VB) theory to chemical thinking is the idea that sp ratios in symmetrical molecules are tightly tied to bond angles and that information about one is all that is needed to obtain the other.[1] The notion is widespread but the argument used to obtain it is deficient because simple VB theory ignores the energies of s and p orbitals in constructing hybrids, relying instead on the maximum overlapping principle to determine orbital utilizations. That s and p orbitals enter molecular orbitals independently has often been reiterated,[2] but the rule is still treated as inviolable. Nevertheless, it will be seen that a relationship between bond angles and hybrid sp ratios does exist, and it deserves to be explored by analysis of electron distributions obtained by calculation at a uniform level for a reasonably wide sample of main-group molecules. First- and second-row hyrides (AH, AH_2, AH_3, AH_4) only are considered in this paper, the analogous substituted compounds being treated in a succeeding report.

s- and p-Orbital Ratios in Molecular-Orbital and Valence-Bond Theory. In its most economical form, the simple VB approach to molecular electronic structure uses atomic wave functions obtained by mixing the basic s and p atomic orbitals (s, p_x, p_y, p_z) of the component atoms at the outset. This step, hybridization, is performed against the external criterion of "maximum overlapping" irrespective of its effect on molecular energy.

In contrast to simple VB theory, the molecular orbital (MO) method allows all atomic orbitals of appropriate symmetry to enter all MOs, optimum utilization of each being determined separately according to the energy criterion; external criteria for sp mixing are not permissible. Of course, there are levels of VB theory which also allow the variational determination of s,p mixing, but it is not from these levels that the common notions of bond angle/hybrid ratio dependence were inherited. In view of the confusion caused by importing the idea of a fixed relationship between sp ratios and bond angles into MO theory, it is important to inspect the electron-density distributions of symmetrical main-group molecules to discover the ranges of utilization of s and p valence orbitals adopted by the central atoms and estimate the actual strength of the relationship.

It is important to distinguish the relationships between sp ratios and bond angles as they apply in simple VB theory and variational

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(1) (a) Grim, S. O.; Plastas, H. J.; Huheey, C. L.; Huheey, J. E. *Phosphorus* **1971**, *1*, 61–66. (b) Bingel, W. A.; Luttke, W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 899–911.

(2) Murrell, J. N.; Kettle, S. F. A.; Tedder, J. M. "Valence Theory"; Wiley: London, 1965; p 183.

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MO theory. Since only p orbitals have direction, the angles that separate hybrids are only deducible in general from the p_x:p_y:p_z ratios in each unless some external rule imposes a fixed relationship between s and p utilization as in simple VB theory. If the molecule has some elements of symmetry, the p_x:p_y:p_z ratios of individual hybrids will exhibit themselves in p_x:p_y:p_z ratios of the total electron distribution around the atom in question. Thus the three central-atom p-orbital populations in tetrahedral compounds will be equal. In regular pyramids and other compounds with a threefold axis, two of the p-orbital populations will be equal but different from the third. The s orbital transforms differently from the degenerate p orbitals, and its population relative to them depends on energy matching and overlap, not geometry; consequently the overall s:p ratio derived from a MO calculation will generally lead to an incorrect bond angle if applied to the usual valence-bond relationship.[8]

In the VB maximum overlap concept, bond energy is the criterion used to determine the degree of s- and p-orbital mixing. However, sp ratios quoted from MO calculations usually suffer from the defect that the populations are averaged over all orbitals (bonding, lone pair, and core MOs)[3] and thus distort a result deemed to apply to the bonding part of the electron distribution alone. It is important that population analysis be used in this study in a way that discriminates between the bonding and nonbonding roles of basis orbitals.

Model Dependence. Electron-population data derived from ab initio calculations are known to fluctuate when calculated at different basis set levels. Values of the sp^n ratio, particularly, are very variable.[4] Consequently, it is necessary to restrict conclusions to those which can be based on general trends and without any suggestion that the results of population analysis are absolute.

Not all population data vary to the same extent when the basis set is changed. As a test of the sensitivity of the quantities critical to this research, the s- and p-orbital contributions to gross atomic and overlap populations have been calculated for examples of two kinds of series which are critical to the discussion: a series of conformations of NH_3 and PH_3 spanning the bond-angle range 90–120°, and the isoelectronic series NH_2^-, NH_3, NH_4^+ and PH_2^-, PH_3, PH_4^+. The test was carried out at minimal basis set level, with intermediate basis sets (with or without polarization functions on the central atom), and, for the isoelectronic series, at the high-level basis set designated 6-311G**.[5] The results of the test suggest that the valence interactions indicated by the population data are stable throughout the whole range of these calculations and that the arguments in the discussion might well have been used on calculations at any of these levels.

As an example, results are given for PH_3 calculated at bond angles of 90 and 120°. The extent of variation of gross atomic populations and overlap populations (in parentheses) for the s and p orbitals of phosphorus in PH_3 between the STO-3G, STO-3G*, 3-21G, 3-21G(*), 4-31G, and 4-31G(*) basis set calculations is as follows:

90°	$3s^{1.77\pm0.07(-0.01\pm0.01)}3p^{3.15\pm0.04(0.62\pm0.04)}$
120°	$3s^{1.39\pm0.06(0.22\pm0.005)}3p^{3.63\pm0.07(0.47\pm0.03)}$

The characteristic trends in the response of atomic and overlap densities for both s and p orbitals to the change in bond angle are unobscured by any of the variations between basis sets including the introduction of polarization functions.

Method of Calculation. The analysis of s- and p-orbital involvement in molecular wave functions has been performed on the results of all-electron MO calculations at the single configuration restricted Hartree–Fock level of MO theory. The calculations were carried out with the Gaussian 80 series of programs.[6] The small "split valence" basis set designated "3-21G"[5] was used for most systems, supplemented, in the case of second-row atoms by polarization functions (the 3-21G$^{(*)}$ set). For oxygen-containing molecules the basis was the 4-31G set and for sulfur, the supplemented 4-31G$^{(*)}$ set.

The quality of the electron distribution as calculated at single-determinant extended basis set level has been discussed recently by Bicerano et al.[7] from which discussion it seems unlikely that post-Hartree–Fock procedures would alter any of the conclusions. Calculations were carried out at optimum geometries, but the results of bond-angle variation studies were obtained at fixed (optimum geometry) A–H bond length.

Results and Discussion

In what follows, Mulliken gross atomic populations[3] for central-atom s and p orbitals are given separately (as superscripts) for a series of first- and second-row hybrides, figures in parentheses being the contributions from each orbital to the overlap density of the A–H bond. The inclusion of this latter figure makes it possible to estimate how much of the s, or p, gross atomic population is due to the atom A one-center density term and how much to the shared A – H bond density. sp^n values calculated from the gross atomic populations are sometimes given; sp^n values in parentheses are calculated from the s- and p-orbital overlap densities.

Hydrides in Maximum Symmetry Conformations. To estimate the variability of s and p orbitals in the absence of geometrical change, compounds with obligatory tetrahedral, triangular, and linear symmetry are taken first.

(a) Tetrahedral Hydrides. Tetrahedral hydrides make more effective use of the s atomic orbital for covalent bonding than any other class; the s-orbital contribution arises entirely from the single MO of a_1 symmetry in the valence shell.

BH_4^-	$2s^{1.04(0.23)}2p^{2.25(0.56)}$	$sp^{2.16}$	$(sp^{2.43})$
AlH_4^-	$3s^{0.99(0.21)}3p^{1.71(0.47)}$	$sp^{1.73}$	$(sp^{2.24})$
CH_4	$2s^{1.50(0.17)}2p^{3.32(0.57)}$	$sp^{2.21}$	$(sp^{3.35})$
SiH_4	$3s^{1.22(0.22)}3p^{2.20(0.52)}$	$sp^{1.80}$	$(sp^{2.36})$
NH_4^+	$2s^{1.68(0.12)}2p^{4.23(0.48)}$	$sp^{2.52}$	$(sp^{4.00})$
PH_4^+	$3s^{1.56(0.15)}3p^{3.00(0.53)}$	$sp^{1.92}$	$(sp^{3.53})$

The populations of both s and p orbitals rise in line with the effective nuclear charge of the central atom but the p-orbital figures change more and, accordingly, the sp^n ratios increase with the electronegativity of the central atom.

Compared with the standard sp^3 model, the sp^n ratios are generally low as viewed through the gross atomic populations and generally high on the overlap density view. This is a reflection of the fact of the large contribution from one-center terms to the s-orbital gross atomic populations and of the fact that the p orbitals make the larger contributions to overlap populations.

(b) Triangular Hydrides. The s- and p-population data for AH_3 hydrides in the "maximum symmetry" planar conformation (D_{3h}

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(3) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833–1840. In the Mulliken formalism, the "net atomic population" of an atom is the sum of the one-center contributions made by its component atomic orbitals, each of the form $n_j = n_i\sum_i c_{ij}^2$ (the summation is over occupied MOs, each with occupation number n_i and the *c*'s are the MO coefficients). They are the diagonal elements of the one-particle density matrix (with a suitable adjustment for multiterm basis functions). "Overlap density populations" (*p*) are two-center quantities of the form (for orbitals φ_j and φ_k on different centers) $p_{jk} = 2n_i\sum_i c_{ij}c_{ik}S_{jk}$, where S_{jk} is the overlap integral between the contribution orbitals, the p_{jk} being off-diagonal elements of the density matrix. The overlap population between two atoms, also called the bond order, is the sum of all such terms between the participating orbitals on the two centers. The "gross atomic population" (q_1) for an atom 1 is made up of the net atomic population plus all the overlap populations (each multiplied by the arbitrary constant 0.5) to which atom 1 contributes: $q_1 = n_1 + 0.5\sum p_{jm}$. Since *N*, the total number of electrons in the system, is given by summing all net atom populations and all overlap populations, the gross atomic populations also sum to *N*, the factor 0.5 preventing double counting of the two-center terms.

(4) Methane is a good example, the net atomic populations at various basis set levels being: STO-3G, $s^{0.748}p^{1.962}$; 3-21G, $s^{1.175}p^{2.155}$; 4-31G, $s^{0.992}p^{2.099}$; 6-311G**, $s^{1.182}p^{1.959}$.

(5) (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.

(6) 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.

(7) Bicerano, J.; Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 732–739.

symmetry) are given below. The data may be used calculate sp^n ratios, the nonbonding p electrons on the heavy atom being excluded from the calculation of the ratios so as to permit comparison with the value for the sp^2 model (see Table IV). As was the case for tetrahedral hydrides, the central-atom s orbital makes its rather large contribution to A–H bonding by means of its presence in a single valence-shell MO.

BH_3*	$2s^{1.16(0.28)}2p_{x,y}{}^{1.74(0.52)}2p_z{}^{0.00(0.00)}$
AlH_3*	$3s^{1.03(0.26)}3p_{x,y}{}^{1.29(0.46)}3p_z{}^{0.00(0.00)}$
CH_3^+*	$2s^{1.62(0.17)}2p_{x,y}{}^{2.58(0.24)}2p_z{}^{0.00(0.00)}$
SiH_3^+*	$3s^{1.32(0.23)}3p_{x,y}{}^{1.72(0.24)}3p_z{}^{0.00(0.00)}$
NH_3*	$2s^{1.59(0.19)}2p_{x,y}{}^{2.36(0.50)}2p_z{}^{2.00(0.00)}$
PH_3*	$3s^{1.45(0.22)}3p_{x,y}{}^{1.78(0.50)}3p_z{}^{2.04(0.00)}$
H_3O^+*	$2s^{1.80(0.11)}2p_{x,y}{}^{2.93(0.40)}2p_z{}^{2.00(0.00)}$
H_3S^+*	$3s^{1.71(0.14)}3p_{x,y}{}^{2.35(0.23)}3p_z{}^{2.03(0.00)}$

* Planar geometry.

(c) Linear ($D_{\infty h}$) Hydrides. Population data for AH_2 hydrides in the maximum symmetry (linear) geometry again reflect the considerable use made of the s orbital in bonding:

NH_2^-*	$2s^{1.46(0.33)}2p_{x,y}{}^{4.00(0.00)}2p_z{}^{0.90(0.39)}$
PH_2^-*	$3s^{1.43(0.30)}3p_{x,y}{}^{4.07(0.00)}3p_z{}^{0.88(0.40)}$
H_2O*	$2s^{1.73(0.20)}2p_{x,y}{}^{4.00(0.00)}2p_z{}^{1.24(0.38)}$
H_2S*	$3s^{1.65(0.24)}3p_{x,y}{}^{4.06(0.00)}3p_z{}^{1.15(0.40)}$

* Linear geometry.

sp^n ratios calculated from these population data are summarized in Table IV. Relative to the sp$^{1.0}$ model, the sp^n ratios are low (high), reflecting, one the one hand, the large nonbonding component in the s-electron density and, on the other, the larger p-orbital contributions to the overlap densities.

The molecules just considered either had lone pairs which took no part in bonding or had no lone pairs at all, but, as the comparison between the overlap density and gross density views of them accentuated, even the putative bonding orbitals are endowed with nonbonding functions. For most other molecules, which have more electron pairs than bonds, the interpretation of electron population data presents even more difficulties, chiefly because of the arbitrariness of any scheme for partitioning the electron cloud into bonding and nonbonding parts. Localization procedures purport to yield orbitals in which lone pairs are spatially separated from bonding pairs, but there are large differences in the extent of the separation produced by different schemes. In turn, differences in the separation of bonding and nonbonding orbitals lead to differences in the contributions of the s and p orbitals of the central atom and these differences may be large. Thus, four different localization schemes yield, for the NH_3 lone pair, s:p ratios based on gross atomic populations corresponding to sp$^{1.1}$, sp$^{1.8}$, sp$^{2.1}$, and sp$^{3.0}$.[9] Daudel et al.[10] have pointed out that the exchange-energy term, which is minimized in the Edmiston–Ruedenberg localization scheme, is less than 1.5% of the total energy, and they question the ability of this concept to sustain the idea of an abrupt contrast between the distributions of different electron pairs in the same valence shell. Bader and Stephens' pair correlation analysis tends to the same conclusion, this time with reference to the spatial characteristics of orbitals.[11] Since there seems to be no demonstrable advantage to this research in using localized wave functions, the analysis here begins with canonical MOs.

(d) AH_2 Hydrides with C_{2v} Symmetry. The effect on the electron populations of H_2O of changing the bond angle over the range 90–180° is detailed in Figure 1. The origins of the changes in H_2O have often been described[12-15] and from a variety of standpoints. Particularly significant is the approach taken by Hall[13] in emphasizing the importance of the 2s–2p energy separation in determining the minimum-energy geometry. He showed that the most stable form of the AH_2 species is linear when the separation is zero and that the lower energies of the bent geometries of H_2O, H_2S, etc., are achieved by the bigger s-orbital occupations allowed, in spite of the loss of s character in the O–H and S–H bonds.[15] The effect of this may be followed in the individual MOs.

(i) The upper lone pair (b_1 symmetry) shows no perceptible change in composition from 180 to 90° since there is no O – H interaction to be affected by bond-angle change. The 0.5-eV drop in energy accompanying the bending is the smallest of the set of four and results from the reduced repulsion between the electron pair in this orbital and the diminishing charge on oxygen.

(ii) The upper a_1 orbital is largely nonbonding. The bonding component is stabilized by reducing the bond angle; $2p_{aO}{:}1s_H$ overlap increases. Combined with the electron repulsion, this produces an overall energy stabilization of 1.7 eV, the largest of the four. Overall, s utilization rises strongly at the expense of p-orbital utilization.

(iii) The b_2 bonding orbital rises in energy, because the effect of the drop in $(ip_{yO}{:}1s_H)$ exceeds the reduction in repulsion energy which follows electron drift from oxygen. The composition change is insubstantial.

(iv) The a_1 orbital is usually described as strongly bonding, in consequence of the favorable $2s_O{:}1s_H$ interaction. This component is unaffected by bond angle and, as a result, the overall change in composition is minimal. However, a small $2p_{zO}{:}1s_H$ interaction is possible in the bent conformation, and, when this is added to the loss of repulsion energy which follows the electron drift, the result is a 1.0-eV orbital energy stabilization across the 180–90° range.

The effects of bond-angle change on individual MOs are fairly small, the biggest being found in the nonbonding a_1 orbital. It is not possible to attribute these effects to changes in bond energy stemming from changes in sp hybridization. Although the s- and p-orbital contributions in individual MOs do move in the expected directions, across the 90 to 120° range, the movement in sp ratios is sp$^{0.62}$ to sp$^{0.54}$ in the two lower orbitals and sp$^{5.1}$ to sp$^{8.9}$ in the upper orbitals; the apparent sp hybrid character in individual MOs is illusory, the overall contribution of the s orbital to bonding being almost miniscule. It is clear that arguments based on individual MO densities must be replaced by an analysis of the electron density as a whole.

Excursus on Electron Population Analysis

The overall electron density of a molecule contains atomic terms (one-center terms like $\varphi_A{}^2$, $\varphi_B{}^2$,. . . for centers A, B,. . .) and overlap terms (two-center terms like $\varphi_A\varphi_B$). Analyzing overlap densities

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(8) Thus Bingel and Luttke (ref 1b) obtain formulas for sp hybrids by requiring that the s and p contribution to four hybrids sum to 1 and 3, respectively. When hybrids are represented $h_i = N(s + a_ip_i)$, they require that $\sum(1 + a_i^2)^{-1} = 1$ and $\sum a_i^2(/(1 + a_i^2) = 3$. Actual MO calculations rarely conform to this requirement. The share of the electron density due to any particular atom varies considerably from one molecule to another; the portions of that share which are attributable to s and p orbitals are also too variable to conform to any such relationship.

(9) Millie, Ph.; Levy, B.; Berthier, G. "Localization and Delocalization in Quantum Chemistry"; Chalvet, O., Daudel, R., Diner, S., Malrieu, J.-P., Eds.; D. Reidel: Dordrecht, 1975; pp 59–97.

(10) Daudel, R.; Stephens, M. E.; Kapuy, E.; Kozmutza, C. *Chem. Phys. Lett.* **1976**, *40*, 194–198.

(11) (a) Bader, R. F. W.; Stephens, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 7391–7399. (b) Bader, R. F. W.; Jones, G. A. *J. Chem. Phys.* **1963**, *38*, 2791–2802.

(12) Gimarc, B. M. "Molecular Structure and Bonding"; Academic Press: New York, 1979.

(13) Hall, M. B. *Inorg. Chem.* **1978**, *17*, 2261–2269; *J. Am. Chem. Soc.* **1978**, *100*, 6333–6338. See also: Palke, W. E.; Kirtman, B. *Ibid.* **1978**, *100*, 5717–5721.

(14) The "p-only" model is expounded in Burdett, J. K. "Molecular Shapes"; Wiley: New York, 1980.

(15) Bernardi, F.; Bottoni, A.; Taddei, M. *J. Mol. Struct.* **1982**, *90*, 183–186. These workers adopt an approach to AH_2 and AH_3 geometries taken by a number of other workers (for references see the paper) in which the bending or linear AH_2 molecules and the pyramidalization of planar AH_3 molecules is attributed to interaction between the HOMO and the LUMO. The fundamental importance of the s–p energy separation and the tendency to adopt a high s electron nonbonding density is not noted. The explanations given for differences in bond angles between first- and second-row hydrides, given in terms of the efficiency of the HOMO/LUMO interaction, are also unnecessary when the observed distances between groups attached to the central atom are related to the minimum nonbonded contact distances for such atoms.

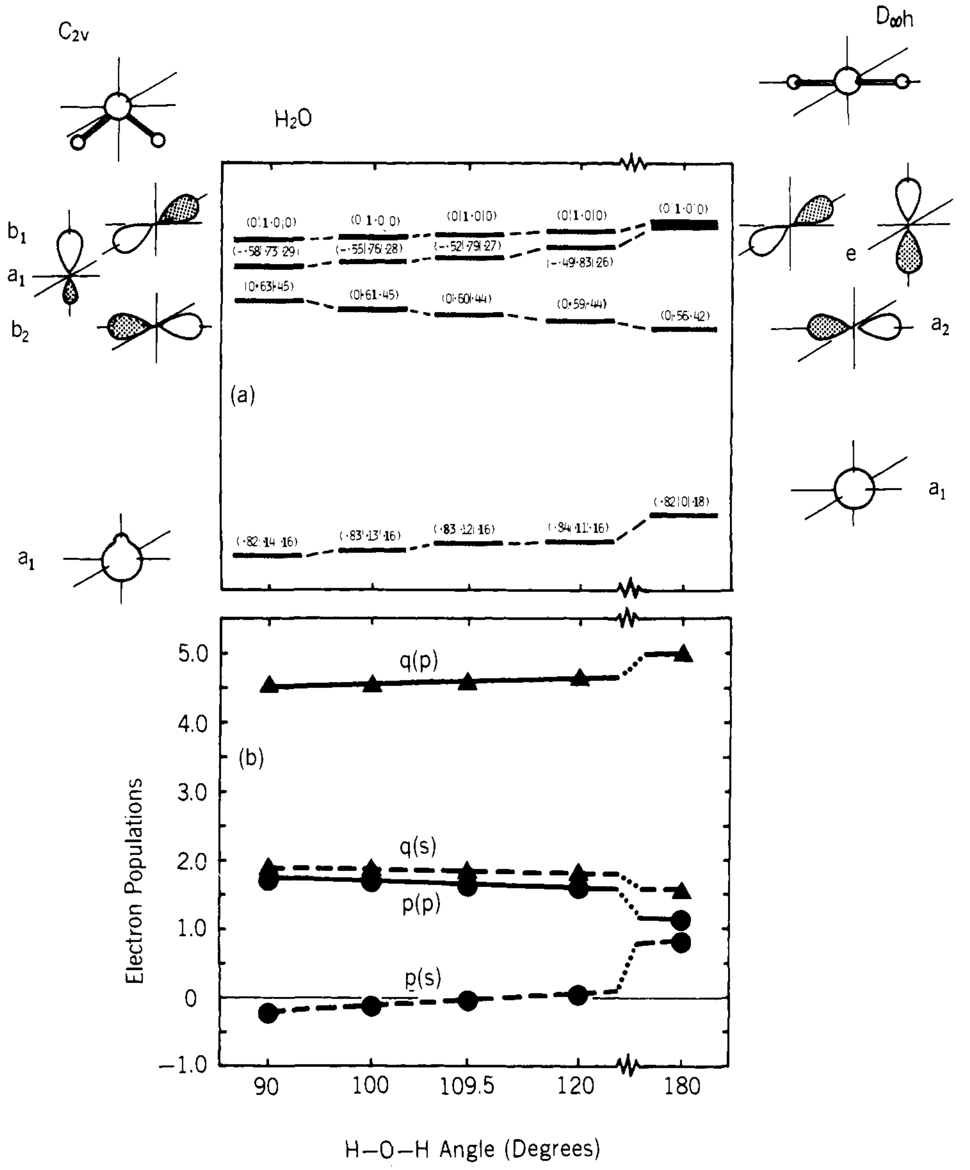

Figure 1. (a) Variation with bond angle of the energies and composition of H_2O MOs (STO-3G results). The figures above each MO energy level are the coefficients of the $3s_O$, $3p_O$, and $1s_H$ orbitals, respectively. The $2p_O$ entry is for the particular p orbital with symmetry appropriate to the MO in question, zero values for the other p orbitals not being included, and $1s_H$ entry is the root-mean-square value for the 1s orbitals of the two H atoms). (b) Bond-angle variation of oxygen electron populations in H_2O. Gross atomic populations (triangles) and total overlap populations for both O – H bonds (circles) are given for the s orbital (dashed curves) and the p orbitals (continuous curves).

into s- and p-orbital contributions provides a useful solution to the confusion between bonding and nonbonding orbitals because there is no ambiguity about their origin. Overlap density necessarily relates to bonding electrons whether it originates from one MO or many. The quantities do not suffer from any uncertainties such as arise in the use of Mulliken atomic populations, and the sign is all that is needed to disclose whether the contribution of a particular AO to the bond energy is favorable or unfavorable. Once the size of the overlap density term in the gross atomic population for an orbital is known, it is much easier to determine the role of the latter in the overall wave function of the molecule. Finally, overlap density data refer to particular bonds, and the information about them is readily extracted from MO wave functions.

Analysis of overlap density data is a useful way to distinguish between utilization of an atomic orbital in the "atomic" and "overlap" parts of the electron density, but its use does not completely eliminate the confusion between the bonding and nonbonding roles of s and p orbitals. As recent studies have emphasized,[16,17] the buildup of electron density in the internuclear region is important in the H_2 molecule, but it is not the only way for molecules to have lower energies than their component atoms. An orbital on an atom may play a part in bonding by virtue of the disposition of the one-center terms it offers to the overall electron density distribution as well as the two-center terms. In cases of very polar bonds or bonds between very electronegative atoms the forces arising from polarization of the core or of π-type AOs may even be more important than those which result from charge buildup (overlap distributions) in the internuclear region.[17,18]

In view of the above, it would be valuable to have a more general index of bonding than the overlap density. Use of the Roby "shared population", recently discussed by Cruickshank and Avramides,[19] would be a step in this direction. It combines one- and two-center population terms in a single datum by projecting the basis functions on one center on to the space of the full set.

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

(17) Bader, R. F. W.; Henneker, W. H.; Cade, P. E. *J. Chem. Phys.* **1971**, *46*, 3341–3363.

(18) (a) Dunitz, J. D.; Schweizer, W. B.; Seiler, P. *Helv. Chim. Acta* **1983**, *66*, 123–133. (b) Coppens, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 32–40.

(19) Cruickshank, D. W. J.; Avramides, E. J. *Phil. Trans. R. Soc. London, Ser. A* **1982**, *304*, 533–565.

Table I. Bond-Angle Variation of s- and p-Orbital Contributions to Overlap Density in H_2O, H_2S, NH_2^-, and PH_2^-

		90°	100°	109.5°	120°	180°
H_2O	p(s)	−0.060	−0.034	−0.008	0.024	0.200
	p(p)	0.578	0.561	0.541	0.516	0.375
H_2S	p(s)	−0.142	−0.116	−0.093	−0.070	0.235
	p(p)	0.672	0.656	0.637	0.613	0.395
NH_2^-	p(s)	−0.196	−0.169	−0.141	−0.101	0.329
	p(p)	0.671	0.653	0.632	0.604	0.393
PH_2^-	p(s)	−0.172	−0.170	−0.172	−0.174	0.279
	p(p)	0.689	0.678	0.663	0.642	0.404

However, pending the development of clearer relationships between calculated population data and experimental measures of bonding, it still seems important to retain the clear distinction made in the Mulliken formalism between one-center and two-center terms in the electron distribution.[3]

Although there is some arbitrariness in the subdivision of the overall electron density of a molecule into atomic and overlap densities, the technique of obtaining "deformation densities"[18b] by subtracting spherical densities appropriate to the atoms from the experimentally determined electron distribution for a molecule gives quasi-observable status to overlap density distributions and justifies its use to explore the structure of the bonding in the molecule. Mulliken's prescription for electron population analysis has an advantage over the Roby method in this connection since in it the total density is conserved (gross atom populations sum to the total number of electrons) and the relation between theoretical and experimental approaches retained.[3] In consequence of this, overlap density contributions made by s and p orbitals, taken in conjunction with gross atomic population data, are here proposed as measures of the participation of these AOs in bonding, allowing estimation of electron drift due to differences in effective nuclear charge of overlapping atoms as well as the relative sizes of the one- and two-center terms in the total density attributable to each orbital. This approach is analogous to that developed formally by Mayer, who also proposes the use of overlap and gross atomic populations for assessing bonding.[20]

AH_2 Hydrides (Continued). The most striking result of analyzing the overlap density in molecules like H_2O is that the contribution to binding made by the s atomic orbital at all bond angles below 110° is negative. The bonding $2s_O{:}1s_H$ interaction in the lower a_1 orbital, almost constant over the wide bond-angle range, is opposed by an antibonding interaction in the upper MO of the same symmetry. Utilization of the s orbital in this MO is not independent of molecular bending, and at low angles the negative overlap term is large enough to exceed the positive overlap density arising from the lower a_1 MO and yield a net negative overall result. This behavior is typical of bent AH_2 molecules (NH_2^-, PH_2^-, H_2O, H_2S) and makes it necessary to use caution in presenting data about the bonding in individual MOs, as was done above. Argument based on a apparent bonding contribution to a MO from the 2s orbital (as in (d) above for the lower a_1 orbital of H_2O) is hard to sustain if the total s-electron bonding in the molecule turns out to be zero or negative. This possibility makes it important to scrutinize the data for the overall density whenever contributions from individual MOs are cited.

Overlap density data for AH_2 group hydrides across the full 90–180° range are presented in Table I and, for H_2O, in Figure 1. Although the crossover between a bonding and an antibonding role for the central atom s orbital occurs at a different point in the bond-angle range for different molecules, all these molecules have s-orbital contributions to bonding in their minimum energy geometries which are negative or close to zero. The large values for the s-orbital density undoubtedly arise from the largely nonbonding role predicted by Pauling many years ago for the s orbital in molecules of this kind.[21] The very favorable energy of the s AO makes it use in bonding unprofitable, he argued, because it would then yield only part of that energy to the molecule. p orbitals, on the other hand, have higher energies and are better direction in space and should be utilized much more. Figure 1 shows just how little this utilization is affected by geometry change.

Both of Pauling's conclusions are reinforced by Hall's calculations on H_2O, already cited,[13] and by the argument of Bader and Jones about the angle dependence of the attraction between the protons and the lone pairs (more favorable for a bent molecule with an s-type lone pair) and the attraction between protons and bonding electrons (also more favorable for a bent molecule with a preponderance of p character in the bonds).[11b]

Thes predictions are well supported by this series of calculations: s orbitals are almost entirely nonbonding. The total s-electron density is little less than that of a lone pair, and the accompanying overlap populations are negative or close to zero. Populations of p orbitals are much lower than maximum because they arise mainly from bonding orbitals. The following atomic population data summarize this situation for the four first- and second-row AH_2 hydrides in their minimum-energy geometries. The figures in parentheses are the contributions to the overlap density of the A–H bond made by each orbital.

H_2O	$2s^{1.90(-0.02)}2p_x^{2.00(0.00)}2p_{y,z}^{2.84(0.55)}$
H_2S	$3s^{1.93(-0.12)}3p_x^{2.03(0.00)}3p_{y,z}^{2.35(0.66)}$
NH_2^-	$2s^{1.85(-0.21)}2p_x^{2.00(0.00)}2p_{y,z}^{2.15(0.68)}$
PH_2^-	$3s^{1.83(-0.17)}3p_x^{2.04(0.00)}3p_{y,z}^{1.96(0.68)}$

Populations for the (lone-pair) p_x orbital are listed separately from those for the other two p orbitals which are responsible for all the bonding in the molecule. sp^n ratios are not given. On the one hand, sp^n ratios calculated from atomic populations fail to discriminate between bonding and nonbonding parts of the electron distribution and so do not represent utilization of the AOs in bonding. On the other hand, the negative values obtained for s-orbital overlap densities scuttle any attempt to use overlap density data as a basis for estimating "bonding" sp^n ratios.

As was the case for the AH_2 hydrides, the behavior of central-atom s and p orbitals in bonding in other classes of molecules is characteristic of each class and quite uniform within the class. Brief descriptions follow for pyramidal AH_3 hydrides and the diatomic AH molecules.

(a) Pyramidal (C_{3v}) Hydrides, AH_3. The response in the canonical orbitals of NH_3 to change in bond angle may be summarized quickly, minimal and extended basis sets results again being closely similar. The changes in individual orbitals over the 90–120° bond-angle range in this molecule (see Figure 2) are more dramatic than in H_2O because of the change in symmetry which takes place at the end of the range. In the pyramid there are two a_1 orbitals, one regarded as strongly bonding and other as a highly directed lone pair. These orbitals reappear in the planar molecule as the a_1' orbital ($2s_N$ and $1s_H$ contributions only) and the a_2'' orbital (a pure p orbital); the energies of both rise. The increase in s character in the a_1' orbital is much less than the p-character increase in the a_2'' orbital. Again, the favorable energy of the 2s orbital ensures its presence in this MO to the almost total exclusion of the $2p_z$ orbital at all angles, not only at 120° where symmetry excludes it. Thus, the overall response of the gross populations, and of the sp ratio, to change in geometry is quite small in contrast to the major change in the s-orbital contribution to bonding.

Once again the overlap density data require an interpretation which contradicts many of the conclusions commonly drawn from the composition of the MOs. The bonding interaction between the s orbital in the lower a_1 is opposed by an antibonding term in the upper orbital of the same symmetry so that the net contribution to bonding is much reduced. In PH_3 the two opposing contributions to the overlap density happen to be equal, and the result is purely nonbonding s orbital. Table II lists the s- and p-overlap density data for AH_3 group hydrides over the bond angle range 90–120°. p orbitals provide almost all the bonding in the lower part of the range, but the s-orbital contribution increases

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(20) Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270–274.

(21) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 111.

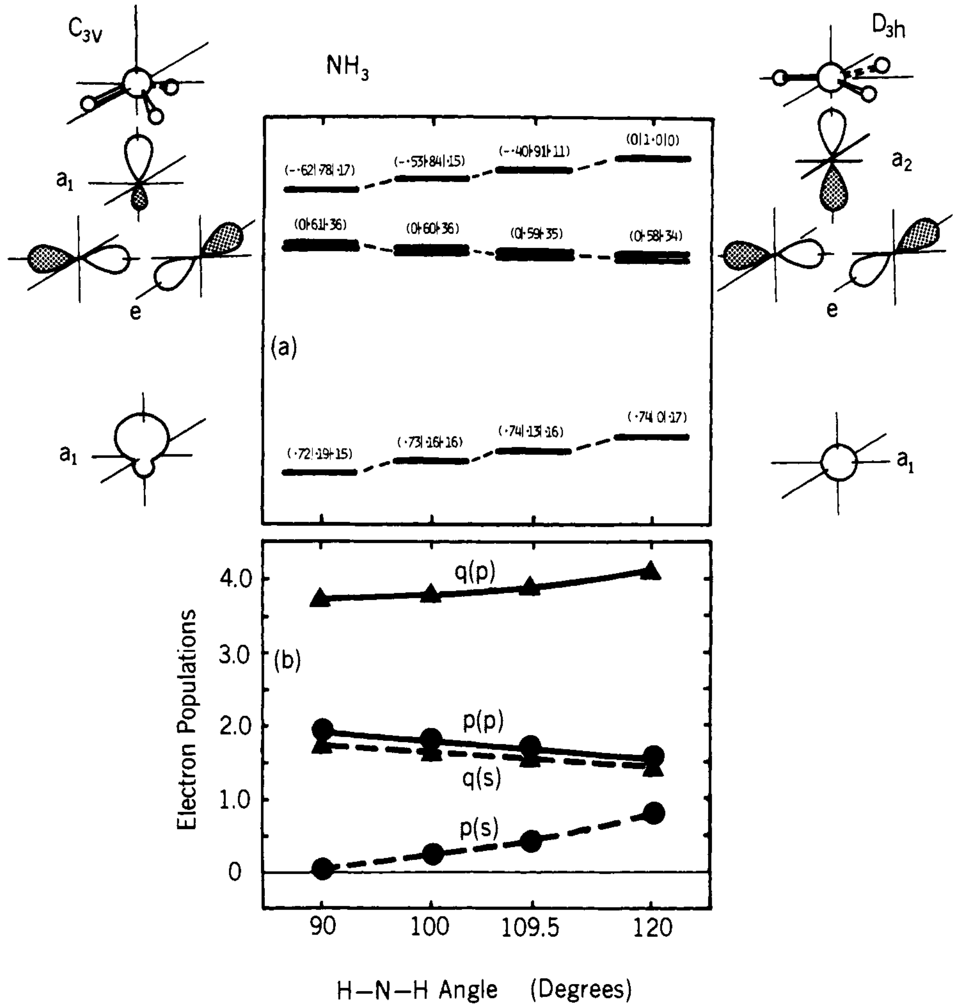

Figure 2. (a) Variation with bond angle of the energies and composition of NH_3 MOs (STO-3G results). MO coefficients above each MO energy level are for the $2s_N$, $2p_N$, and $1s_H$ orbitals, respectively, the $2p_N$ orbital figure being the coefficient for the p orbital which enters the MO, zero values for the other p orbitals not being included, and the $1s_H$ figure being the root-mean-square value of the coefficients of the three 1s AOs of the three H atoms. (b) Bond-angle variation of nitrogen electron populations in NH_3. Gross atomic populations (triangles) and total overlap populations for the three N – H bonds (circles) are given for the s orbital (dashed curves) and the p orbitals (continuous curves).

Table II. Bond-Angle Variation of s- and p-Orbital Contributions to Overlap Density in NH_3 and PH_3

		90°	100°	109.5°	120°
NH_3	p(s)	−0.004	0.054	0.114	0.190
	p(p)	0.616	0.585	0.548	0.496
PH_3	p(s)	−0.024	0.028	0.087	0.220
	p(p)	0.654	0.620	0.577	0.500
H_3O^+	p(s)	−0.004	0.032	0.066	0.108
	p(p)	0.490	0.465	0.437	0.398
H_3S^+	p(s)	−0.015	0.021	0.059	0.138
	p(p)	0.567	0.553	0.527	0.461

as the planar geometry is approached. At 120°, the bond angle for maximum symmetry, there is no negative s overlap term to offset the positive contribution from the lowest MO.

Although the crossover between negative and positive s-orbital overlap occurs at different angles for different molecules, the overall behavior is the same. For NH_3, PH_3, H_3O^+, and H_3S^+ in their minimum-energy geometries the atomic population data are as follows, with the contributions of each atomic orbital to the A – H overlap density given in parentheses, as before:

NH_3	$2s^{1.67(0.10)}2p_{x,y}^{2.32(0.49)}2p_z^{1.90(0.05)}$
PH_3	$3s^{1.77(0.00)}3p_{x,y}^{1.76(0.45)}3p_z^{1.55(0.19)}$
H_3O^+	$2s^{1.80(0.11)}2p_{x,y}^{2.93(0.40)}2p_z^{2.00(0.00)}$
H_3S^+	$3s^{1.93(0.01)}3p_{x,y}^{2.28(0.42)}3p_z^{1.70(0.13)}$

The $2p_z^2$ contribution in H_3O^+ occurs because, unlike the other molecules, the minimum-energy conformation for H_3O^+ is planar in the 3-21G basis and the orbital in question ceases to have any bonding function.

(b) Diatomic AH Hydrides. The picture of sp hybridization in diatomic hydrides like HF, with one hybrid utilized in bonding and the other pointing in the opposite direction, accommodating lone-pair electrons, is very familiar but, again, at odds with electron-population analysis on HF and similar molecules. The phenomenon of negative s-orbital overlap density is again present but more markedly than in the other hydrides. The bonding is provided exclusively by the p orbitals, s-orbital densities being close to the s^2 configuration expected when the s–p energy difference is as great as it is in elements to the right of the periodic table. The atomic population data for HF, HCl, OH^-, and SH^- are given below with the contributions to A – H bond overlap densities in parentheses. The p_x, p_y orbitals are nonbonding.

HF	$2s^{1.98(-0.08)}2p_{x,y}^{4.00(0.00)}2p_z^{1.48(0.51)}$
HCl	$3s^{2.00(-0.14)}3p_{x,y}^{4.03(0.00)}3p_z^{1.31(0.62)}$
OH^-	$2s^{1.96(-0.33)}2p_{x,y}^{4.00(0.00)}2p_z^{1.08(0.63)}$
SH^-	$3s^{1.97(-0.28)}2p_{x,y}^{4.07(0.00)}3p_z^{1.06(0.70)}$

General Discussion

Patterns of s- and p-Orbital Bonding. An overall comparison of the results of subdividing atomic and overlap densities into s and p contributions is now possible. The largest contributions made by the s atomic orbital to the electron density in the bonding region occurs for the tetrahedral class. Even though the bond angle may be the same, s- and p-orbital bonding in hydrides of different symmetry is generally quite different: the lower the symmetry

Table III. sp^n Ratios in AH_4, AH_3, and AH_2 Hydrides in Maximum Symmetry Geometries

symmetry		ratios of atomic populations[a]	ratios of overlap populations[b]
T_d	BH_4^-	2.16	2.43
	AlH_4^-	1.73	2.24
	CH_4	2.21	3.35
	SiH_4	1.80	2.36
	NH_4^+	2.52	4.00
	PH_4^+	1.92	3.53
D_{3h}[c]	NH_3	1.49	2.61
	PH_3	1.23	2.27
	H_3O^+	1.62	3.62
	H_3S^+	1.37	3.34
$D_{\infty h}$[c]	NH_2^-	0.61	1.19
	PH_2^-	0.62	1.36
	H_2O	0.72	1.88
	H_2S	0.70	1.68

[a] sp^n ratios calculated from s and p gross atomic populations. [b] sp^n ratios calculated from s- and p-orbital contributions to overlap populations. [c] Ratios calculated for the bonding orbitals only: s, p_x, p_y orbitals for planar AH_3 hydrides, s, p_x orbitals for linear AH_2 hydrides.

Table IV. sp^n Ratios for Main-Group Hydrides

hydride group	symmetry type	total density[a] sp^n ratios	overlap density sp^n ratios
AH_4	T_d	$sp^{1.8}$–$sp^{2.2}$	$sp^{2.4}$–$sp^{4.0}$
AH_3	D_{3h}	$sp^{1.3}$–$sp^{1.6}$	$sp^{1.0}$–$sp^{3.6}$
	C_{3v}	$sp^{1.9}$–$sp^{2.5}$	
AH_2	$D_{\infty h}$	$sp^{0.6}$–$sp^{0.7}$	$sp^{1.4}$–$sp^{1.9}$
	C_{2v}	$sp^{1.1}$–$sp^{1.5}$	
AH	$C_{\infty v}$	$sp^{0.5}$–$sp^{0.8}$	

[a] Calculated from Mulliken gross atomic populations for the central atom orbitals contributing to the σ-type MOs only.

Table V. Overlap Density Contributions as Fractions of Total Gross Atomic Populations: s- and p-Orbital Data for First- and Second-Row Hydrides

	NH_2^-	NH_3	NH_4^+
nitrogen orbitals			
2s	−0.11	0.12	0.14
$2p_x$	0.00	0.63	0.23
$2p_y$	0.40	0.63	0.23
$2p_z$	0.24	0.07	0.23
hydrogen orbital			
1s	0.22	0.48	0.56
	PH_2^-	PH_3	PH_4^+
phosphorus orbitals			
3s	−0.09	0.00	0.19
$3p_x$	0.00	0.38	0.35
$3p_y$	0.42	0.38	0.35
$3p_z$	0.30	0.19	0.35
hydrogen orbital			
1s	0.50	0.35	0.43

of the arrangement of H atoms around A, the more complete the segregation of the s orbital to the nonbonding part and the p orbitals to the bonding part of the electron distribution. Overlap densities decline toward negative values across sequences in which symmetry is reduced, such as CH_4, NH_3, H_2O, HF, as the following population data make clear (gross atomic populations for s and p orbitals of A; s and p overlap density contributions to the A − H bond in parentheses):

CH_4	$2s^{1.50(0.17)}2p^{3.32(0.57)}$
NH_3	$2s^{1.67(0.10)}2p^{4.22(0.54)}$
H_2O	$2s^{1.90(-0.02)}2p^{4.84(0.55)}$
HF	$2s^{1.98(-0.08)}2p^{5.48(0.51)}$
SiH_4	$3s^{1.22(0.22)}3p^{2.20(0.52)}$
PH_3	$3s^{1.77(0.00)}3p^{3.31(0.64)}$
H_2S	$3s^{1.93(-0.12)}3p^{4.38(0.66)}$
HCl	$3s^{2.00(-0.14)}3p^{5.34(0.62)}$

The trends in the data for these molecules do not appear solely as the result of symmetry change; also clear is the much remarked fall in the importance of sp hybridization as s–p promotion energy increases which is shown in the steady movement toward the $2s^2$ configuration. Comparison of isostructural molecules such as BH_4^-, CH_4, NH_4^+ or BH_3, CH_3^+, NH_3, H_3O^+ is readily made from the data presented in the earlier sections. The rise in s-orbital density parallels the increase in 2s–2p energy separation (7.4–22.9 eV for carbon to fluorine and 6.6–15.4 eV for silicon to chlorine). p-Orbital densities rise at the expense of the electron density around the H atoms, but the effectiveness of the p orbitals in A − H bonds is relatively unchanged. Also apposite are the data which show the relative sizes of the overlap and atomic density parts of the gross atomic density values for the s and p orbitals (see Table V). The fraction of overlap density for the p orbital is generally much larger than the s-orbital fraction, reflecting the effective use made of p orbitals in bonding compared with the concentration of s character in the nonbonding part of the distribution.

These results confirm Hall's conclusions about the importance of s-orbital energies[13] and are also consistent with the study on CH_4, NH_3, H_2O, and H_2S by Jarvie et al.[22] This work provided the substance for an early critique of the Gillespie–Nyholm qualitative approach to molecular geometry. Although an explanation of its wide success has not been found, the VSEPR approach has come increasingly under criticism. The removal of the central-atom s orbital from the set was shown by Jarvie et al. to have very little effect on the geometry of the four molecules and provoked the conclusion that hybridization was relatively unimportant in determining equilibrium shapes of such molecules. Jarvie et al. showed that the nature of the potential-energy curve for bond-angle change was relatively unaffected by removal of the s orbital from the calculation, a conclusion consistent with the observations in this study of s-orbital populations close to 2.0. In such a case no component of the angular deformation potential energy could arise from the s orbital which, lacking overlap with other orbitals, is spherical.

Foster and Weinhold have recently presented a method for the calculation of hybrid ratios from population data and have discussed the wide variety of methods used by other workers, including maximum overlap methods.[23] It is interesting to note that their density matrix method, which ignores the distinction between utilization of an orbital in bonding and nonbonding roles, leads to hybrid ratios much closer to the idealized (maximum overlap) values than those quoted in this paper. This is so in spite of the fact that the maximum overlapping principle is rationalized on the basis of effectiveness in bonding, an approach which must surely require attention to role, not just the total density. The reason is fairly clear: total atomic densities for both s and p orbitals in hydrides are generally in the range 1.5–2.0 and ratios are thus likely to be close to $sp^{1.0}$, $sp^{2.0}$, $sp^{3.0}$ as one, two, and three p orbitals are brought into the reckoning.

Foster and Weinhold's method allows them to determine a priori "Lewis structures" for molecules, a procedure which could be misleading if it were suggested that the hybrid ratios were actually involved in bonding. The heavy involvement of the s orbital in the nonbonding part of the electron distribution means that they are not.

Whitehead and Zeiss have recently proposed methods of improving the quality of maximum overlap wave functions, which "suffer from excessive s–p promotion", suggesting their wider usage because of the economy with which they can be obtained.[24] They show that, when maximum overlap wave functions are constrained to reproduce certain experimental (or calculated) expectation

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(22) Jarvie, J.; Willson, W.; Doolittle, J.; Edmiston, C. *J. Chem. Phys.* **1973**, *59*, 3020–3026.

(23) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218.

(24) Whitehead, M. A.; Zeiss, G. D. *Can. J. Chem.* **1983**, *61*, 675–679.

values for one-electron properties, the excesses of ignoring the energies of the atomic orbitals are largely reversed.

Bond-Angle Change and s- and p-Orbital Utilization. The general pattern of the response in s- and p-orbital utilizations to bond-angle change in AH_2 and AH_3 hydrides is obvious in Tables I and II and Figures 1 and 2. It is important because these are the species to which the hybridization rule is most often applied. The contributions made by central-atom s and p orbitals in these molecules arise mainly from different MOs, the segregation becoming complete in the maximum symmetry conformations (the linear $D_{\infty h}$ conformation for AH_2 and the planar D_{3h} conformation for AH_3). (See the MO figures in Figures 1 and 2.) Adherence to the bond-angle/sp-ratio relationship is thus restricted to the disappearance of the respective minor components of the upper and lower a_1 MOs as the bond angle increases from 90° to the maximum. Because the s and p contributions go to zero in the upper and lower a_1 MOs, respectively, the sp^n ratios in these MOs vary catastrophically. In contrast, the s and p gross atomic populations for the molecule as a whole show only slight dependence on angle, the major effect being the change in the s-orbital overlap density component from its negative value at 90°, through zero, to the point at the top of the range where it provides a significant part of the gross density and contributes strongly to A–H binding. In contrast, the p-orbital overlap contribution undergoes only very minor change.

These results provide a general corroboration of further conclusions drawn by Hall from his study of H_2O.[13] The hybridization ratio varies little with bond angle, he suggests, because it is intrinsic to the topology of the system and the number of electrons it contains. His arguments apply equally to pyramidal molecules and explain the bent geometry (for AH_2 hydrides) and pyramidal geometry (for AH_3 hydrides) as resulting from the need to maximize the occupation of the low-lying 2s orbital; low 2s–2p separations would subject the AH_2 and AH_3 hydrides to repulsive forces between bond pairs (Pauli forces) only and leave the AH_2 hydrides linear and the AH_3 hydrides planar. One change in Hall's commentary is necessary: he ascribes the 104° bond angle in H_2O to the effect of Pauli forces on what would otherwise be a 90° geometry, overlooking the fact that at 104° the hydrogen atoms are in close contact, as they are also in NH_3 at the experimental geometry. The explanation for the smaller angles in second-row hydrides, PH_3, H_2S, etc., is unnecessary; the larger kernel size of the atoms in the next row naturally permits a greater reduction of the bond angle before contact between attached atoms halts it.

It is important to notice the way that s- and p-overlap density terms vary with change in bond angle because this is the analogue, in the "total density" view of the molecule, of the variation with bond angle of individual MOs as portrayed in Walsh diagrams. Substantially the same overall behavior is observed for the AH_3 and AH_2 hydrides: an initially negative s-overlap density contribution passing through zero to become positive at higher angles. The crossover occurs at different points in the range (see Tables I and II), and this explains why the s orbital is antibonding in some molecules (e.g., H_2O), nonbonding in some (e.g., PH_3), and bonding in others (e.g., NH_3).

Significance of Negative Overlap Density Terms. Comparison of results for a series of hydrides with the same central atom is helpful. The overlap densities for the NH_2^-, NH_3, NH_4^+ series are:

	p(s)	p(p)
NH_2^-	−0.200	0.651
NH_3	0.137	0.535
NH_4^+	0.115	0.478

In all three species there is a large contribution from the 2s AO to the lowest valence-shell MO. The 1s orbitals of the hydrogens are too high in energy to contribute very strongly to this orbital, but such interaction as there is produces a bonding $2s_N$:$1s_H$ contribution to the charge density of the molecule; this is offset by negative contributions from higher lying orbitals of the same symmetry, producing a net negative s-overlap term for NH_2^- and a much reduced positive term for NH_3. NH_4^+ has no upper a_1 orbital and, consequently, no reduction of the s-overlap density term. Analogous results are obtained from the second-row molecules PH_2^-, PH_3, PH_4^+ with the exception that in PH_3, where the bond angle is much smaller, the contributions to the s-orbital overlap density from the two a_1 MOs completely cancel each other, giving a zero overall result. The bonding is thus entirely due to the p orbitals, the 3s AO being involved only in a nonbonding role.

In molecules with lower than maximum symmetry the s-orbital overlap densities sometimes take quite large negative values. This feature establishes the fact that the low energy of the s AO is sufficient to ensure the presence of nonbonding s density even at the expense of an antibonding interaction with the attached atoms if the topology of the system produces this, as in the AH_3, AH_2, and AH hydride classes. There are two important consequences of this. Firstly, since the net s-overlap density usually comes about when positive overlap in a low-lying orbital is counteracted by an antibonding term in a higher orbital, very small or negative overlap densities may result even when the s orbital in some particular MO appears to be strongly bonding. (See, for example, the $2s_O$ and $1s_H$ MO coefficients in the lowest valence-shell MO displayed in Figure 1.) An illusory contribution to binding in a molecule imposes a serious restriction on the use of arguments drawn from the electron distribution in particular MOs—as when Walsh diagrams are used. When it is remembered that MO energies exaggerate the effect of electron repulsion (counted twice when MO energies are summed), the possibility that the s-electron overlap densities inferred from MOs may not exist in the total electron density must be noted. If they are nonexistent in the latter, it is not wise to base arguments on their existence in the former. Secondly, it must not be overlooked that participation of an orbital in the molecular electron distribution is not dependent on its contribution to binding, and that a MO which lies low in the valence shell is not necessarily a bonding MO.

The presence of negative overlap contributions from the s orbital makes it a rather hazardous procedure to cite s:p ratios in connection with bonding by s and p orbitals. The wisest conclusion may be to desist from the attempt to compress all the data into a single parameter and instead to quote the utilizations of s and p orbitals (in the Mulliken or some other convention) with overlap density contributions appended, as above. This gives maximum information about the involvement of orbitals and obviates the difficulties which arise from the common but unsuspected antibonding s-orbital contributions.

Summary

In main-group hydrides, sp mixing is governed by the following circumstances.

(a) As predicted by Pauling and elaborated most recently by Hall, the advantage gained by isolating s electrons in a nonbonding role often offsets any potential value of sp mixing in bonding. Hybridization in lower symmetry molecules is frequently negligible and the ground-state conformations of many molecules, particularly second-row hydrides, are configured with central-atom s-orbital populations close to s^2 and with bonding provided exclusively by p orbitals. Molecules in maximum symmetry conformations (tetrahedral AH_4 hydrides, planar AH_3 hydrides, and linear AH_2 hydrides) retain substantial s-orbital bonding, but the degree of participation is highly variable.

(b) Reducing the bond angle increases s-orbital density in AH_3 and AH_2 group hydrides and lowers the energy until the process is halted by steric constraints. Consequently, hybridization is most in evidence in first-row hydrides; because the kernels are smaller, reduction of the bond angle is halted about 10° earlier than in second-row molecules.

(c) A relationship exists between bond angle and orbital occupations: s-orbital occupations show the expected decline over the 90–120° bond-angle range (for AH_3 hydrides) and 90–180° (for AH_2 hydrides), but the relationship is not general because it chiefly depends on mechanisms to maximize the nonbonding s-orbital population. p-Orbital occupations, a much greater fraction of which are made up of overlap density terms, show much

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 bewteen 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, sp^n 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 sp^n 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 sp^n 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.

Acknowledgment. I was rescued from several faux pas by advice from Professor D. P. Craig.

Registry No. CH_4, 74-82-8; SiH_4, 7803-62-5; NH_4^+, 14798-03-9; PH_4^+, 16749-13-6; BH_3, 13283-31-3; AlH_3, 7784-21-6; CH_3^+, 14531-53-4; SiH_3^+, 41753-67-7; NH_3, 7664-41-7; PH_3, 7803-51-2; H_3O^+, 13968-08-6; H_3S^+, 18155-21-0; PH_2^-, 13937-34-3; H_2O, 7732-18-5; H_2S, 7783-06-4; NH_2^-, 17655-31-1; HF, 7664-39-3; HCl, 7647-01-0; OH^-, 14280-30-9; SH^-, 15035-72-0; BH_4^-, 16971-29-2; AlH_4^-, 19469-81-9.

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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 AX_4, AX_3, AX_2, and AX series (X = CH_3, 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 AX_4 compounds and the planar and linear conformations, respectively, of AX_3 and AX_2 compounds), but in lower symmetry AX_n compounds and the partly substituted AH_3X, AH_2X, and AHX groups bonding is provided almost entirely by the p orbitals, with s orbital densities tending toward the s^2 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 hyrides.

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 AH_4 systems, planar AH_3 systems, and linear AH_2 systems), but in the normal ground-state geometries of AH_3 and AH_2 hydrides, the s orbital contributions to bonding (as measured by overlap densities) are meager. The s electron density often approaches the nonbonding s^2 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]

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 s^2 nonbonding configuration. (c) Substituted AX_2 and AX_3 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 sp^n ratio and bond angle,[3]

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[1] Undergraduate level chemistry textbooks often present the notion that sp^n 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.

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

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