The Shapes of Simple Polyatomic Molecules and Ions. II. The Series AH_2, AH_3, and AH_4

B. M. Gimarc

Contribution from the Department of Chemistry,
University of South Carolina, Columbia, South Carolina 29208.
Received May 9, 1970

Abstract: The rough features of the shapes of molecules with the general formulas AH_2, AH_3, and AH_4 are discussed in terms of simple molecular orbital pictures and energy-level correlation diagrams deduced from relative atomic orbital energies, orbital symmetry considerations, and the rule of maximization of atomic orbital overlap. Extended-Hückel correlation diagrams are presented to support the qualitative ones. Comparisons are made between the qualitatively predicted molecular shapes and those determined by experiment and by *ab initio* calculations. Relative barriers to inversion in ammonia and methane are discussed.

The shapes of small polyatomic molecules are explained in most textbooks by a qualitative model of electrostatic repulsions among lone pairs and bonding pairs of valence electrons. In contrast, most quantum-mechanical calculations of molecular electronic structure are based on molecular orbital theory which assumes that the electrons are free to move throughout the molecule. The qualitative, localized, electrostatic-repulsion model and the quantitative, delocalized molecular orbital (MO) model can be related by the notion of localized orbitals. Practical procedures have been developed for producing localized orbitals from calculated molecular orbitals, but a simple, qualitative MO model of molecular shapes and electronic structure would still be of great conceptual value to most chemists. Such a qualitative model does exist, although it has been much neglected over the years. It was originally formulated by Mulliken[1] and Walsh.[2] The object of the present series of papers is to put this qualitative MO model into a more systematic, practical form which chemists could use easily, without calculations, to predict or at least rationalize molecular shapes. Paper I in this series developed some rules for the qualitative model and used them to study the shapes of A_2H_2 and A_2B_2 molecules.[3] Another article used the same ideas to discuss the geometries of the H_3 and H_4 transition states in hydrogen-exchange reactions.[4]

The most important rules in the qualitative MO model are Walsh's rules and the rule of maximization of overlap. The atoms which form the molecules of a particular series contribute the same kinds of atomic orbitals (AO's) which can then be combined to form MO's. The MO's for each series must, therefore, be qualitatively similar and the molecules differ only in the number of valence electrons occupying the MO system. The summarizations of observations of how the number of valence electrons determines molecular shapes are usually called Walsh's rules. The rule of maximization of overlap says that changes in molecular shape which increase the in-phase overlap between two AO's in the same MO will lower the energy of that MO. Changes in shape which increase the out-of-phase AO overlaps will raise the energy of the MO. In terms of semiempirical MO theory, this rule follows from the assumption of the overlap proportionality of the off-diagonal matrix elements of the Hamiltonian: $H_{kl} = KS_{kl}$. By applying this rule to simple MO pictures, one can construct MO correlation diagrams which show how energy levels change with changing molecular shape. In simple MO theory the total energy of the molecule is just the sum of energies of the individual valence electrons; therefore, the molecular shape of minimum total energy is determined by a balance of maximizations of overlaps among the AO's in the occupied MO's. The term shape is used here to denote only the point group to which the molecule belongs or just the rough features of the angular arrangement of the hydrogens about the central A atom. Precise estimates of bond angles and variations in bond length are beyond the capability of the crude model described here.

The qualitatively deduced correlation diagrams are similar to those calculated by semiquantitative MO methods, such as the extended-Hückel method,[5] and to those obtained by quantitative, *ab initio* MO calculations. All three types of correlation diagrams–qualitative, semiquantitative, and *ab initio*—are similar to the pictures Walsh, using somewhat different arguments, presented in his classic series of papers. The extended-Hückel calculations mentioned in the present paper, in support of the qualitative model, were all done for NH_n systems using fixed N–H bond distances and the relation $H_{kl} = KS_{kl}$, where $K = -42$ eV. Since only qualitative results are of interest here, further quantitative details have been omitted.

Herzberg[6] has tabulated a great many experimental structures of small polyatomic molecules. Other structures are listed in ref 7. For several interesting species, which are as yet undetected or for which no experimental structural information is available, some very good *ab initio* calculations predict shapes for comparison.

The qualitative features of molecular shapes have recently received much attention,[8] but the present scheme

---

[1] R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 204 (1942).

[2] A. D. Walsh, *J. Chem. Soc.*, 2260 (1953); *Photoelec. Spectrom. Group Bull.*, **13**, 348 (1961).

[3] B. M. Gimarc, *J. Amer. Chem. Soc.*, **92**, 266 (1970).

[4] B. M. Gimarc, *J. Chem. Phys.*, **53**, 1623 (1970).

[5] R. Hoffmann, *ibid.*, **39**, 1397 (1963).

[6] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. III. "Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1965, p 583.

[7] L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11** (1958); **No. 18** (1965).

[8] L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968); R. M. Gavin, Jr.,

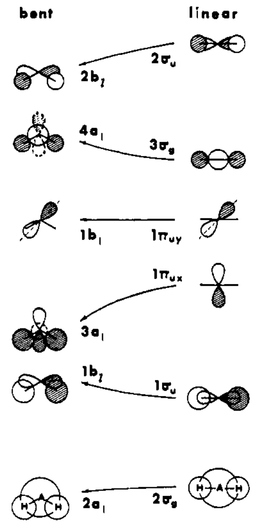

Figure 1. Molecular orbital pictures and qualitative correlation diagram for bent and linear AH_2 molecules. Open and cross-hatched areas represent orbitals or parts of orbitals of different phase. Changes in shape which increase in-phase overlaps between atomic orbitals lower the molecular orbital energy.

should appeal to a wide audience of chemists because it requires neither calculations nor a detailed knowledge of group theory.

The AH_2 Series

Walsh has already used qualitative MO theory to explain the shapes of molecules of the general formula AH_2. Many of his arguments and most of his conclusions are the same as those presented here. There are some differences, however, which justify the following reexamination of the AH_2 molecules. This series provides a textbook example for the application of the qualitative MO model. Table I lists some AH_2 molecules. With only three atoms, these molecules can be only either linear or bent. Figure 1 contains schematic MO diagrams for the typical AH_2 molecule in linear and bent geometries, and Figure 2 is a correlation diagram calculated by the extended-Hückel method. Comparable *ab initio* SCF-MO diagrams can be found elsewhere.[9-12] It is easier to start the discussion with linear geometry. From s, p_x, p_y, and p_z AO's on the central A atom and from one 1s AO on each hydrogen, one can form six MO's. The four MO's of lowest energy are essentially the four AO's of the central A atom perturbed by mixing with hydrogen 1s orbitals. Take the z axis as the molecular axis. The hydrogens lie on the nodal planes of the p_x and p_y AO's and therefore the hydrogen 1s AO's cannot mix with p_x or p_y to form MO's. The hydrogen 1s AO's do combine with p_z to form a σ_u MO of lower energy than either p_z or 1s individually. The 1s AO's also combine with the A atom s orbital to form a σ_g MO of lower energy than s or 1s. The p_x and p_y orbitals on A constitute, unchanged, the degenerate π_u pair of linear AH_2 MO's.

Table I. Shapes of AH_2 Molecules

AH_2	No. of valence electrons	Shape	Ref
LiH_2^+	2	Bent	13, 14
BeH_2^+	3	Linear	13
BeH_2, BH_2^+	4	Linear	9, 10
BH_2, AlH_2	5	Bent	6
CH_2, BH_2^-, NH_2^+, SiH_2	6	Bent	6, 9, 11, 12
NH_2, PH_2	7	Bent	6, 7
NH_2^-, H_2O, H_2S, H_2Se, H_2Te	8	Bent	6, 7

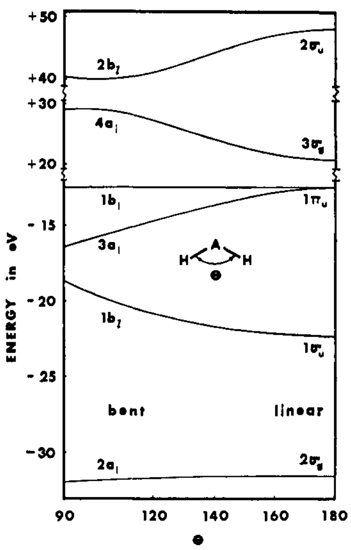

Figure 2. Extended-Hückel correlation diagram for AH_2 molecules.

The lowest energy valence MO in linear geometry, $2\sigma_g$, is mainly the s AO on A plus contributions from in-phase overlapping hydrogen 1s orbitals. By symmetry, p_x, p_y, and p_z are eliminated from σ_g orbitals. The orbital $2a_1$ which results from bending $2\sigma_g$ is slightly lower in energy than $2\sigma_g$ itself, because the hydrogen 1s orbitals move into better overlap with each other and with the p_x AO (x axis vertical) which can be a component of the bent $2a_1$ orbital. Because the p_x contribution to $2a_1$ is small and not essential to the energy lowering of $2a_1$, p_x has been omitted from the $2a_1$ picture in Figure 1. (If p_x were included in that figure, the lower lobe would be in phase with the two hydrogen 1s orbitals). The energy lowering of $2a_1$ on bending is small. As a rule, the nodeless MO's of lowest energy change very little on varying bond angles. When higher orbitals are occupied, the $2a_1$–$2\sigma_g$ orbital has no influence on molecular shape, but the qualitative model predicts the two-electron ion LiH_2^+ to be bent, in agreement with *ab initio* calculations.[13,14] In Walsh's picture,[2] the energy of the $2a_1$–$2\sigma_g$ orbital increases on bending and one would expect LiH_2^+ to be linear.

Next higher in energy is the $1\sigma_u$ MO. This is the p_z AO on A combined with in-phase overlapping 1s orbitals from the hydrogens. The $1\sigma_u$ orbital has a

---

J. Chem. Educ., **46**, 413 (1969); R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).

(9) S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, **45**, 734 (1966).

(10) J. J. Kaufman, L. M. Sachs, and M. Geller, *ibid.*, **49**, 4369 (1968).

(11) J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, **91**, 807 (1969).

(12) L. M. Sachs, M. Geller, and J. J. Kaufman, *J. Chem. Phys.*, **52**, 974 (1970).

(13) R. D. Poshusta, J. A. Haugen, and D. F. Zetik, *ibid.*, **51**, 3343 (1969).

(14) N. K. Ray, *ibid.*, **52**, 463 (1970).

nodal plane perpendicular to the molecular axis and passing through the A atom. The nodal surface eliminates A atom s, p_x, and p_y atomic orbitals from $1\sigma_u$ and from the related $1b_2$ orbital of bent geometry. The $1b_2$ orbital has higher energy than $1\sigma_u$ because bending pulls the hydrogen 1s AO's out of overlap with the lobes of p_z. The $1\sigma_u$–$1b_2$ level controls the shape of three- and four-valence electron AH_2 molecules such as BeH_2^+, BeH_2, and BH_2^+ and holds them linear. Although there is no experimental structural information about these species, very reliable *ab initio* calculations indicate that they should be linear.[9,10,13]

Next higher in energy are the doubly degenerate $1\pi_u$ orbitals. These can be denoted $1\pi_{ux}$ or $1\pi_{uy}$ to indicate that they consist of individual p_x or p_y AO's on A. Each of these molecular orbitals has a nodal plane which contains all three nuclei and eliminates hydrogen 1s and A atom s and p_z contributions to the MO's for linear geometry. On bending, $1\pi_{ux}$ becomes $3a_1$, the hydrogens move off the nodal surface of p_x, and in-phase overlapping of the hydrogen 1s orbitals with the bottom lobe of p_x lowers the energy of $3a_1$ relative to $1\pi_{ux}$. In the bent shape, the A atom s orbital can add to $3a_1$. To make $3a_1$ different from $2a_1$, however, the s orbital must add to $3a_1$ with phase opposite to that of the hydrogen 1s orbitals. The s contribution to $3a_1$ is shown by the dashed circle in Figure 1. When the $1\pi_{uy}$ orbital is bent to form $1b_1$, the hydrogens remain on the nodal surface of p_y, preventing hydrogen 1s contributions to $1b_1$. Since the same nodal surface excludes s, p_x, and p_z, the $1b_1$ MO must remain pure p_y and therefore has the same energy as $1\pi_{uy}$. Clearly, the $1\pi_{uy}$–$1b_1$ level has no direct influence on AH_2 shapes.

For molecules with five through eight valence electrons, molecular shapes are determined by $1\pi_{ux}$–$3a_1$ which falls in energy as the HAH angle decreases. This means that the $1\pi_{ux}$–$3a_1$ level must fall faster than the $1\sigma_u$–$1b_2$ level rises below it. That this is true can be seen from the following argument based on the rule of maximization of overlap. The overlap between an A atom p orbital and a hydrogen 1s orbital is proportional to the cosine of the angle ϕ between the axis of the p orbital and the A–H bond axis. Maximum p,1s overlap (call this S_{max}) occurs if the hydrogen is on the p orbital axis: $S = S_{max} \cos \phi$. Figure 3 plots the function S/S_{max} and shows the arrangement of orbitals. With the hydrogen tilted 30° away from the p-orbital axis, the p,1s overlap S is 87% of the maximum S_{max}. At 60° from the axis, the p,1s overlap is still 50% of S_{max}, and at 90° the hydrogen is on the nodal plane of the p orbital and the overlap is zero. It is easy to see that moving a hydrogen a few degrees away from the p-orbital nodal plane, as happens in $1\pi_{ux}$–$3a_1$, makes a big change in overlap, and therefore the energy, while tilting a hydrogen a few degrees from the p-orbital axis, as is the case for $1\sigma_u$–$1b_2$, produces a much smaller change in overlap and energy. For example, imagine decreasing the angle HAH from 180° (linear) to 120° (bent). Each of two $1s,p_z$ overlaps in $1\sigma_u$–$1b_2$ decreases from 100 to 87% of S_{max}, while each of two $1s,p_x$ overlaps in $1\pi_{ux}$–$3a_1$ increases from 0 to 50% of S_{max}. Therefore, even a single electron in the $1\pi_{ux}$–$3a_1$ orbital can control the shape of molecules such as BH_2 and AlH_2.

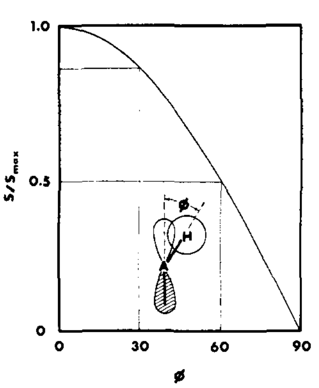

Figure 3. Overlap dependence on the angle ϕ between the A–H bond and the p-orbital axis.

Of the 17 molecules listed in Table I, the most chemically interesting is CH_2. Harrison and Allen[11] have recently published a comprehensive study of this species. Their work includes *ab initio* valence-bond and MO calculations plus a reinterpretation of the spectroscopic observations. They conclude that the triplet ground state of CH_2, previously thought to be linear, is bent with a rather large HCH angle, while the excited singlet is bent with a smaller HCH angle. These results seem to vindicate Walsh's simple MO model which predicts bent CH_2. In the triplet state $3a_1$ and $1b_1$ would each hold one electron; in the lowest singlet state $3a_1$ would be doubly occupied. Since $3a_1$ is the MO that bends the molecule, the wider HCH angle in the triplet state is easily rationalized. *A priori* application of the Pauli principle and Hund's rule to the simple MO energy level diagrams leads one to conclude that the $(3a_1)^2$ singlet state should have lower energy than the $(3a_1)^1(1b_1)^1$ triplet. This conclusion is wrong for CH_2, but the other known six-electron AH_2 molecules do have singlet ground states.

For the molecules discussed here, the high-energy $3\sigma_g$–$4a_1$ and $2\sigma_u$–$2b_2$ MO's in Figures 1 and 2 contain no electrons and hence have no influence on molecular shapes. Nonetheless, a discussion of how their energies change with bond angle is of interest because of similarities to more complicated series, to be discussed elsewhere, for which the arguments are a bit harder to see. They also demonstrate that all the details of the calculated correlation diagram can be understood qualitatively. The $4a_1$ MO, related to $3\sigma_g$, can contain p_x from the A atom, but p_x must combine in such a way that the lobe it presents for overlap with the hydrogen 1s orbitals provides out-of-phase overlap. This must be so to keep $4a_1$ different from $3a_1$. Since the hydrogens are immediately adjacent to the added p_x orbital, the effect of bending is to raise the energy of $4a_1$ relative to $3\sigma_g$ because of the increased out-of-phase overlaps. For HAH angles of 90° or less, however, the in-phase overlap between the two hydrogen 1s orbitals themselves comes into play and this tends to lower the energy of $4a_1$ for small angles.

For the $2\sigma_u$–$2b_2$ MO there are also two effects. At first, bending $2\sigma_u$ to $2b_2$ moves the hydrogens away from strong out-of-phase overlap with the p_z AO on A, and this lowers the energy of $2b_2$ relative to $2\sigma_u$. For small HAH angles, however, the hydrogens oppose each other out of phase across the nodal plane and this

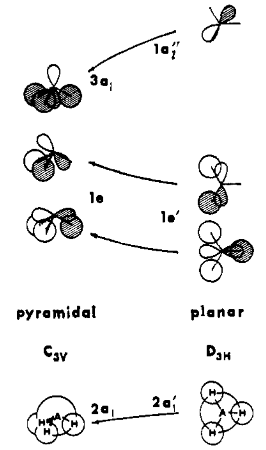

Figure 4. Molecular orbital pictures and qualitative correlation diagram for AH_3 molecules in pyramidal C_{3v} and planar-triangular D_{3h} shapes. The D_{3h} orbitals are seen along the threefold axis, while the C_{3v} orbitals are viewed perpendicular to the axis.

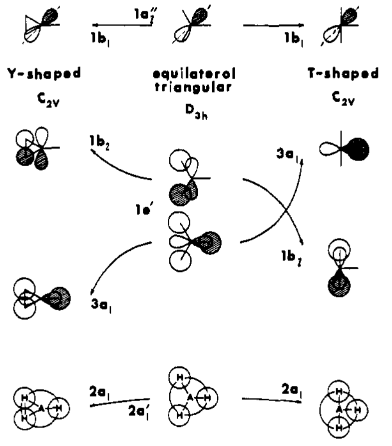

Figure 5. Molecular orbital pictures and qualitative correlation diagram for AH_3 molecules in planar Y-shaped, T-shaped, and centered-equilateral-triangular geometrices.

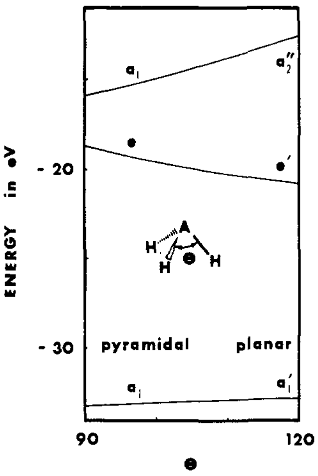

Figure 6. Extended-Hückel correlation diagram for AH_3 molecules in planar D_{3h} and pyramidal C_{3v} shapes.

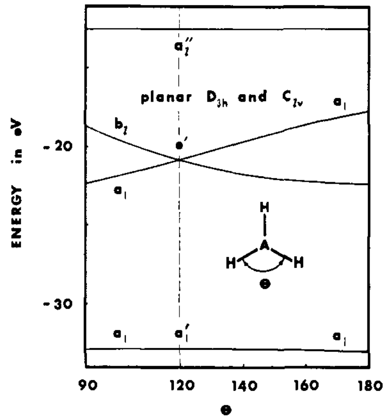

Figure 7. Extended-Hückel correlation diagram for AH_3 molecules in planar Y-shaped ($\theta < 120°$), T-shaped ($\theta > 120°$), and equilateral-triangular geometries.

tends to raise the energy of $2b_2$ for small angles. Walsh concluded that the energy of $2b_2$–$2\sigma_u$ should rise on bending, even for wide HAH angles.

Summarizing the conclusions for AH_2 molecules: those molecules containing one or two valence electrons should be bent, those with three or four electrons should be linear, and those with five through eight electrons should be bent. Notice that no arbitrary assumptions about orbital hybridization are necessary. The conclusions follow easily from very simple symmetry considerations and the rule of maximization of overlap.

The AH_3 Series

Table II lists some molecules with the general formula AH_3. Figure 4 contains qualitative pictures of MO's for AH_3 in planar, equilateral-triangular D_{3h}, and pyramidal (nonplanar) C_{3v} shapes. Figure 5 shows similar orbital pictures for the planar structures: Y-shaped C_{2v} ($\theta < 120°$), D_{3h} ($\theta = 120°$), and T-shaped ($\theta > 120°$). Figures 6 and 7 are the corresponding energy-level diagrams as calculated by the extended-Hückel method. Since AH_3 molecules have more than three atoms, more than two different shapes are possible and therefore intersecting correlation diagrams are necessary. Figures 4 and 6 intersect their counterparts, Figures 5 and 7, through the planar D_{3h} structure. Correlation diagrams obtained by *ab initio* SCF calculations for D_{3h} and C_{3v} structures only are available.[9,15]

Table II. Shapes of AH_3 Molecules

AH_3	No. of valence electrons	Shape	Ref
LiH_3^+	3	Y shaped, C_{2v}	13
BeH_3^-, BH_3, CH_3^+	6	Planar, D_{3h}	9
CH_3	7	Planar, D_{3h}	6, 17
NH_3, PH_3, H_3O^+	8	Pyramidal, C_{3v}	6, 7

It seems easier first to discuss the MO's for the planar D_{3h} arrangement and then to show how the various structural alterations change the energies of these orbitals. The lowest energy valence orbital $2a_1'$ for D_{3h} geometry is composed of the s orbital on the central A atom with in-phase overlapping 1s orbitals on the three hydrogens. Changes from D_{3h} to pyramidal C_{3v} or planar C_{2v} shapes increase the 1s,1s overlaps and lower the energy of the related MO's. These energy

---

(15) M. E. Schwartz and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 1466 (1970).

changes are small, however, and never control molecular shapes unless the higher orbitals are vacant.

The three degenerate p AO's on A mix in phase with the three 1s hydrogen orbitals to form the three MO's which affect the geometry of AH_3 molecules with three through eight electrons. For shapes with a threefold rotational axis, symmetry requires that two of these three MO's be degenerate. In planar D_{3h} geometry these are the e′ orbitals made from the two p AO's which lie in the plane of the molecule. As drawn in Figure 4, one of the two e′ MO's contains a p orbital in 100% overlap with one hydrogen 1s and 50% overlap with each of two others. The other e′ MO has its p orbital in nearly 90% overlap with two hydrogen 1s orbitals, while the third hydrogen lies on the nodal plane of the p orbital. With no symmetry arguments at all one can see that the two MO's designated e′ should have nearly the same energy. This is also a good place to point out that the simple overlap considerations are only qualitative for comparisons between MO's with differing AO compositions. The $1a_2''$ MO of D_{3h} geometry is just that p AO the axis of which is perpendicular to the molecular plane. Because the hydrogens lie on the nodal surface of this p orbital, their 1s orbitals cannot mix into $1a_2''$. It is clear that the pure p orbital $1a_2''$ is much higher in energy than the 1e′ pair.

Now imagine symmetrically pushing the hydrogens out of the original molecular plane to give AH_3 the pyramidal C_{3v} geometry. The degenerate 1e′ orbitals of planar D_{3h} geometry become the degenerate 1e pair in the nonplanar structure. The 1e orbitals must rise in energy relative to 1e′ because the hydrogen 1s orbitals are pulled out of overlap with the lobes of the p orbitals. Notice that the p orbitals remain locked to the Cartesian axes and only the hydrogens move. As the hydrogens are pushed below the nodal plane of the p orbital in $1a_2''$, the 1s orbitals can overlap with the bottom lobe of the p orbital to form $3a_1$. The energy of $3a_1$ drops rather sharply from that of $1a_2''$ because of the relatively large increase in overlap; each of three hydrogen 1s orbitals goes from zero to about 30% of maximum overlap with the p orbital. In contrast, the increases in 1e compared to 1e′ are small. For molecules with three through six valence electrons, the occupied 1e–1e′ orbitals hold AH_3 planar. For molecules with eight electrons, such as NH_3 and PH_3, the doubly occupied $3a_1$–$1a_2''$ orbital produces the pyramidal shape. For the seven-electron case the qualitative MO model gives an equivocal result. Experiment[6] and SCF–MO calculations[16,17] agree that the seven-electron radical CH_3 is planar. Even the extended-Hückel method, the semiquantitative scheme on which the qualitative MO model is based, predicts the planar shape for CH_3. Apparently, two electrons in $3a_1$–$1a_2''$ can override the planar preference of four electrons in 1e–1e′, but a single electron in $3a_1$–$1a_2''$ cannot.

The $C_{3v} \rightarrow D_{3h}$ motion is the ammonia inversion process, for which the D_{3h} MO's present a relatively low-energy barrier.

Now consider distortions of the planar D_{3h} orbitals to planar C_{2v} geometry, both T shaped and Y shaped. These distortions remove the threefold axis and break up the degeneracy of the 1e′ orbitals. For the Y shape, two hydrogen 1s AO's in $3a_1$ move into better overlap with the p orbital and with each other, lowering the energy of $3a_1$ relative to 1e′. In $1b_2$ the 1s orbitals move out of overlap with the lobes of the p orbital and oppose each other out of phase across a nodal surface; therefore the energy of $1b_2$ is higher than that of 1e′. Just the reverse occurs for the T shape: the energy of $3a_1$ goes higher and that of $1b_2$ goes lower than the 1e′ energy. Since the hydrogens are on the nodal surface in $1a_2''$ and in the related $1b_1$ orbital of both T and Y shapes, the $1b_1$–$1a_2''$–$1b_1$ MO remains pure p and of constant energy and it does not affect the shape of AH_3 molecules.

It is clear from Figure 5 that three- and four-electron AH_3 molecules should be either T or Y shaped, not the centered-equilateral-triangular D_{3h} arrangement. Overlap considerations show that $3a_1$ of the Y shape should have lower energy than $1b_2$ of the T shape. The $3a_1$ Y-shape orbital has one hydrogen 1s in 100% overlap with one p lobe and two hydrogens each near 90% overlap with the other lobe. The $1b_2$ T-shape orbital has only two 1s orbitals, both in 100% overlap with opposite lobes of the p orbital. The Y shape has much more overlap and therefore lower energy.

What about the five- and six-electron cases? Again, overlap considerations suggest that the upper $1b_2$ and $3a_1$ orbitals should be much higher in energy above 1e′ than the corresponding lower $3a_1$ and $1b_2$ orbitals are below 1e′, and therefore five- and six-electron AH_3 molecules should be planar D_{3h}. Once more the results of the extended-Hückel calculations agree. The conclusions about the shapes of seven- and eight-electron species are not affected by considering planar C_{2v} possibilities.

Summarizing the conclusions for this series: those AH_3 molecules with one or two valence electrons should be pyramidal, those with three or four electrons should be Y shaped, those with five, six, or seven electrons should be planar D_{3h}, and those with eight electrons should be pyramidal.

Very little information is available against which to test these rules. Several eight-valence-electron molecules and ions are known and they are, without exception, pyramidal.[6,7] The seven-electron CH_3 radical is planar.[6,16,17] Borane, BH_3, with six electrons has been prepared.[18] Although experimental structural information is not yet available, *ab initio* SCF,[9] semiempirical SCF,[16] and extended-Hückel MO calculations all predict planar D_{3h} geometry. A valence-bond calculation for LiH_3^+ indicates that this hypothetical three-electron radical ion should be Y shaped.[13] A similar calculation shows that the ion H_4^+, though not bound, would have lowest energy in the Y shape.[13] The rules summarized above are at least consistent with all the information at hand.

The AH_4 Series

Some of the more plausible shapes for AH_4 molecules, all involving a central A atom, are considered in the qualitative MO correlation diagrams in Figures 8 and 9.

---

(16) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

(17) K. Morokuma, L. Pedersen, and M. Karplus, *ibid.*, **48**, 4801 (1968).

(18) P. S. Ganguli and H. A. McGee, Jr., *ibid.*, **50**, 4658 (1969); G. W. Mappes and T. P. Fehlner, *J. Amer. Chem. Soc.*, **92**, 1562 (1970).

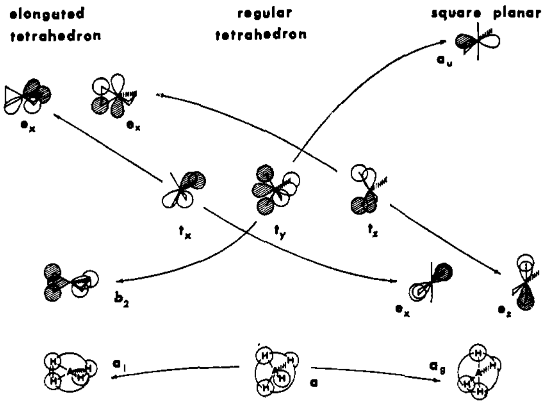

Figure 8. Molecular orbital pictures and qualitative correlation diagram for AH_4 molecules in regular-tetrahedral, elongated-tetrahedral, and square-planar shapes.

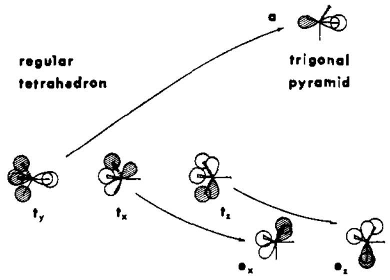

Figure 9. Molecular orbital pictures and correlation diagram for higher energy valence orbitals of AH_4 molecules in regular-tetrahedral and trigonal-pyramidal shapes.

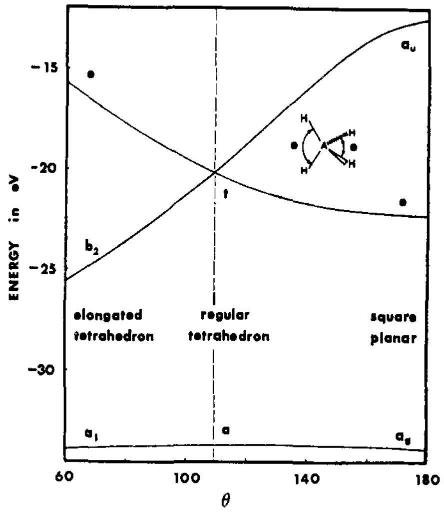

Figure 10. Extended-Hückel correlation diagram for AH_4 molecules in regular-tetrahedral, elongated-tetrahedral, and square-planar shapes.

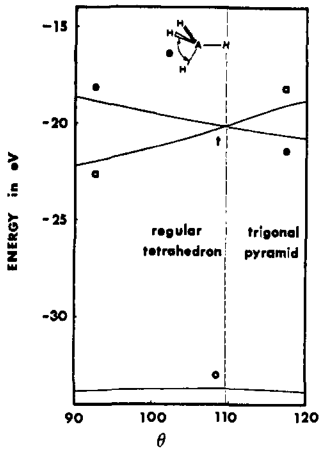

Figure 11. Extended-Hückel correlation diagram for AH_4 molecules in tetrahedral and trigonal-pyramidal shapes.

Figures 10 and 11 are the corresponding diagrams obtained from extended-Hückel calculations.

The midsection of Figure 8 shows the four valence MO's of lowest energy for AH_4 in regular-tetrahedral geometry. Symmetry requires that there be one MO at low energy and a triply degenerate set at higher energy. All four of these orbitals are doubly occupied in the eight-valence-electron, regular-tetrahedral species BH_4^-, CH_4, and NH_4^+.[7] The lowest energy MO a is primarily the s AO on A with in-phase overlapping hydrogen 1s orbitals. Each of the triply degenerate orbitals t_x, t_y, t_z is composed of a valence p AO on A and hydrogen 1s orbitals overlapping in phase with the nearest p lobes.

In square-planar geometry, symmetry requires a degenerate MO pair. Figure 8 shows the conversion of orbitals of regular-tetrahedral geometry into those of square-planar geometry by squashing the tetrahedron into the *xz* plane (vertical, perpendicular to plane of page). Again, the energy of the nodeless, lowest energy MO changes only slightly and has no affect on molecular shapes. Energy changes in the higher levels control the geometry of AH_4 molecules. For the regular-tetrahedral-to-square-planar squashing, the t_x and t_z MO's drop in energy to become e_x and e_z, the hydrogen 1s orbitals moving into maximum possible overlap with the lobes of the A atom p_x and p_z orbitals. In the same process, the t_y orbital of regular-tetrahedral geometry becomes the high-energy a_u MO in square-planar geometry; an isolated p_y AO on the central atom. In a_u the hydrogens lie on the nodal surface of p_y and therefore the 1s orbitals cannot contribute to a_u. The decreases in overlap for the $t_y \rightarrow a_u$ process are much larger in magnitude than the corresponding overlap increases for $t_x,t_z \rightarrow e_x,e_z$. In $t_y \rightarrow a_u$ each of four 1s,p overlaps decreases from about 60% of maximum to zero, while for $t_x,t_z \rightarrow e_xe_z$ each 1s,p overlap increases from 80 to 100% of maximum.

With eight valence electrons, CH_4, NH_4^+, and BH_4^- are tetrahedral and have completely filled t_x,t_y,t_z orbitals. Squashing these molecules to the square-planar shape would produce a net increase in total energy because of the very high energy of a_u relative to t_y. A six-electron molecule, such as the hypothetical BeH_4, would be square planar because the a_u MO would be empty. This qualitative MO model is too weak to give a reliable prediction for the seven-electron ion CH_4^+, but surely removal of one electron from a_u would give a push toward square-planar geometry. The *ab initio* SCF-MO results of Handler and Joy[19] and Arents and Allen[20] predict that CH_4^+ should be a flattened tetrahedron, partway between the regular tetrahedron and the plane. Even the extended-Hückel calculations agree.

---

(19) G. S. Handler and H. W. Joy, *Int. J. Quantum Chem., Symp.*, 3, 529 (1970).

(20) J. Arents and L. C. Allen, *J. Chem. Phys.*, 53, 73 (1970).

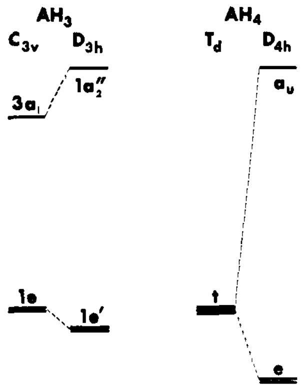

Figure 12. Comparison of higher energy valence levels in pyramidal (C_{3v}) and planar-equilateral-triangular (D_{3h}) shapes for AH_3 and in tetrahedral (T_d) and square-planar (C_{4v}) shapes for AH_4. The much smaller energy gap between $3a_1$ and $1a_2''$ compared to that between t and a_u lets eight-electron AH_3 molecules invert much more easily than eight-electron AH_4 molecules.

The qualitative MO pictures also explain why ammonia inverts but methane does not. Figure 12 shows relative energy levels in pyramidal (C_{3v}) and planar-triangular (D_{3h}) shapes for AH_3 molecules and in tetrahedral (T_d) and square-planar (D_{4h}) shapes for AH_4 molecules. (Compare Figures 4 and 8 for the rationale for Figure 12.) In eight-electron AH_4 molecules the a_u level is quite high in energy relative to t. In eight-electron AH_3 molecules an electron pair in $3a_1$ is much closer to $1a_2''$ and therefore inversion is much easier.

On displacing the AH_4 regular tetrahedron to the trigonal pyramid (Figure 9), the triply degenerate t orbitals break up into the degenerate e_x,e_z pair at lower energy and the a orbital at higher energy. Because it contains one hydrogen 1s orbital in maximum overlap with the central atom p_y, the a orbital in trigonal geometry has lower energy than the corresponding a (pure p_y) in square-planar geometry. On the other hand, the trigonal e pair is higher in energy than the corresponding square-planar e pair because the 1s AO's are not in maximum overlap with the central atom p orbital. Still, the overlap increase for $t_x,t_z \rightarrow e_x,e_z$ (trigonal) is smaller than the overlap decrease for $t_y \rightarrow$ a (trigonal), and the eight-electron AH_4 molecule would have lower total energy in regular-tetrahedral geometry. With seven electrons, the energy levels for the trigonal pyramid could allow CH_4^+ to shift toward the trigonal shape. The qualitative MO model cannot give direct energy comparisons between the flattened tetrahedron and the trigonal pyramid for the seven-electron case, but the *ab initio* SCF calculations of Arents and Allen[20] and semiempirical extended-Hückel results predict that CH_4^+ has slightly lower energy in the flattened tetrahedral shape. For a six-electron AH_4 molecule, a trigonal isomer is possible but it would definitely have higher energy than the square isomer.

Stretching the regular tetrahedron to the elongated-tetrahedral shape (Figure 8) removes the degeneracy of the t orbitals. In this case the nondegenerate level b_2 goes to lower energy and the doubly degenerate e levels move to higher energy relative to the regular tetrahedral t levels. The diagrams in Figure 8 suggest that a four-electron species such as the LiH_4^+ ion would have the elongated-tetrahedral shape. *Ab initio* calculations indicate that LiH_4^+ and H_5^+ are bound and have elongated tetrahedral geometry.[13] LiH_4^+ is unknown, but H_5^+ has been observed in mass spectra. The completely bonding lower occupied orbital a_1 and the H–H bonding parts of the higher occupied b_2 must be sufficient to stabilize H_5^+ without a strong contribution from a p orbital on the central atom.

Summarizing the conclusions about AH_4 geometries: those species with four electrons should be elongated tetrahedral in shape, those with six electrons should be square planar, and those with eight electrons should be regular tetrahedral. AH_4 species with five electrons should have elongated-tetrahedral and square-planar isomers; those with seven electrons should have trigonal-pyramidal and flattened-tetrahedral isomers. The isomers in each set should be of nearly equal energy and will be prevented from converting one into the other by the principle of conservation of orbital symmetry.[21]

Conclusions

From simple, qualitatively deduced molecular orbital diagrams, the rule of maximization of overlap, and simple symmetry arguments involving molecular orbital degeneracies and the nodal properties of atomic and molecular orbitals, one can predict the shapes of small polyatomic molecules and ions. In some cases involving odd numbers of electrons the model cannot give firm conclusions, but even in these situations it provides a rationalization of the experimental structure or of the results of *ab initio* calculations. The model matches the energy-level ordering and structural conclusions of the extended-Hückel method on which it is based in a qualitative way.

Acknowledgments. The author expresses his thanks to his colleagues E. E. Mercer and S. I. Goldberg for several helpful discussions and to J. Arents and L. C. Allen for communicating the results of their CH_4^+ calculations prior to publication. The Computer Center of the University of South Carolina generously provided the computer time required.

(21) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).