$0.023$ cm$^{-1}$ to the previously described $D_n{}^{ss}$ curves. When appended by this spin–orbit contritution, the Harrison–Liedtke[37] curve predicts $D = 0.745$ cm$^{-1}$ at the computed equilibrium angle of 133°, while that of Langhoff and Davidson[14] predicts $D = 0.807$ cm$^{-1}$ at this same angle. While both estimates are in reasonable agreement with the experimental number,[23] $0.76 \pm 0.02$ cm$^{-1}$, it is somewhat disconcerting that the more complete theoretical study of Langhoff and Davidson is outside of the experimental range. Indeed, if we ask what HCH angle the theoretical curves would predict, given the experimental $D$, we see that the Harrison–Liedtke curve is consistent with a range of angles from 145 to 135° while the Langhoff–Davidson calculation suggests an angle less than 125°. However, given the complexity of both the experimental interpretation and theoretical calculations, mutual agreement, even at the $\pm 5\%$ level, must be regarded as a satisfying accomplishment.

### Concluding Remarks

While theory and experiment concur on many of the characteristics of $CH_2$, a few loose ends remain. Most notable is the energy of the $^1B_1 \leftarrow {}^1A_1$ 0–0 transition. Experiment places this at 20 kcal/mol while a larger separation, perhaps 33 kcal/mol, is suggested theoretically. Also, while an analysis of the spectrum arising from the $^3A_2 \leftarrow {}^3B_1$ transition fixes the angle of the $^3B_1$ state at 136°, it also demands that the $^3A_2$ state be strongly bent with a bond angle of 125°. The nature of this $^3A_2$ state has not been characterized theoretically.[45]

That $CH_2$ was predicted[3] to be a bent triplet by *ab initio* calculations at least 10 years before it was experimentally substantiated[17,19,20] speaks to both the difficulty of doing the experiments and the reliability of current computational techniques and suggests that similar calculations can play a significant, if not major, role in elucidating the electronic structure of other reactive intermediates.[46]

(45) This problem is being studied in our laboratory by Mr. David Wernette.

(46) J. F. Harrison and C. W. Eakers, *J. Amer. Chem. Soc.*, **95**, 3467 (1973).

# Applications of Qualitative Molecular Orbital Theory

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Much information of chemical interest can be obtained from molecular orbital (MO) theory without resort to any calculations at all. Considerations of symmetry properties, nodal surfaces, and atomic orbital (AO) overlaps in MO's have been used quite fruitfully in recent years by Woodward and Hoffmann[1] to elucidate mechanisms of chemical reactions. In this Account I will use similar arguments to predict, understand, or at least rationalize the shapes, *i.e.*, the gross geometrical features, of small polyatomic molecules in both ground and excited states. In some cases these considerations lead naturally to discussions of other properties such as hydrogen bonding, barriers to inversion and rotation, and hydrogen bridging.

In most introductory chemistry textbooks, molecular shapes are explained by an electrostatic model of repulsions among lone pairs and bonding pairs of valence electrons. This valence-shell electron-pair repulsion (VSEPR) model has been summarized at various stages in its development by Sidgwick and

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Powell,[2] Gillespie and Nyholm,[3] and Bartell.[4] It has recently been extended by Wolfe[5] to rationalize rotational conformations about single bonds. Schnuelle and Parr[6] have discussed a related qualitative model of molecular shapes based on ideas from crystal field theory.

Molecular orbital theory offers an alternative qualitative model for explaining or rationalizing molecular shapes. It began with the work of Mulliken[7] in the 1930's and '40's. It blossomed in the 1950's when Walsh[8] published a series of papers containing qualitative or empirically deduced MO correlation diagrams showing how orbital energies change with changes in molecular shape. Recent years have seen an increase in interest in MO-based models for molecular shapes. Gavin[9] has discussed some of the qualitative aspects of extended Hückel MO calcula-

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

(2) N. V. Sidgwick and H. M. Powell, *Proc. Roy. Soc., Ser. A*, **176**, 153 (1940).

(3) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 339 (1957); R. J. Gillespie, *J. Chem. Educ.*, **47**, 18 (1970).

(4) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968).

(5) S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972).

(6) G. W. Schnuelle and R. G. Parr, *J. Amer. Chem. Soc.*, **94**, 8974 (1972).

(7) R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 204 (1942); *Science*, **157**, 13 (1967).

(8) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953), and the papers immediately following.

(9) R. M. Gavin, *J. Chem. Educ.*, **46**, 413 (1969).

tions as they apply to molecular shapes. Pearson[10] has developed a symmetry rule based on the second-order Jahn–Teller effect and the symmetry of MO's. Other authors have sought to understand the success of Walsh's rules from rigorous considerations of MO theory[11] and the Hellman–Feynman theorem.[12] Nakatsuji[13] has used the Hellman–Feynman theorem to develop an electrostatic force theory to explain chemical bonding, molecular shapes, and other properties. The relationship between *ab initio* SCF MO calculations and Walsh's rules has recently been reviewed by Buenker and Peyerimhoff.[14]

In this Account I will present the rules of qualitative MO theory and review some of the highlights of their application. I must acknowledge a debt to the published work of Walsh.[8] The qualitative MO model is a practical method which can be easily used to understand molecular properties. Because of its simplicity and generality, this approach will soon occupy an important place in chemical education. It will also provide a means for the kind of guided speculation about molecular properties that could lead to new experiments or detailed quantum mechanical calculations.

The basic assumptions, features, and rules of qualitative MO theory are these.

(i) Electrons in molecules are completely delocalized and move in molecular orbitals which extend over the entire molecular framework.

(ii) For properties that can be explained by qualitative MO theory, only the valence electrons need be considered.

(iii) Satisfactory molecular orbitals can be formed from linear combinations of atomic orbitals. This is the well-known LCAO–MO approximation.

(iv) The atoms which form the molecules of a particular series or class contribute the same kinds of valence AO's from which molecular orbitals can be constructed. Therefore the MO's for each series or type of molecular framework must be qualitatively similar and individual molecules differ primarily in the number of valence electrons occupying the common MO system. At least for small molecules this rule holds quite well, and the results of experiment[15,16] and *ab initio* SCF MO calculations[17] support it.

(v) The total energy of the molecule is the sum of the orbital energies of the individual valence electrons, or, more accurately, changes in the total energy parallel those of the orbital energy sum. Allen and coworkers[18] have shown that this assumption results from a fortuitous cancellation of energy terms.

(vi) No explicit considerations of electron–electron

(10) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 1252, 4947 (1969); *J. Chem. Phys.*, **52**, 2167 (1970); *Chem. Phys. Lett.*, **10**, 31 (1971).

(11) L. C. Allen, *Theor. Chim. Acta*, **24**, 117 (1973).

(12) C. A. Coulson and B. M. Deb, *Int. J. Quantum Chem.*, **5**, 411 (1971).

(13) H. Nakatsuji, *J. Amer. Chem. Soc.*, **95**, 345, 354, 2084 (1973).

(14) R. J. Buenker and S. D. Peyerimhoff, *Chem. Rev.*, **74**, 127 (1974).

(15) G. Herzberg, "Molecular Spectra and Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N.J., p 312.

(16) D. W. Turner, A. D. Baker, C. Baker, and C. R. Brundle: "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970.

(17) L. C. Snyder and H. Basch, "Molecular Wave Functions and Properties," Wiley-Interscience, New York, N.Y., 1972.

(18) S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, **45**, 734 (1966); L. C. Allen and J. D. Russell, *ibid.*, **46**, 1029 (1967).
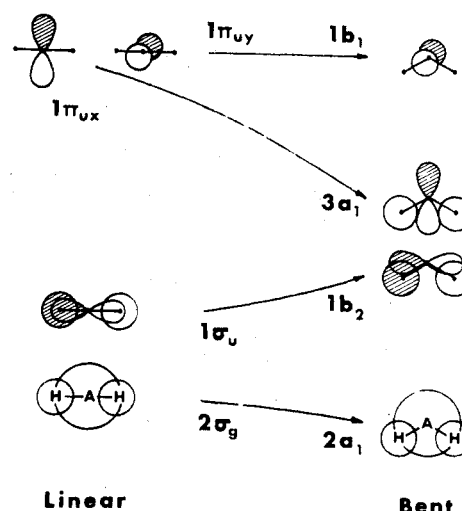
**Figure 1.** Qualitative MO correlation diagram for linear and bent $AH_2$ molecules. Changes in geometry which increase in-phase overlaps between AO's lower the MO energy.

or nuclear–nuclear repulsions are included in this simple model.

(vii) Molecular orbitals must be either symmetric or antisymmetric with respect to the symmetry operations of the molecule. These symmetry restrictions severely limit the number and kinds of AO's that combine in a particular MO. This makes the job of forming the MO's even easier, since most small molecules have high symmetry. To use qualitative MO theory, the only part of group theory necessary is a knowledge of symmetry classifications.

(viii) From the properties of AO's available on component atoms it is possible, at least for small molecules, to draw pictures of what the MO's must be like and to establish the approximate order of energies without calculations.

(ix) Changes in molecular shape which increase the in-phase overlap between two or more AO's in a MO tend to lower the energy of that MO. Conversely, changes in shape which decrease in-phase overlap or increase out-of-phase overlap among AO's in a MO tend to raise the energy of the MO. This can be called the overlap rule.

(x) No *a priori* assumptions about orbital hybridization are needed.

### The AH₂ Series

With only three atoms, the molecules in the series $AH_2$ can be only either linear or bent in shape.[19] Molecules with three or four valence electrons are linear; those with one or two or five through eight electrons are bent. Herzberg has recently reviewed the experimental structural data for several of the members of this series with five electrons or more.[20]

Consider the four valence MO's of lowest energy for a linear $AH_2$ molecule.[21] These can be made from the s and three p valence AO's on the central atom A by combining them in phase with the 1s orbitals on the hydrogens. Figure 1 shows how this is done. The lowest energy valence MO for linear geometry is $2\sigma_g$.

(19) Most of the structural data used in this review come from these sources: L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 11 (1958), No. 18 (1965); ref 15.

(20) G. Herzberg, *Science*, **177**, 123 (1972).

(21) B. M. Gimarc, *J. Amer. Chem. Soc.*, **93**, 593 (1971).

It is mainly the s AO on A plus in-phase overlapping 1s AO's from the hydrogens. The $p_z$ AO points directly at the 1s orbitals on the hydrogens and these can overlap in phase with $p_z$ to form the $1\sigma_u$ orbital which is of lower energy than $p_z$ alone. In the two $1\pi_u$ orbitals, the hydrogens are located on the nodal surfaces of the $p_x$ and $p_y$ orbitals and hence the hydrogen 1s AO's cannot enter either $1\pi_{ux}$ or $1\pi_{uy}$. These two MO's are pure $p_x$ or $p_y$, and they remain degenerate in energy. Starting with six AO's on the three separated atoms one can make six MO's for $AH_2$. Only the four of lowest energy are included in Figure 1.

Figure 1 correlates orbitals and energies for linear and bent $AH_2$. On bending, the two hydrogen 1s orbitals in $2\sigma_g$ move closer together in $2a_1$ and therefore into better overlap with each other. Thus the $2a_1$ orbital of bent geometry will have lower energy than the related $2\sigma_g$ orbital of the linear shape. If the molecule contains only one or two valence electrons, these will find lower energy in bent geometry in $2a_1$. The ions $H_3^{2+}$, $H_3^+$, and $LiH_2^+$ are indeed bent.[22,23] The energy difference between linear $2\sigma_g$ and bent $2a_1$ is not large, however. To a first approximation, these nodeless MO's of lowest energy are almost spherical.[24] When higher energy orbitals are occupied, the energy changes for the nodeless orbitals will be negligible by comparison.

The energy of the $1\sigma_u$ orbital increases on bending because the hydrogen 1s AO's are pulled out of overlap with the lobes of the $p_z$ AO on the central atom and pushed toward each other across the nodal surface of the orbital $1b_2$ of bent geometry. The $1\sigma_u$–$1b_2$ MO controls the shapes of three- and four-electron $AH_2$ molecules such as $BeH_2^+$, $BeH_2$, and $BH_2^+$ which are linear[25] because the electrons are at lower energy in the linear $1\sigma_u$ orbital. The $p_z$ AO on the central atom is not required to explain why $H_3$ is linear; the energy of $1\sigma_u$–$1b_2$ still increases on bending because the terminal hydrogen 1s AO's approach each other out of phase on opposite sides of the nodal surface.[26]

When $1\pi_{uy}$ is bent, the hydrogens move on the nodal surface (the $xz$ plane) of $1b_1$; no change in overlap is possible and therefore $1\pi_{uy}$ and $1b_1$ have the same AO composition and the same energy. The $1\pi_{uy}$–$1b_1$ MO system has no geometry preference and no direct influence on molecular shapes. As $1\pi_{ux}$ is bent, the hydrogens move off the nodal surface of $p_x$ (the $yz$ plane), and in-phase overlapping of the hydrogen 1s orbitals with the bottom lobe of $p_x$ lowers the energy of the orbital $3a_1$ thus formed. The shapes of molecules with five through eight electrons are bent because $3a_1$ falls rapidly in energy as the valence angle HAH decreases. In $BH_2$ and $AlH_2$ the $3a_1$ orbital contains only one electron. Since $BH_2$ and $AlH_2$, are both bent it means that the energy of the singly occupied $3a_1$ orbital falls at least twice as

rapidly as that of the doubly occupied $1b_2$ rises below it. That this might be so can be seen from the following overlap argument. The overlap between a p orbital and a hydrogen 1s orbital is proportional to the cosine of the angle $\phi$ between the axis of the p orbital and the A–H bond axis. The position of maximum overlap has the hydrogen 1s AO resting squarely on the p orbital axis ($\phi = 0$). With the hydrogen tilted 30° away from the p orbital axis, the 1s,p overlap is still 87% of maximum and at $\phi = 60°$ the overlap is 50% of maximum. At $\phi = 90°$ the 1s AO is on the p orbital nodal surface and the overlap is zero. If the size of the energy change is related to the amount of overlap change, then tilting a hydrogen a few degrees away from the p-orbital axis should produce a relatively small energy increase. Moving the hydrogen a few degrees off the p-orbital nodal surface should lead to a significant energy lowering. For example, imagine decreasing the angle HAH from 180° (linear) to 120° (bent). Each of two 1s,p overlaps in $1b_2$ decreases from 100% to 87% of maximum, producing a modest rise in energy, while each of two 1s,$p_x$ overlaps in $3a_1$ increase from 0 to 50% of maximum for a substantial energy lowering or stabilization. Therefore, even a single electron in $3a_1$ can force molecules such as $BH_2$ and $AlH_2$ to be bent.

In its ground state $BH_2$ has a valence angle of 131°. The linear excited state of $BH_2$ is known for which the electron configuration is $(2a_1)^2$-$(1b_2)^2(1b_1)^1$. In this case an electron has been removed from the MO $3a_1$ that holds ground-state $BH_2$ bent; the excited electron occupies $1b_1$ which has no geometry preference and the excited molecule is therefore linear because of the electron pair in $1\sigma_u$–$1b_2$.

Simply assigning electrons to the lowest available MO energy levels for $AH_2$ leads one to the conclusion that for six-valence-electron molecules the $(3a_1)^2$ singlet configuration should have lower energy than the $(3a_1)^1(1b_1)^1$ triplet. Both experiment[27] and *ab initio* SCF MO calculations[28] show that this conclusion is wrong for $CH_2$ and apparently for $NH_2^+$ as well.[29] The ground states of these species are, in fact, triplets, $(3a_1)^1(1b_1)^1$. The valence angles for these ground-state triplets are 136° ($CH_2$) and 140–150° ($NH_2^+$), rather wide angles, comparable to that for the $BH_2$ ground state and consistent with the notion that $3a_1$ is singly occupied. Each of these species has a singlet state at higher energy with $3a_1$ doubly occupied, and hence a sharper valence angle. For the $(3a_1)^2$ singlets, the angles are 105° ($CH_2$) and 115–120° ($NH_2^+$). The singlets of still higher energy, the $(3a_1)^1(1b_1)^1$ configuration, have wide valence angles similar to those of the ground-state triplets: 140–150° for $CH_2$ and around 150° for $NH_2^+$. The ground state of $SiH_2$ is a singlet $a_1^2$ and has a valence angle of 97°.[30] Higher in energy is the triplet configuration $a_1^1b_1^1$ with the wider angle of 124°. Still higher is

(22) H. Conroy and B. L. Bruner, *J. Chem. Phys.*, 47, 921 (1967).

(23) R. D. Poshusta, J. A. Haugen, and D. F. Zetik, *J. Chem. Phys.*, 51, 3343 (1969).

(24) For accurate MO contour diagrams, see: T. H. Dunning, Jr., R. M. Pitzer, and S. Aung, *J. Chem. Phys.*, 57, 5044 (1972).

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

(26) B. M. Gimarc, *J. Chem. Phys.*, 53, 1623 (1970).

(27) E. Wasserman, W. A. Yager, and V. J. Kuck, *Chem. Phys. Lett.*, 7, 409 (1970); G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, 54, 2276 (1971).

(28) J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, 91, 807 (1969); S. V. O'Neil, H. F. Schaefer III, and C. F. Bender, *J. Chem. Phys.*, 55, 162 (1971).

(29) S. Y. Chu, A. K. Q. Siu, and E. F. Hayes, *J. Amer. Chem. Soc.*, 94, 2969 (1972).

(30) B. Wirsam, *Chem. Phys. Lett.*, 14, 214 (1972).

the $a_1{}^1b_1{}^1$ singlet with a comparable angle, 126°. While the simple notion of sums of orbital energies fails to give the proper energy order of states of $CH_2$ and $NH_2{}^+$, the qualitative model does represent the correct trends in bond angles for those states.

The ground-state electron configuration of the seven-valence electron molecule $NH_2$ is $(3a_1)^2(1b_1)^1$ and the valence angle of 103° is consistent with double occupancy of $3a_1$. Excitation to the configuration $(3a_1)^1(1b_1)^2$ moves one electron from the orbital that holds $NH_2$ bent to an orbital with no geometry preference. A single electron in $3a_1$ is enough to keep excited $NH_2$ bent, but at the wider valence angle of 144°. $PH_2$ shows a similar increase of valence angle from the ground state (92°) to excited state (123°).

$AH_2$ molecules with eight-valence electrons, of which water is an example, are bent due to double occupancy of the $3a_1$ orbital.

### The AH₃ Series

Molecules of the general formula $AH_3$ with eight valence electrons ($NH_3$, $PH_3$, $H_3O^+$, $CH_3{}^-$) are pyramidal or nonplanar. Those with six electrons ($BeH_3{}^-$, $BH_3$, $CH_3{}^+$) are planar and equilateral triangular. The $CH_3$ radical and the $NH_3{}^+$ radical ion[31] are apparently also planar. Figure 2 is a qualitative MO correlation diagram for planar and pyramidal shapes. Only the four valence MO's of lowest energy appear in Figure 2. The lowest of these is the nodeless $2a_1'-2a_1$ system. Because the 1s,1s overlaps are greater in $2a_1$ (pyramidal), this orbital is slightly more stable than $2a_1'$ (planar). Therefore the two-electron ion $H_4{}^{2+}$ should have lowest energy in the tetrahedral (pyramidal) shape[32] since this arrangement would give the maximum in-phase overlap among four hydrogen 1s orbitals.[26] For molecules and ions with more than two electrons, the $2a_1'-2a_1$ MO system does not control molecular geometry.

Doubly degenerate MO's occur for molecules with geometries which have a symmetry axis of threefold or greater. For planar and pyramidal $AH_3$ molecules these degenerate orbitals are $1e'-1e$. As shown in Figure 2, one of the two $e'$ MO's for planar geometry contains a p orbital in 100% overlap with one hydrogen 1s AO and 50% overlap with each of the two other 1s orbitals. The other $e'$ MO has its p orbital in about 87% overlap with each of two hydrogen 1s orbitals while the third hydrogen lies on the nodal plane of the MO. Thus even without symmetry arguments one can see that the two MO's designated $e'$ should have nearly equal energies. This is also a good place to emphasize that the simple overlap considerations are only qualitative for comparisons between MO's with different AO compositions. Suppose the valence angle decreases from 120° (planar) to 110° (pyramidal). The 1s,p overlap decreases are small, but they are large enough to hold molecules with three through six valence electrons planar. In the planar–pyramidal transformation, the three hydrogens in $1a_2''$ move off the nodal surface. As they do so their 1s AO's can enter the resulting $3a_1$ MO and overlap one of the lobes of the central atom $p_x$ AO. Since this overlap starts from zero, it increases rap-
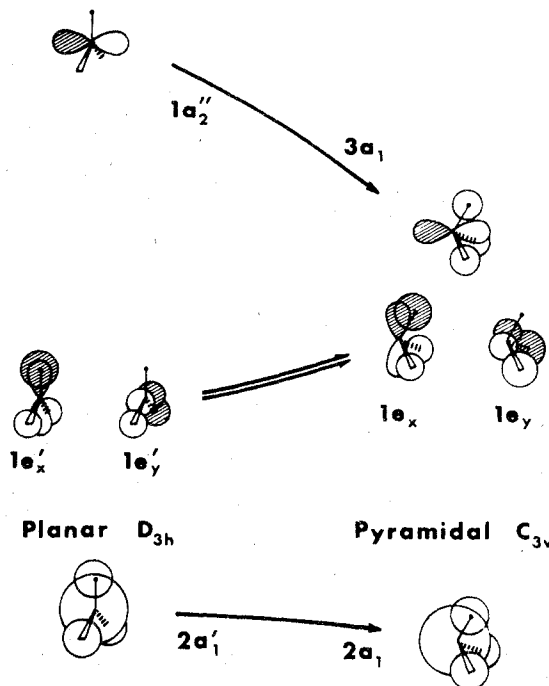
(31) W. R. Harshbarger, *J. Chem. Phys.*, **56**, 177 (1972).
(32) H. Conroy and G. Malli, *J. Chem. Phys.*, **50**, 5049 (1969).

**Figure 2.** Qualitative MO correlation diagram for an $AH_3$ molecule in planar and pyramidal shapes.

idly; hence the energy of $3a_1$ must fall sharply, much faster than the two 1e orbitals which rise below it. For eight-electron molecules such as $NH_3$, the $1a_2''-3a_1$ orbital is doubly occupied and the molecules are pyramidal rather than planar. For the seven-electron methyl radical, with only one electron in $1a_2''-3a_1$ but two pairs in $1e'-1e$, the total overlap increases in $3a_1$ are comparable with the decreases in 1e and the qualitative MO model is inconclusive. However, extended Hückel calculations and the more rigorous *ab initio* SCF MO calculations agree that $CH_3$ is planar.

Still other geometries are accessible to $AH_3$ molecules. The transformation Y-shape ($C_{2v}$)–equilateral triangular ($D_{3h}$)–T-shape ($C_{2v}$) is a geometry change that intersects the planar–pyramidal change.
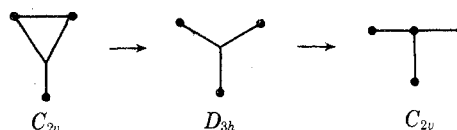


Intersecting correlation diagrams are available which permit energy comparisons.[21] These comparisons do not change the conclusions we have already reached concerning one and two or five, six, seven, and eight electron molecules, but they do predict that three- and four-electron $AH_3$ molecules should be Y-shaped. Valence bond calculations for the three-electron radical ions $H_4{}^+$ and $LiH_3{}^+$ and for the four-electron ion $HeH_3{}^+$ offer evidence that these hypothetical ions should be Y-shaped.[23]

### The AH₄ Series

The tetrahedral structure of methane can be explained without assuming tetrahedral hybrid orbitals. Figure 3 correlates valence MO's for tetrahedral ($T_d$) and square-planar ($D_{4h}$) structures for $AH_4$. The lowest energy or nodeless orbital $a_1-a_{1g}$ does not
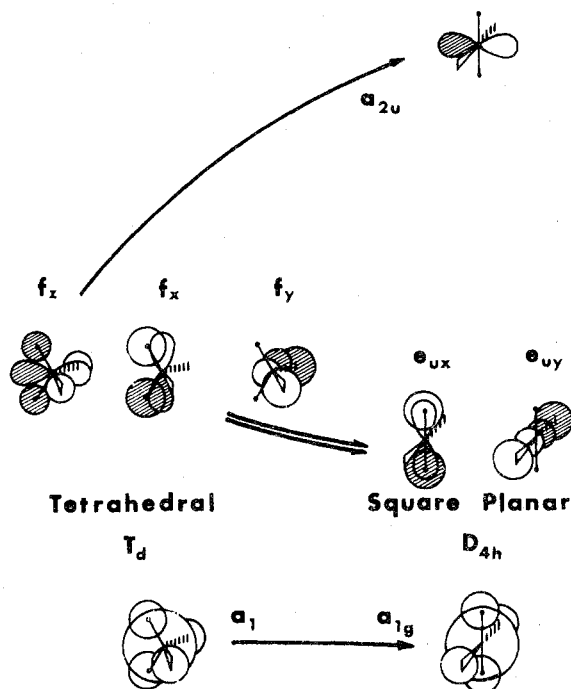
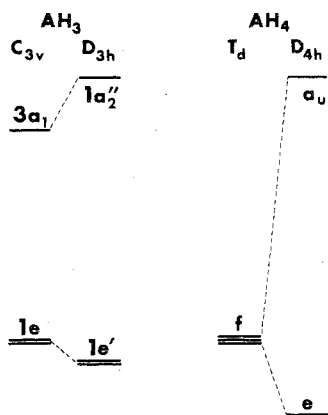Figure 3. Molecular orbital pictures for $AH_4$ in tetrahedral and square-planar geometry.



Figure 4. Comparison of higher energy valence levels of $AH_3$ in pyramidal and planar shapes and for $AH_4$ in tetrahedral and square-planar shapes. The relatively small gap between $3a_1$ and $1a_2''$ permits inversion of eight-electron $AH_3$ molecules. Inversion of eight-electron $AH_4$ molecules is much harder because of the large gap between f and $a_u$.
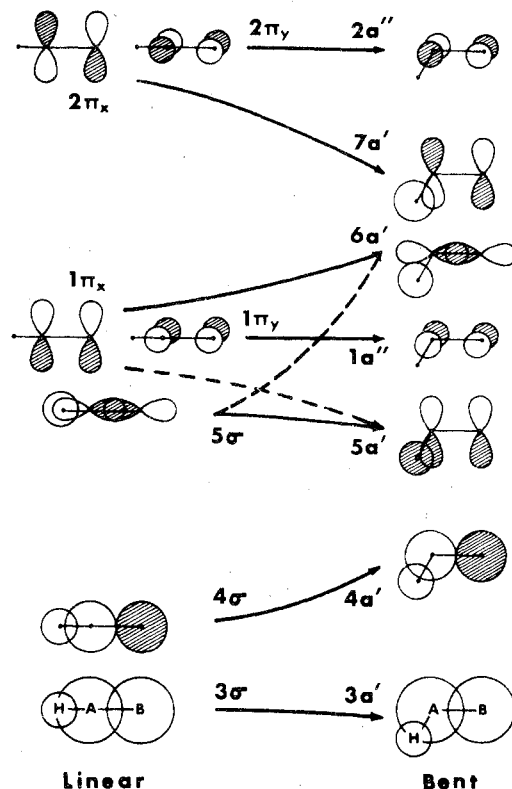


Figure 5. Qualitative correlation diagram for linear and bent HAB molecules. Dashed arrows indicate intended correlations which are blocked by the noncrossing rule.

influence the shape of the molecules to be considered here. Tetrahedral geometry requires a set a triply degenerate MO's, the f orbitals of Figure 3. While the particular set of AO composition pictures in Figure 3 is not the one that shows the degeneracy most clearly, that set does demonstrate most conveniently the orbital energy differences between tetrahedral and square-planar shapes. These energy changes can be readily deduced from the overlap rule. In the tetrahedral orbitals $f_x$ and $f_y$ the hydrogen 1s AO's are already in good overlap with the lobes of the adjacent p orbital. In square-planar shape the overlaps are even better though the increases are small, leading to a small lowering of energy. For $f_z$–$a_{2u}$ the overlap decrease is large, all overlaps going to zero for $a_{2u}$, producing a correspondingly large energy rise. For $BH_4^-$, $CH_4$, and $NH_4^+$, each with eight valence electrons, the high energy of $a_{2u}$ prohibits square-planar geometry and makes these species tetrahe-

dral. Molecules with six electrons, $BeH_4$ for instance, should be square planar. That the pair of square-planar MO's $e_{ux}$ and $e_{uy}$ must be doubly degenerate is easy to see from the diagrams in Figure 3.

## Inversion

Qualitative MO pictures can show why ammonia inverts but methane does not. The most straightforward comparison for this purpose would be between $NH_3$ and $NH_4^+$. Figure 4 contains energy levels in pyramidal ($C_{3v}$) and planar-triangular ($D_{3h}$) shapes for $AH_3$ compared with those for $AH_4$ in tetrahedral ($T_d$) and square-planar ($D_{4h}$) shapes. Figures 2 and 3 form the basis for Figure 4. The $a_{2u}$ level of planar $AH_4$ is prohibitively high in energy relative to the f orbitals of tetrahedral geometry, while the $3a_1$ orbital of pyramidal $AH_3$ is much closer to $1a_2''$ of planar shape, making the inversion of $AH_3$ much cheaper energetically.

## The HAB Series

Molecules of the series HAB are either linear or bent. The occupied valence MO's for linear HAB molecules can be derived from those for the diatomic molecule AB by combining a hydrogen 1s AO in-phase with the $\sigma$ MO's of AB.[33] The nodal planes of the $\pi$ orbitals prevent any 1s contributions to those MO's. Figure 5 shows schematic MO pictures correlating orbitals for linear and bent HAB. Orbitals for bent HAB must be either symmetric (a') or antisymmetric (a'') with respect to reflection in the symmetry plane. Orbital energy changes are easy to interpret by the overlap rule with the exceptions of $5\sigma$–

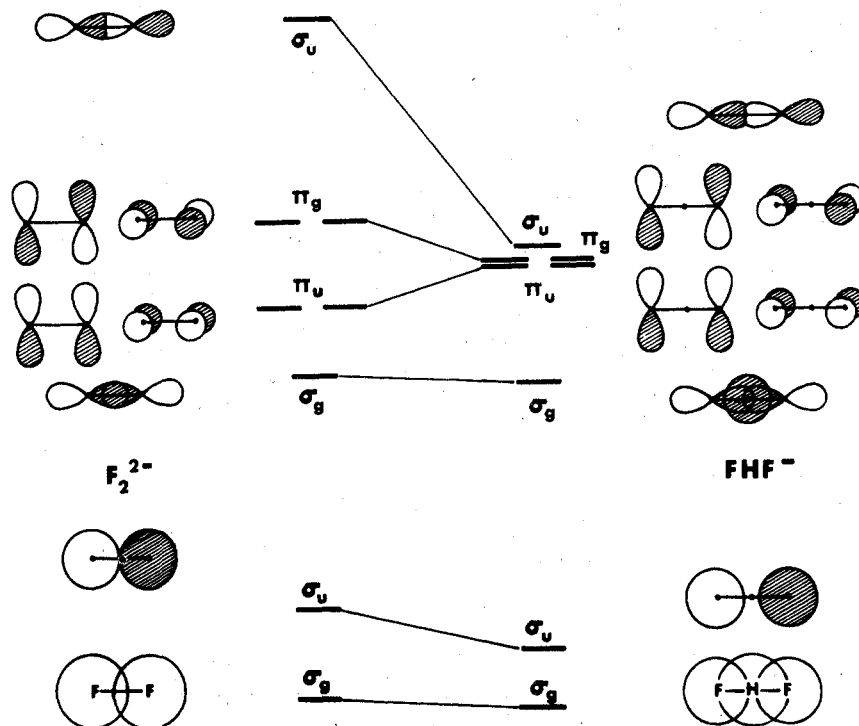(33) B. M. Gimarc, *J. Amer. Chem. Soc.*, 93, 815 (1971).

**Figure 6.** Relative energy levels and MO pictures for $F_2^{2-}$ and $FHF^-$. Energy levels shown were obtained by extended Hückel calculations.

$5a'$ and $1\pi_x-6a'$. Both $5\sigma$ and $1\pi_x$ must yield orbitals of $a'$ symmetry in bent geometry. Intended orbital correlations are shown by dashed arrows in Figure 5. The crossing of two $a'$ orbitals is forbidden by the noncrossing rule. Instead, these two orbitals mix and diverge as shown by the solid arrows for $5\sigma-5a'$ and $1\pi_x-6a'$.

With ten valence electrons, HCN is linear, the highest occupied MO being $1\pi_x-6a'$. The first excited state of HCN is bent. Excitation transfers an electron from $1\pi_x-6a'$, the orbital that holds the molecule linear, to $2\pi_x-7a'$, an orbital that goes to significantly lower energy in the bent shape. Thus, ten-electron molecules should have linear ground states and bent excited states. The 11-electron radical HCO should be bent in its ground state with one electron in $7a'$. Excitation removes this electron from $7a'$, the orbital that makes HCO bent, and adds it to $2\pi_y-2a''$, an orbital having no geometry preference. Lower occupied orbitals, the same ones that make the HCN ground state linear, give excited HCO linear geometry. Molecules with 12 through 14 electrons (HNO, HNF, HOCl) should be bent in both ground and excited states because at least one electron will be in $7a'$.

## Hydrogen Bonding

Unlike the other HAB species, the 16 electron ions $FHF^-$, $ClHCl^-$, etc., are linear and symmetric with the hydrogen on the axis and midway between the two halogens. One can think of an ordinary HAB molecule (14 electrons or less) as an $AB^-$ ion with a proton attached to one end. In fact, HCN, HNO, and HOCl are all weak acids, and the corresponding $AB^-$ ions are known. One would not expect the ion $F_2^{2-}$ (16 electrons, isoelectronic with $Ne_2$) to be bound because equal numbers of bonding and antibonding orbitals are occupied. For the $FHF^-$ system, the insertion of a hydrogen with its 1s AO between

the two halogens stabilizes the antibonding $\sigma_u$ and $\pi_g$ orbitals (particularly the highest occupied $3\sigma_u$ which has $p_z$ AO's pointing directly at each other out of phase) by separating the antibonding or out-of-phase fragments, thereby lowering their out-of-phase overlaps and making them nonbonding. At the same time, the central hydrogen 1s orbital provides in-phase overlaps to maintain the bonding character of the $\sigma_g$ MO's. Figure 6 contains schematic diagrams of these orbitals. Only the bonding $\pi_u$ orbitals are raised in energy (to become nonbonding) by the increased separation of the two fluorine atoms. In the $\pi_u$ MO's the hydrogen is on the nodal surface, and its 1s AO cannot participate in any overlap stabilization. The result is a change from four bonding and four antibonding MO's for $X_2^{2-}$ to two bonding and six nonbonding MO's for $XHX^-$.

Pimentel and Spratley[34] predicted that FHeF should be stable, arguing from analogy with the isoelectronic ion $FHF^-$ and FXeF. On the basis of *ab initio* valence bond and SCF MO calculations Allen and coworkers[35] and Noble and Kortzeborn[36] conclude that, while $FHF^-$ is stable, FHeF should be unstable. Those conclusions can be rationalized by means of the qualitative MO model. Hydrogen bonding results from antibonding or out-of-phase pieces of MO's being separated far enough to make all antibonding orbitals nonbonding while at the same time some of the bonding orbitals retain their bonding character through new overlaps provided by the inserted 1s AO. Now the larger charge of the He nucleus makes a He 1s AO considerably smaller than a hydrogen 1s. In order to maintain effective in-phase overlaps in the two $\sigma_g$ MO's, a He 1s orbital cannot

(34) G. C. Pimentel and R. D. Spratley, *J. Amer. Chem. Soc.*, **85**, 826 (1963).

(35) L. C. Allen, R. M. Erdahl, and J. L. Whitten, *J. Amer. Chem. Soc.*, **87**, 3769 (1965).

(36) P. N. Noble and R. N. Kortzeborn, *J. Chem. Phys.*, **52**, 5375 (1970).
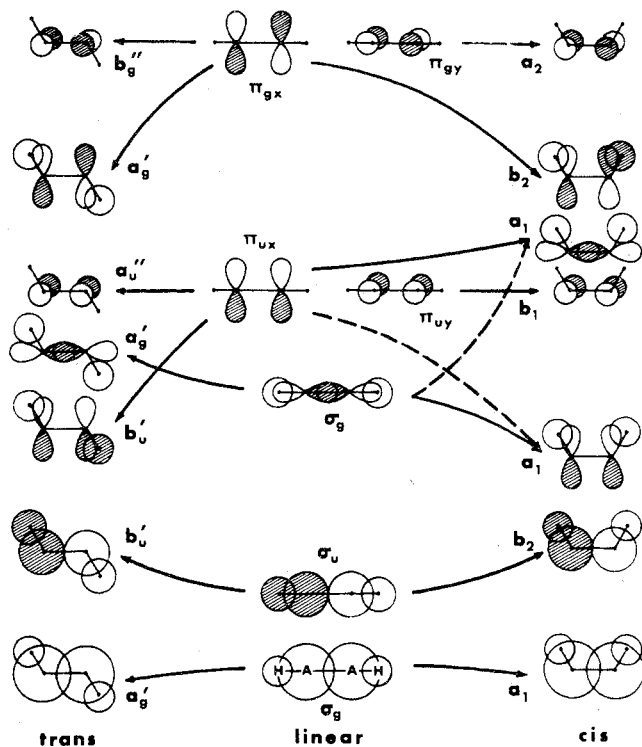
Figure 7. Qualitative correlation diagram for HAAH in linear and nonlinear (cis and trans) shapes.

separate the F atoms far enough to stabilize significantly the antibonding MO's. Therefore net bonding in FHeF is not likely.

## $C_2H_2$, $N_2H_2$, and $H_2O_2$

The $A_2H_2$ series is a simple extension of the HAB series.[37] Figure 7 displays the valence MO's for linear and nonlinear, cis and trans, geometries of a typical $A_2H_2$ molecule. Orbital energy changes can be interpreted by the overlap rule. A case of noncrossing of orbitals of the same symmetry for cis geometry exactly parallels the HAB model. With ten electrons, acetylene ($C_2H_2$) is linear. Diimide ($N_2H_2$; 12 electrons) has planar cis and trans isomers because of the lower energies of $b_2$ (cis) and $a_g'$ (trans) that stem from the $\pi_{gx}$ MO of linear geometry. Hydrogen peroxide ($H_2O_2$; 14 electrons) should also be nonlinear. To see why $H_2O_2$ is actually nonplanar, or gauche, look at Figure 8 which contains pictures of the two highest occupied MO's for $H_2O_2$ and shows how their energies change as the molecular framework is twisted from planar, trans, through nonplanar, gauche, to planar, cis. For the purposes of Figure 8, this twisting takes place in such a way that the molecular twofold symmetry axis remains perpendicular to the page, passing through the midpoint of the A–A bond. Also the p AO's are locked parallel to the cartesian axes and are not twisted or rotated. Only the hydrogens move. In the orbital $b_g''$–b–$b_2$, the hydrogens move away from the nodal surface in $b_g''$ (trans) and into positions where their 1s orbitals can overlap well with the p orbital lobes in $b_2$ (cis). This produces a lowering of energy from $b_g''$ to b to $b_2$. At the same time, the hydrogens in $a_g'$–a–$a_2$ move out of good overlap in $a_g'$ (trans) and towards the nodal surface of $a_2$ (cis) for an energy in-

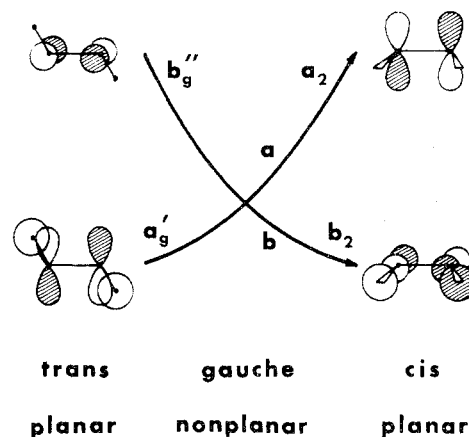(37) B. M. Gimarc, *J. Amer. Chem. Soc.*, 92, 266 (1970).



Figure 8. Correlations for the highest occupied pair of MO's in $H_2O_2$ on rotation from trans to cis through skewed or nonplanar geometry.

crease from $a_g'$ to a to $a_2$. Now the energy of $b_g''$–b should drop rapidly because the overlap increases from zero while the energy of $a_g'$–a should increase more slowly because the overlap decreases from near maximum. Therefore the energy at which orbitals a and b cross in gauche geometry is lower than the average of either $b_g''$ and $a_g'$ for trans or $a_2$ and $b_2$ for cis. (It turns out that a similar crossing of a and b MO's for hydrazine ($N_2H_4$) makes that molecule gauche also.)[38] While this naive model gives an appealing rationale for the gauche shape of $H_2O_2$, the actual situation is more complicated. Extensive mixing among orbitals of a symmetry and among orbitals of b symmetry for the gauche shape makes the crossing of these a and b orbitals occur at higher energy. Gauche geometry of $H_2O_2$ arises from a delicate balance among all the occupied a and b valence orbitals.

## Orbitals for Ethylene

Qualitative MO's for the planar $A_2H_4$ molecule can be constructed by taking in-phase and out-of-phase combinations of the MO's for separated, bent $AH_2$ fragments.[38] Figure 9 correlates relative energy levels and MO's for planar $A_2H_4$ and two isolated $AH_2$ molecules. Compared with $3a_1$ ($AH_2$) the energy of $3a_g$ ($A_2H_4$) should be quite low and that of $3b_{3u}$ (not shown, off the top of Figure 9) should be quite high because of the bonding and antibonding p–$\sigma$ type overlaps that result as the two $AH_2$ fragments are joined. The splittings that occur as a result of the two $1b_2$ and the two $1b_1$ combinations are much smaller because of their $\pi$-type overlap. One might be concerned that the A–A antibonding orbital $1b_{1g}$ lies below the bonding orbital $1b_{1u}$. The four 1s,p overlaps available to $1b_{1g}$ but not to $1b_{1u}$ give $1b_{1g}$ a lower energy. For ethylene (12 electrons), the bonding $\pi$-orbital $1b_{1u}$ is the highest occupied MO. The lowest unoccupied MO is the antibonding $\pi$ orbital $1b_{2g}$.

Now consider twisting one $AH_2$ group relative to the other about the A–A bond. Figure 10 is the correlation diagram for this process. For convenience, the two valence MO's of lowest energy, $2a_g$–$2a_1$ and

(38) J. R. Durig, B. M. Gimarc, and J. D. Odom in "Vibrational Spectra and Structures," Vol. II, J. R. Durig, Ed., Marcel Dekker, New York, N.Y., 1973.
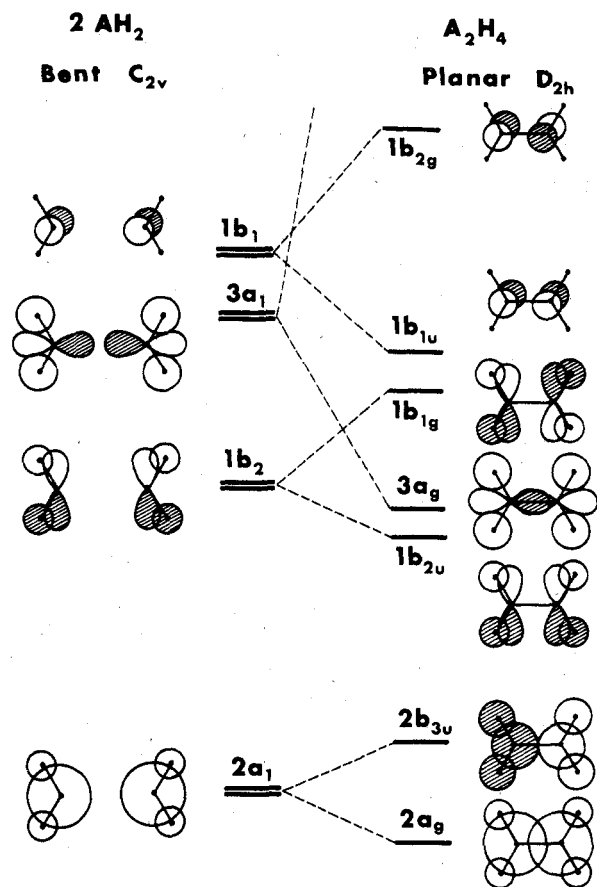
**2 AH₂**

**Bent C₂ᵥ**



Figure 9. Formation of MO's for planar $A_2H_4$ by taking in-phase and out-of-phase combinations of the MO's of bent $AH_2$ fragments.

**Planar　Twisted　Staggered**

**$D_{2h}$　$D_2$　$D_{2d}$**



Figure 10. Qualitative correlation diagram for planar and staggered ethane. The degenerate orbital pair 1e has about the same energy as $3a_1$ (staggered).

$2b_{3u}$–$2b_1$, are not shown in Figure 10. These orbitals, as well as $3a_g$–$3a_1$, are axially symmetric and their energies change very little on rotation. Symmetry requires that each $b_1,b_2$ pair of $D_{2h}$ or $D_2$ geometry becomes degenerate in $D_{2d}$. Both $1b_{1u}$ and $1b_{1g}$ of $D_{2h}$ become $b_1$ in intermediate $D_2$ geometry. Intended correlations, indicated by dashed arrows in Figure 10, are $1b_{1g}$–2e and $1b_{1u}$–1e. Because $1b_{1u}$ lies above $1b_{1g}$ in energy, the intended correlations are blocked by the noncrossing rule. It is the rising energy of the MO $1b_{1u}$–$b_1$–2e that makes ethylene planar. Other MO correlation diagrams are available which summarize the various shapes of the remaining members of the $A_2H_4$ series.[38]

### Ethane and Diborane

Figure 11 correlates the orbital energies of an $A_2H_6$ molecule of the staggered ethane conformation with those for a bridged or diborane shape.[39] For simplicity, the pair of valence MO's of lowest energy has not been included in the diagram. Those two orbitals have no significance for the ethane–diborane structural transformation. In fact, only two MO's undergo large energy changes. Look at $3a_{1g}$–$3a_g$. On rocking from the staggered form to the bridged shape, four hydrogens in $3a_{1g}$ move to terminal positions in $3a_g$ and two hydrogens move to bridging positions. All six move to positions of increased overlap. Each of the bridging hydrogens overlaps two p orbitals. This
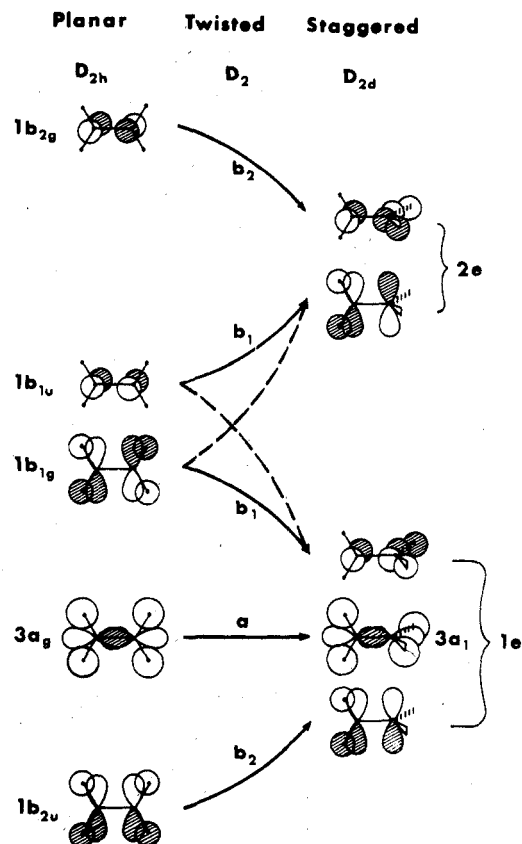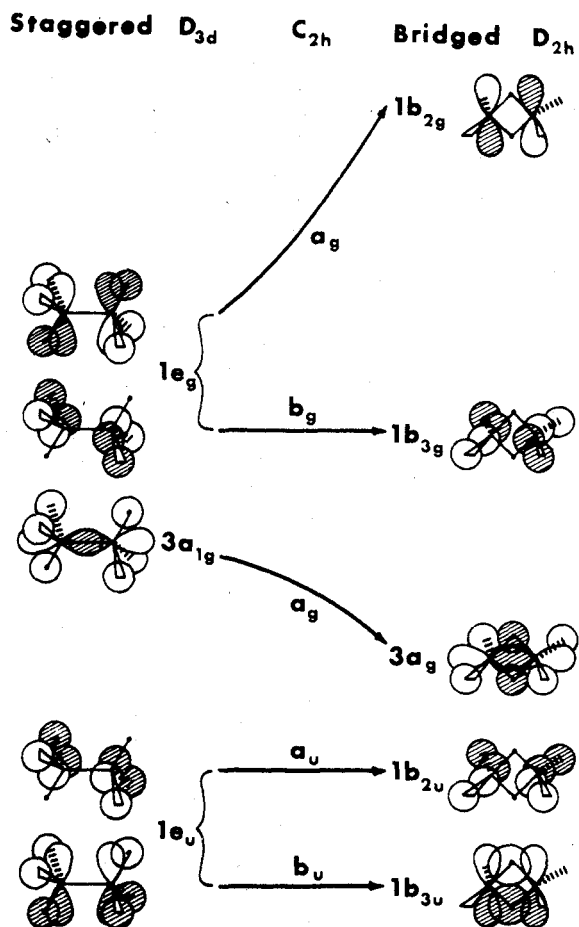
(39) B. M. Gimarc, *J. Amer. Chem. Soc.*, **95**, 1417 (1973); R. Hoffmann and J. E. Williams, Jr., *Helv. Chim. Acta*, **55**, 67 (1972).

**Staggered $D_{3d}$　$C_{2h}$　Bridged $D_{2h}$**



Figure 11. Qualitative correlation diagram for an $A_2H_6$ molecule in staggered $D_{3d}$ and bridged $D_{2h}$ shapes.

considerable increase in overlap makes the bridged form $3a_g$ much lower in energy than the staggered form $3a_{1g}$. Now consider the $1e_g$-$1b_{2g}$ orbital. In the staggered form ($1e_g$) all six hydrogens are in good overlap with the p orbitals of the principal atoms. In the bridged form ($1b_{2g}$) all six hydrogens lie on nodal surfaces of the MO and the overlap is zero. Therefore the energy of $1b_{2g}$ is considerably higher than that of $1e_g$. This increase is even larger than the decrease of $3a_g$ relative to $3a_{1g}$. While individual overlaps in $1e_u$-$1b_{3u}$ do change, they change in such a way as to cancel each other. Overlap changes in $1e_u$-$1b_{2u}$ and $1e_g$-$1b_{3u}$ are negligible compared to those described already.

Diborane, with 12 valence electrons, has $1b_{3g}$ as its highest occupied MO. The favorable overlap arrangement of the bridging hydrogens in $3a_g$ is responsible for the bridged structure of diborane. For ethane (14 electrons) the steeply rising energy of the occupied $1e_g$-$1b_{2g}$ orbital holds ethane in staggered geometry. In MO theory, bridge bonds arise in a natural way. For the valence bond model the basic rules must be amended and additional concepts such as electron deficiency must be introduced to account for hydrogen bridging.

## Conclusion

Are these qualitative speculations and interpretations verifiable? The correlation diagrams presented here compare very favorably with those obtained from extended Hückel MO calculations[21,33,37-39] and, where available, *ab initio* SCF MO calculations.[11,40] The relation between the qualitative MO model and semiempirical MO methods is quite close. The overlap rule enters the extended Hückel method through the overlap proportionality chosen to represent the off-diagonal elements of the Hamiltonian matrix in the secular equation.[41] Thus, the qualitative arguments can be checked by comparable quantitative methods. Unfortunately this means that if the calculations give the wrong answer the qualitative model will also lead to the wrong conclusions. An example is the failure of both qualitative MO theory and the extended Hückel calculations to predict the correct geometry for hydroxylamine ($H_2NOH$), presumably because of the failure of either method to include changes in internuclear repulsions (assumption vi).[33] However, it should still be considered an advance in valence theory to have a qualitative model that corresponds so closely to easily performed calculations.

It is hard to suppress the urge to refine the qualitative pictures. Streitwieser and Owens[42] have compiled a book of computer-drawn MO contour diagrams for small molecules. Surely, those diagrams present a more accurate picture of the MO's than do the qualitative AO composition diagrams that accompany this Account but energy changes arising from changes in molecular shape are easier to interpret with the qualitative AO composition diagrams.

What about qualitative MO's for larger molecules? The same overlap and symmetry arguments should apply, but unfortunately problems rapidly become more complicated because of the larger number of MO's involved and the fact that these orbitals lie much closer together in energy, and the extent of mixing among orbitals of the same symmetry is therefore likely to be greater. This MO mixing together with energy differences due to different atomic electronegativities may cause a reordering of close-lying MO energies (failure of rule iv). But even this presents no difficulty as long as highest occupied and lowest unoccupied orbitals are not reversed. Several approaches for extension to larger systems may be useful. First is the formation of MO's of large molecules from those of small molecules as we have done for $A_2H_4$ and $A_2H_6$. Another possibility is that one might hope to resolve only those MO's of chemical interest from the traditional valence bond structures much as Woodward and Hoffmann have done in their studies of mechanisms of concerted organic reactions.[1] Finally, it is always possible to use the qualitative MO model to interpret the results of MO calculations.

The familiar, remarkably simple, and often powerful qualitative concepts of MO theory lead to some very appealing interpretations of chemical properties. The model is applicable to molecular excited states as well as ground states and it can account in a very natural way for such phenomena as hydrogen bridging in diborane and the skewed geometry of hydrogen peroxide, problems not so easily explained by valence bond theory or the VSEPR model. Finally, the qualitative MO explanations can easily be checked by performing MO calculations.

(40) D. C. Pan and L. C. Allen, *J. Chem. Phys.*, 46, 1797 (1967); R. J. Buenker, *ibid.*, 48, 1368 (1969); W. H. Fink, D. C. Pan, and L. C. Allen, *ibid.*, 47, 895 (1967); R. J. Buenker, S. D. Peyerimhoff, L. C. Allen, and J. L. Whitten, *ibid.*, 45, 2835 (1966).
(41) R. Hoffmann, *J. Chem. Phys.*, 39, 1397 (1963).

(42) A. Streitwieser, Jr., and P. H. Owens, "Orbital and Electron Density Diagrams," Macmillan, Riverside, N.J., 1973.