466. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part I. AH_2 Molecules.*

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The electronic orbitals possible for an AH_2 molecule when linear are correlated with those possible for the molecule when non-linear. Qualitative curves of binding energy *versus* $\angle HAH$ are given for the various orbitals. These curves are then used to explain and predict (i) the shapes and (ii) the electronic spectra and associated characteristics of AH_2 molecules. AH_2 molecules containing 4 valency electrons should be linear in their ground states. AH_2 molecules containing 5—8 valency electrons should be bent in their ground states.

THE purpose of this paper is first to correlate the electronic orbitals of a bent with a linear AH_2 molecule, next to decide whether a given orbital becomes more or less tightly bound with increase of the angle HAH, and then to use the resulting graphs of binding energy *versus* apex angle to explain and predict the shapes and spectra of AH_2 molecules.

Linear AH_2 Molecules.—The lowest-energy intra-valency-shell orbitals of a linear AH_2 molecule, may, on the assumption that these are built solely from s and p atomic orbitals, be described as follows : (i) Two orbitals binding the hydrogen atoms to the central atom. These may be thought of as each formed by the overlap of an sp hybrid atomic orbital on A with the $1s$ orbital of hydrogen. If so regarded they will be orbitals of σ-type predominantly localized one in each A–H distance. If, however, one were discussing a transition involving excitation of an electron from one of the bonding orbitals, one could not regard the electron as coming from one A–H link or the other—the two are indistinguishable. If one first conceives of the orbitals as completely localized one has to take combinations of them in order to express this indistinguishability. These combinations are either in-phase or out-of-phase and may be labelled σ_g and σ_u respectively. (ii) A π_u orbital. This is simply a p orbital localized on the central atom and pointing in a direction at 90° to the HAH line. It is non-bonding. Since there are two such directions that are independent but equivalent (except for a rotation by 90°), the orbital is two-fold

degenerate. If the apex angle were changed from 180°, the degeneracy must become split.
The order of decreasing binding energy of these orbitals is σ_g, σ_u, π_u.

Bent AH_2 *Molecules.*—A bent AH_2 molecule belongs to the symmetry class C_{2v}. The definitions of the symbols appropriate to the non-localized orbitals of such a molecule are given below. The z axis bisects the HAH angle and lies in the molecular plane. The y axis also lies in the molecular plane and is parallel with the $H \cdots H$ line. $C_2(z)$ means a rotation by 180° about the z axis. $\sigma_v(y)$ means a reflection in the xz plane. $+$ and $-$ mean respectively that the wave function does not or does change sign when one of the symmetry operations $C_2(z)$ or $\sigma_v(y)$ is carried out.

	$C_2(z)$	$\sigma_v(y)$
a_1	$+$	$+$
a_2	$+$	$-$
b_1 *	$-$	$+$
b_2 *	$-$	$-$

* Certain authors reverse the definitions of b_1 and b_2.

The lowest-energy intra-valency-shell orbitals of an AH_2 molecule whose apex angle is 90° are then as follows : (i) Two orbitals binding the hydrogen atoms to the central atom. These may be thought of, in the first place, as each formed by the overlap of a pure p atomic orbital on A with the $1s$ orbital of H. This would be to think of the orbitals as predominantly localized, one in each A–H distance. As with the bonding orbitals of the linear molecule, however, for discussions of spectroscopic transitions involving these orbitals they must be regarded as non-localized. The equivalent non-localized orbitals are simply the in-phase or out-of-phase combinations of the two localized orbitals, and, being no longer localized, may, by the above table of definitions, be labelled a_1 and b_2 respectively. (ii) A p orbital on atom A pointing in the x direction. The foregoing Table shows that the molecular symbol to be applied to this orbital is b_1. (iii) An s orbital on atom A. It is non-bonding. The Table shows that the molecular symbol to be applied to this orbital is a_1.

Correlation of the Orbitals for Bent and Linear Molecules.—Clearly, if the HAH angle is gradually increased, the a_1 and the b_2 bonding orbitals must eventually become the σ_g and the σ_u orbitals respectively of the linear molecule. At the same time the binding energy of the orbitals must increase. The reasons for this may be seen by thinking of the orbitals in either their localized or their non-localized forms. For the localized forms, the reasons are : (1) the orbitals are built solely from p atomic orbitals of A in the 90° molecule but partly from an s atomic orbital of A in the linear molecule; (2) an sp hybrid valency gives rise to a stronger bond than does a pure p valency (see Walsh, *Discuss. Faraday Soc.*, 1947, **2,** 18).

When considering the non-localized forms, it is convenient to form first the two possible group orbitals of the H_2 group, *viz.*, $1s + 1s$ and $1s - 1s$. To do this automatically takes account of the symmetry of the molecule. The components from which the non-localized molecular orbitals are built may then be written as follows :

Bent molecule		Linear molecule	
$1s + 1s$, a_1	p_z, a_1	$1s + 1s$, σ_g	$p_x p_x$, π_u
$1s - 1s$, b_2	p_y, b_2	$1s - 1s$, σ_u	p_y, σ_u
s_A, a_1	p_x, b_1	s_A, σ_g	

Components of the same species may then be " mixed " to form the actual molecular orbitals. This procedure leads to the same end as taking combinations of the localized orbitals. We now introduce three principles : (i) in the 90° molecule the s_A orbital does not mix (" hybridize ") with the other orbitals *; (ii) whether or not an orbital becomes more tightly bound with change of angle is determined primarily by whether or not it changes from being built from a p orbital of A to being built from an s orbital of A; and (iii) if no change of A valencies from which the orbital is built occurs when the angle is changed, the following subsidiary effect determines whether the orbital becomes more

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* Introduced to make the description of the non-localized bond orbitals consistent with that of the localized ones.

or less tightly bound : if the orbital is anti-bonding between the end atoms it is most tightly bound when the latter are as far apart as possible (*i.e.*, in the linear molecule) ; if it is bonding between the end atoms it is most tightly bound when the latter are as near together as possible (*i.e.*, in the 90° molecule). The a_1–σ_g bond orbital is thus built from a combination of $1s + 1s$ and p_z in the 90° molecule, from a combination of $1s + 1s$ and s_A in the linear molecule, and from a combination of $1s + 1s$, s_A, and p_z in the intermediate molecule. It follows that the orbital is more tightly bound in the linear than in the bent molecule. The b_2–σ_u orbital is built from a combination of the $1s - 1s$ and p_y components in both the bent and the linear molecule; but from principle (iii), it is more tightly bound in the linear molecule since it is anti-bonding between the end atoms.

Clearly, as the HAH angle is increased, the b_1 orbital of the bent molecule must become one of the two π_u orbitals of the linear molecule. To a first approximation, the orbital is the same when the apex angle is 90° as when it is 180°. We may therefore suppose its binding energy to remain approximately constant as the angle changes.
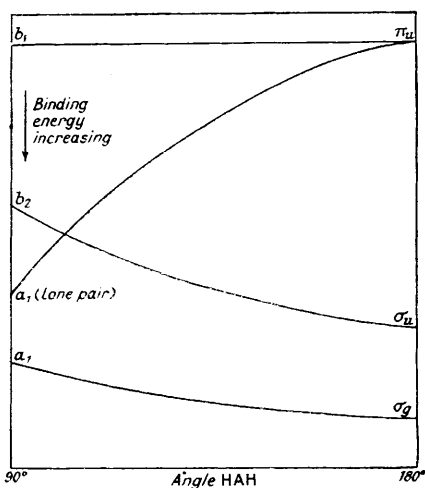
Increase of the apex angle from 90° implies mixing of the $a_1 s_A$ orbital with the $a_1 p_z$ orbital on A. The a_1 bond orbital, instead of being built from a pure p valency of A, becomes more and more built also from the s orbital of A; while at the same time the non-bonding orbital, instead of being built solely from the pure s orbital of A, becomes more and more built from a p_z orbital on A. In the linear molecule, the bonding orbital has become built from an orbital of A that is solely s, while the non-bonding orbital has become built solely from a p_z orbital of A. In other words, as the HAH angle increases from 90° to 180°, the bond orbital increases in binding energy, while the non-bonding orbital originally labelled $a_1 s_A$ decreases in binding energy until at 180° it becomes one of the degenerate π_u orbitals.

At 90° the non-bonding $a_1 s_A$ orbital must be much more tightly bound than the non-bonding $b_1 p$ orbital. Where it lies in relation to the b_2 and a_1 bond orbitals is best decided by appeal to experimental facts.

Shapes of Actual AH$_2$ *Molecules.*—The Figure is a correlation diagram between the orbitals possible for bent and linear AH$_2$ molecules. It incorporates the conclusions reached above as to whether a particular orbital rises or falls in energy as the HAH angle is changed.*

The Figure does not include *all* the possible intra-valency-shell orbitals, but only the lowest-lying ones. Two others are possible and are referred to below. There is no particular reason to make the Figure include all and only all the intra-valency-shell orbitals; for an infinite number of extra-valency-shell orbitals is also possible, the lowest of which (see the discussion below of the spectrum of water vapour) will be comparable in energy with the highest intra-valency-shell orbitals. It is just as arbitrary to make the Figure show six orbitals as to make it show four; and, indeed, for the purpose of interpreting observed spectra it is less desirable since it is the highest intra-valency-shell orbitals that are most likely to lie above or mix with the lowest extra-valency-shell orbitals. There is no doubt about the four lowest-lying orbitals—they are intra-valency-shell in type; but the fifth and sixth orbitals in order of energy are probably not both simple intra-valency-shell orbitals. A similar point should be borne in mind in reading all the

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* *Added in Proof.*—The drop from left to right of the a_1–σ_g orbital curve, due to principle (ii), is offset by a smaller rise due to principle (iii). The rise from left to right of the a_1–π_u orbital curve is not offset. The Figure has therefore been drawn with the a_1–σ_g and b_2–σ_u curves falling from left to right by similar amounts; and both falling considerably less than the a_1–π_u curve rises.

papers of this series, where the correlation diagrams show what are thought to be the lowest energy orbitals and do not necessarily include *all* the intra-valency shell orbitals.

Each of the curves must be a maximum or a minimum on the 180° line, since from 180° to 270° the curves must repeat their behaviour from 180° to 90°. The two most tightly bound orbitals have a minimum on the 180° line. One therefore expects that all AH_2 molecules containing only four valency electrons will be linear in their ground states. As far as is known, this is true. As examples, the BeH_2 and HgH_2 molecules are expected to be linear in their ground states. On the other hand, the ground states of AH_2 molecules containing 5, 6, 7, or 8 valency electrons are expected to be bent because at least one electron has to be placed in the a_1 non-bonding orbital. Similarly, the first excited state of HgH_2 or BeH_2 should be bent. This a_1 orbital rises steeply from left to right in the Figure because, as already explained, it changes from a pure *s* orbital to a pure *p* orbital. The ground state of the H_2O molecule, with eight valency electrons, has therefore a bent nuclear configuration. The CH_2 molecule, with six valency electrons, is similarly expected to be bent. The actual value of the apex angle cannot be predicted, while the Figure remains merely qualitative. If the angle is close to 180°, the ground state of the molecule may be a triplet, the configuration

$$(a_1)^2(b_2)^2(a_1)(b_1),^3B_1 \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

lying lower in energy than

$$(a_1)^2(b_2)^2(a_1)^2,^1A_1 \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

because the existence of electron repulsion offsets the small energy difference of the (a_1) and (b_1) orbitals. If, on the other hand, the apex angle is considerably less than 180°, the ground state will be a singlet, having the configuration (2). By analogy with H_2O and in view of the fact that the two most weakly bound electrons of the H_2O molecule lie in the b_1 orbital and should therefore have comparatively little effect on the apex angle, the second possibility seems the more likely.

The small decrease that has been observed in the apex angle in the series H_2O, H_2S, H_2Se, H_2Te may be due either to the a_1–π_u curve rising even more steeply or to the bonding orbital curves falling less steeply as one passes from H_2O to H_2Te. However, the total range of the decrease is only 14°.

Spectra of AH_2 *Molecules.*—(i) *Spectrum of* H_2O. In the ground state of the H_2O molecule all the orbitals represented in the Figure are fully occupied. These are the only low-lying orbitals of the molecule. No electronic spectrum of H_2O is therefore expected until comparatively short wave-lengths are reached. In agreement, the first absorption of the molecule occurs as a continuum between 1830 and 1500 Å ($\lambda_{max.}$ *ca.* 1675 Å; Hopfield, *Phys. Review*, 1950, **77**, 560).

In the Figure the b_2 and the upper a_1 curve have been drawn to cross at an angle of *ca.* 110°. The reason for this is as follows. Three ionization potentials of H_2O are known (Price and Sugden, *Trans. Faraday Soc.*, 1948, **44**, 108, 116), *viz.*, 12·61 v, 14·5 ± 0·3 v, 16·2 ± 0·3 v. A good Rydberg series is known leading to the first limit (Price, *J. Chem. Phys.*, 1936, **4**, 147). A cruder Rydberg series is also known leading to the third limit (Henning, *Ann. Physik*, 1924, **13**, 599). Rydberg series are only likely for the excitation of lone-pair electrons (or, sometimes, of weakly bonding or anti-bonding electrons); excitation of an electron from a strongly bonding orbital is hardly likely to give a series of discrete transitions. For this reason it seems best to interpret the first and third limits as due respectively to ionization from the (b_1) and (a_1) lone-pair orbitals; leaving the second limit to represent ionization of the (b_2) bonding electrons. The ground state configuration of H_2O is therefore written as $(a_1)^2(a_1)^2(b_2)^2(b_1)^2$ instead of $(a_1)^2(b_2)^2(a_1)^2(b_1)^2$. The main conclusions of this paper would not, however, be altered if the order of the (a_1) and (b_2) orbitals were reversed.*

Two intra-valency-shell orbitals other than those shown in the Figure are possible. These are highly anti-bonding in nature, being obtained by considering out-of-phase overlap of an oxygen valency with the hydrogen 1*s* valency. The lower of the two is of

* Price and Sugden (*loc. cit.*) assume that (b_2) is more tightly bound than (a_1).

species $\bar{a}_1$–σ_g, where the bar indicates the anti-bonding nature. For spectroscopic purposes it must be considered as non-localized and therefore built by the in-phase overlap of the two hydrogen $1s$ atomic orbitals, these interacting out-of-phase with an oxygen valency that is $2s$ in the linear molecule and $2p_z$ in the 90° molecule. Because of its anti-bonding nature, it may well lie so high that transition to it requires as much energy as transition to the lowest extra-valency-shell (Rydberg) orbital. In other words, the longest wave-length allowed transition of H_2O may be formulated

$$(a_1)^2(a_1)^2(b_2)^2(b_1)(a_1),{}^1B_1 \longleftarrow (a_1)^2(a_1)^2(b_2)^2(b_1)^2,{}^1A_1$$
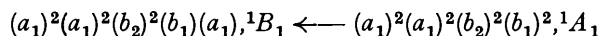
where the uppermost (a_1) orbital refers either to the anti-bonding intra-valency-shell orbital or to the $3s$ orbital of the oxygen atom. The 1830—1500-Å absorption has already been interpreted as due to transition of an electron from (b_1) to $(3sa_1)$ (Mulliken, *J. Chem. Phys.*, 1935, **3**, 506; Price, Teegan, and Walsh, *Proc. Roy. Soc.*, 1950, *A*, **201**, 600). Its continuous nature, however, makes it best considered as involving also transition to a repulsive upper state containing an electron in the anti-bonding $(\bar{a}_1)$ orbital (cf. Walsh, unpublished work).

According to Wilkinson and Johnston (*J. Chem. Phys.*, 1950, **18**, 190) the absorption actually consists of three diffuse bands superimposed on a continuum. Rathenau (*Z. Physik*, 1934, **87**, 32) had earlier found structure in the continuum, stating that a frequency difference ~1300 cm.$^{-1}$ was present. The diffuse bands found by Wilkinson and Johnston are at 1608, 1648, and 1718 Å. It is possible that they represent the Rydberg transition while the continuum represents the intra-valency-shell transition. The maximum molecular extinction coefficient is about 1000.* It seems therefore that the transition(s) must be regarded as allowed, in agreement with the present assignments. Because of this, one expects either or both of the two totally symmetrical vibrational frequencies of the upper state to appear in the spectrum. It is possible that the separation of the 1608 and the 1648 Å band (1520 cm.$^{-1}$) represents the bending vibration ν_2 (1595 cm.$^{-1}$ in the ground state), and that the separation of the 1608 and the 1718 Å band (3388 cm.$^{-1}$) represents the stretching vibration ν_1 (3655 cm.$^{-1}$ in the ground state). The smallness of the reductions in these frequencies from the ground-state values would accord with only one quantum of each vibration appearing. It seems that comparatively little change of the molecular dimensions occurs on excitation, in agreement with the transition being of an electron from one non-bonding orbital (whose binding energy changes little with change of HOH angle) to another.

(ii) *Spectrum of* NH_2. In the ground state of the NH_2 radical only one electron lies in the (b_1) orbital. A long-wave-length transition

$$\cdots (a_1)(b_1)^2,{}^2A_1 \longleftrightarrow \cdots (a_1)^2(b_1),{}^2B_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$
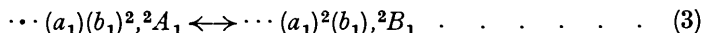
should therefore be possible. It represents an allowed transition. The further, long-wave-length, transition

$$\cdots (b_2)(b_1)^2,{}^2B_2 \longleftrightarrow \cdots (b_2)^2(b_1),{}^2B_1$$
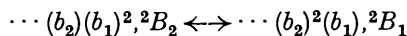
is forbidden. The allowed transition should be polarized in the x direction, *i.e.*, perpendicularly to the molecular plane. Since the transition involves transfer of an electron from the orbital represented in the Figure by the steep a_1–π_u curve to the orbital represented by the approximately horizontal b_1–π_u line, it should result in an increase of the apex angle in the equilibrium form of the upper state. On the other hand, since the (a_1) and the (b_1) orbital are non-bonding, there should be little change of N–H length.

The so-called " ammonia α " band, lying in the visible region, has long been attributed (though without proof) to the NH_2 radical. It was first observed by Eder (*Denkschr.*

* Wilkinson and Johnston record intensities in terms of the atmospheric absorption coefficient at 30° c. Their values have been multiplied by $(22\cdot4 \times 303)/(2\cdot30 \times 273)$ in order to obtain molecular extinction coefficients. The present discussion assumes that the bands observed by them in the continuum are not due to impurities. There is some doubt of this, however, since Rathenau's findings are not entirely in agreement with those of Wilkinson and Johnston.

Wien. Akad., 1893, **60**, 1) in the ammonia–oxygen flame. It was later found to occur (more weakly) in the spectrum of an uncondensed discharge through ammonia (Rimmer, *Proc. Roy. Soc.*, 1923, *A*, **103**, 696). The latter method of obtaining it supports the identification of the emitter as a decomposition product of NH_3. The band also occurs in the spectra of the hydrogen–nitrous oxide (Fowler and Badami, *ibid.*, 1931, *A*, **133**, 325; Gaydon, *ibid.*, 1942, *A*, **181**, 197) and the methane–nitrous oxide flames (Gaydon, *loc. cit.*). Infra-red bands observed in the spectrum of the former flame have been provisionally assigned to an extension of the band (Gaydon, *loc. cit.*). Rimmer's high-resolution photographs showed the great complexity of the band and the many lines (some 3000) present. The fine structure appears much too complex for the emitter to be the diatomic radical NH. Its attribution to NH_2 therefore seems very plausible. If the attribution is correct, then the interpretation of the band can hardly be other than as the emission transition (3). Analysis of the observed rotational structure should proceed in the light of the expectations formulated above.* That the structure should be so complex is not surprising (i) if the HNH angle is such that the molecule is not even an approximate symmetric top † and (ii) if, as expected here, the apex angle changes markedly in the transition.

(iii) *Spectrum of* CH_2. If the ground state of the molecule is a singlet, then the following is the longest-wave-length absorption transition :

$$K^2(a_1)^2(b_2)^2(a_1)(b_1),{}^1B_1 \longleftarrow K^2(a_1)^2(b_2)^2(a_1)^2,{}^1A_1$$
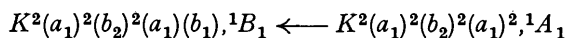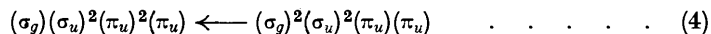
Mulliken (quoted by Venkateswarlu, *Phys. Review*, 1950, **77**, 676) has earlier made the same assignment. The transition is allowed, with polarization perpendicular to the main symmetry axis. It should probably occur at quite long wave-lengths (cf. the supposed NH_2 transition above). It would result in an increase of apex angle in the equilibrium form of the upper state. On the other hand, there should be little change of C–H length. The Figure thus enables very specific statements to be made about the expected spectrum of CH_2, which should be helpful in the search currently being undertaken in various laboratories for that spectrum.
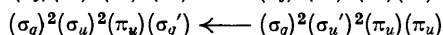
It is worth noting what the expectations would be if the ground state of the CH_2 molecule should turn out to be a triplet. This implies that the molecule is nearly linear in the ground state and we shall therefore use the $\sigma, \pi, \cdots$ nomenclature for its orbitals. Consider only transitions with no change of multiplicity : the lowest energy transition, *viz.*,

$$(\sigma_g)^2(\sigma_u)(\pi_u)^2(\pi_u),{}^3\Pi_g \longleftarrow (\sigma_g)^2(\sigma_u)^2(\pi_u)(\pi_u),{}^3\Sigma_g^-$$
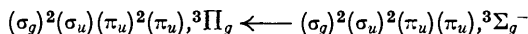
is forbidden. There will be no allowed transitions until comparatively short wave-lengths (probably, by analogy with H_2O, not until wave-lengths <2500 Å). The longest wave-length allowed transition will be ${}^3\Pi_u \longleftarrow {}^3\Sigma_g^-$ whose interpretation may be

$$(\sigma_g)(\sigma_u)^2(\pi_u)^2(\pi_u) \longleftarrow (\sigma_g)^2(\sigma_u)^2(\pi_u)(\pi_u) \qquad \cdots \cdots \quad (4)$$

or

$$(\sigma_g)^2(\sigma_u)^2(\pi_u)(\sigma_g') \longleftarrow (\sigma_g)^2(\sigma_u')^2(\pi_u)(\pi_u)$$

where (σ_g') stands for either the 3*s* carbon atom orbital or the anti-bonding orbital referred to above in the discussion of the H_2O spectrum.

If the CH_2 molecule is found to have a strong transition at wave-lengths considerably longer than 2500 Å, it should be safe to conclude that (*a*) the apex angle in the ground state is considerably less than 180° and (*b*) the ground state is a singlet.

* Since this paper was written, Dr. D. A. Ramsay has informed me that Professor Herzberg and he have now (*a*) proved that the ammonia α bands are due to NH_2, (*b*) obtained the system in absorption between 4500 and 7400 Å, and (*c*) shown, in agreement with the present expectations, that the upper and the lower state differ considerably in the geometrical arrangement of the nuclei (see Herzberg and Ramsay, *J. Chem. Phys.*, 1952, **20**, 347; *Discuss. Faraday Soc.*, 1953, **14**, 11). Dr. Ramsay has also pointed out to me that the same assignment of the bands as made here has been given earlier by Mulliken and quoted as a personal communication in a paper by Swings, McKellar, and Minkowski (*Astrophys. J.*, 1943, **98**, 142).

† According to the Figure the apex angle in the ground state should be close to that of the H_2O molecule.

Relation to Other Work.—In the following papers we shall show that, as with AH_2 molecules, the shape of a molecule in its ground state depends primarily on the number of valency electrons. In general terms, the recognition of this is of course not new (see, *e.g.*, Cassie, *Nature*, 1933, **131**, 438; Penney and Sutherland, *Proc. Roy. Soc.*, 1936, *A,* **156**, 654), though the newer data now available frequently enable the older generalizations to be extended and made more precise. There seems, however, to have been only one previous attempt to plot a correlation diagram between the orbitals possible for a polyatomic molecule in each of two nuclear configurations, and to use such a diagram to discuss both the shapes (in excited as well as ground states) and electronic spectra of molecules. This was by Mulliken (*Rev. Mod. Phys.*, 1942, **14**, 204) who plotted a correlation diagram for the limited case of AB_2 molecules. He did not specifically apply his diagram to AH_2 molecules. He also said that he was unable to give any simple explanation of why particular curves should rise or fall with increase of angle. His diagram was either empirical or based upon unpublished computations.

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