

Factors determining bond angles from a classical valence bond perspective. Covalent structure of H₂O

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We identify the energy contributions that govern the interorbital and internuclear angles in the classical covalent structure of H₂O. The central atom valence state term plays a primary role in H₂O and other AH₂ molecules as well. Lone pair interactions of three different types are also of major significance.

Key words: Classical valence bond theory — Bond angles — Valence state energy — Water

1. Introduction

In a number of recent studies [1-3] it has been shown that, as the internuclear angle varies away from equilibrium in a series of AH_n molecules, the optimum hybrid bond orbitals at the central atom remain essentially fixed in direction. This "orbital stasis" phenomenon suggests that the angle between the hybrids and, hence, the equilibrium internuclear angle may depend to a far greater extent on some atomic property than has, heretofore, been appreciated.

The most appropriate theoretical framework for investigating such a question is the valence bond model of electronic structure since it gives the hybrid bond orbitals directly without requiring an arbitrary localization procedure. This model has been used, from an intuitive point of view, as the basis of VSEPR theory [4]. According to the latter the equilibrium internuclear angle is determined by repulsions between electrons in the various bond and lone pair orbitals. It is assumed that the angle between the bond orbitals is coincident with the angle

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between nuclei. Although VSEPR theory has had much success, quantitative investigations have revealed that its basic assumptions are invalid [5]. Thus, there is a clear need for an explanation of the equilibrium internuclear angle which is consistent with the results of *ab initio* valence bond computations.

Recently, some progress has been made along these lines [6] using a generalized valence bond description of second row AH_2 molecules. In that description the number of σ lone pair electrons (in a symmetry constrained wavefunction) turns out to be crucial. Here, however we wish to utilize the "classical" valence bond treatment of Heitler, London, Slater, and Pauling (HLSP) to examine, particularly, the covalent structure of H_2O .

Not surprisingly, the HLSP wavefunction leads to a perspective on the factors governing orbital and nuclear angles that is rather different from the one which emerges from the generalized valence bond analysis mentioned above. We are hopeful that the two viewpoints will complement one another just as the molecular orbital Walsh rules complement VSEPR theory.

Our anatomization of the HLSP wavefunction reveals that certain lone pair interactions are of particular importance for both the orbital and nuclear geometry. But the classical analysis shows that valence state energies are probably more significant. We have found that for second row AH_2 molecules in general there is a correlation between the equilibrium internuclear angle and the minimum in the valence state energy of the neutral central atom. This can be rationalized on the grounds that the valence state energy plays the major role in determining the angle between the hybrid orbitals and that the nuclei follow these orbitals (even though, when the situation is reversed, the orbitals do *not* follow the nuclei).

2. Computational details

In the computations described here we have used the experimental O-H distance of [7] $1.8111a_0$. Calculations were performed for H-O-H angles of 90° , 95° , 100° , 105° , 110° , 120° , 150° , and 180° . For the oxygen atom a double-zeta basis set with the best atom orbital exponents of Huzinaga and Arnau [8] was employed. For the hydrogen $1s$ orbital the exponent was taken to be 1.2. This basis was contracted to a $2s, 1p/1s$ set using Huzinaga and Arnau's atomic wavefunctions. The integrals were obtained by means of Stevens' program [9].

As we will see later the above basis set, in conjunction with the classical covalent wavefunction, reproduces the experimental equilibrium angle quite well and gives the vibrational force constant with reasonable accuracy. Although the hybrid bond orbitals are only slightly bent at equilibrium, they remain almost stationary in direction over a wide range of internuclear angles as found in other calculations.

3. Covalent structure of H_2O

For H_2O the classical perfect-pairing covalent wavefunction, including only valence orbitals, may be written as:

$$\psi_{\text{H}_2\text{O},\text{cov}} = N[|l_1 \bar{l}_1 l_2 \bar{l}_2 b_1 b_2 \bar{h}_1 \bar{h}_2| - |l_1 \bar{l}_1 l_2 \bar{l}_2 \bar{b}_1 b_2 h_1 \bar{h}_2| - |l_1 \bar{l}_1 l_2 \bar{l}_2 b_1 \bar{b}_2 \bar{h}_1 h_2| + |l_1 \bar{l}_1 l_2 \bar{l}_2 \bar{b}_1 \bar{b}_2 h_1 h_2|]. \quad (1)$$

In Eq. (1) the oxygen orbitals are a set of mutually orthogonal hybrids of the form

$$\begin{aligned} b_1 &= \frac{1}{\sqrt{2}} [\sqrt{1-\alpha^2} s + p_y + \alpha p_x] \\ b_2 &= \frac{1}{\sqrt{2}} [\sqrt{1-\alpha^2} s - p_y + \alpha p_x] \\ l_1 &= \frac{1}{\sqrt{2}} [\alpha s + p_z - \sqrt{1-\alpha^2} p_x] \\ l_2 &= \frac{1}{\sqrt{2}} [\alpha s - p_z - \sqrt{1-\alpha^2} p_x] \end{aligned} \quad (2)$$

where b_1 and b_2 are the bonding orbitals while l_1 and l_2 are the lone pairs. Here x is the symmetry axis and, for convenience, b_1 and b_2 are taken to be in the xy plane. The hybridization parameter α is equal to $\cot(\theta_{\text{orb}}/2)$, where θ_{orb} is the angle between the bond orbitals. Thus, the hybridization and orbital angle are not separately variable.

To simplify the energy expression and its interpretation each hydrogen orbital was orthogonalized to all other orbitals except for the oxygen hybrid to which it is paired. In doing so the two hydrogen orbitals were constrained to be symmetrically equivalent. This results in a set of non-linear simultaneous equations for the mixing coefficients which were solved numerically. The above strong orthogonality restriction leaves only one overlap integral $S(b_1, h_1) = S(b_2, h_2) = S$ different from zero. Neither the total energy [10] nor the bending potential is significantly affected. A symmetric orthogonalization was not done because, from our viewpoint (as discussed in the Introduction) it was desirable to maintain the integrity of the central atom orbitals. For reasons analogous to those just cited, and with similar effect, the $1s$ core orbital on oxygen was orthogonalized to all the valence orbitals.

For the hydrogen molecule the energy formula corresponding to the classical covalent VB wavefunction, i.e.

$$\psi_{\text{H}_2,\text{cov}} = \frac{1}{\sqrt{2(1+S^2)}} [|\phi_a \bar{\phi}_b| - |\bar{\phi}_a \phi_b|] \quad (3)$$

is sometimes written as:

$$E_{\text{H}_2,\text{cov}} = E_a + E_b + \frac{J_{ab} + K_{ab}}{1 + S^2} \quad (4)$$

where

$$J_{ab} = \langle aa|bb \rangle - \langle a|\frac{1}{r_B}|a \rangle - \langle b|\frac{1}{r_A}|b \rangle + \frac{1}{R_{AB}},$$

$$K_{ab} = \langle ab|ba \rangle + 2S \left[\langle a|-\frac{1}{2}\nabla^2|b \rangle - \langle a|\frac{1}{r_A}|b \rangle - \langle a|\frac{1}{r_B}|b \rangle \right] + \frac{S^2}{R_{AB}},$$

and E_a, E_b are the molecular valence-state energies (including normalization) of atoms A and B. This formalism lumps one-electron and nuclear repulsion terms together with two-electron contributions. The quantity $J_{ab} + K_{ab}$ is indicative of an attractive bonding interaction between electrons in atomic orbitals a and b . On the other hand $J_{ab} - K_{ab}$ would be indicative of a repulsive antibonding interaction while $J_{ab} - 1/2 K_{ab}$ would correspond to a nonbonding interaction. The terms in the energy expression for H₂O can be combined in a similar manner to yield a sum of valence state energies, bonding, and nonbonding interactions.

There are, all together, twelve separable contributions to the energy of the covalent structure of H₂O as obtained for wavefunction (1). These include the valence state terms for oxygen and hydrogen and a bond pair term for the two OH bonds. The remainder consists of various non-bonded interactions. All twelve contributions are given below.

1. Oxygen molecular valence state term

$$E_{vs}^{\text{mol}}(\text{O}) = E_{\text{core}} + 2\langle l_1|-\frac{1}{2}\nabla^2 - \frac{Z_{\text{O}}}{r_{\text{O}}} + V_{\text{core}}|l_1 \rangle + 2\langle l_2|-\frac{1}{2}\nabla^2 - \frac{Z_{\text{O}}}{r_{\text{O}}} + V_{\text{core}}|l_2 \rangle$$

$$+ \langle l_1 l_1|l_1 l_1 \rangle + 4\langle l_1 l_1|l_2 l_2 \rangle - 2\langle l_1 l_2|l_2 l_1 \rangle + \langle l_1 l_2|l_2 l_1 \rangle$$

$$+ \left[\langle b_1|-\frac{1}{2}\nabla^2 - \frac{Z_{\text{O}}}{r_{\text{O}}} + V_{\text{core}}|b_1 \rangle + \langle b_2|-\frac{1}{2}\nabla^2 - \frac{Z_{\text{O}}}{r_{\text{O}}} + V_{\text{core}}|b_2 \rangle \right.$$

$$+ 2\langle b_1 b_1|l_1 l_1 \rangle - \langle b_1 l_1|l_1 b_1 \rangle + 2\langle b_1 b_1|l_2 l_2 \rangle - \langle b_1 l_2|l_2 b_1 \rangle$$

$$+ 2\langle b_2 b_2|l_1 l_1 \rangle - \langle b_2 l_1|l_1 b_2 \rangle + 2\langle b_2 b_2|l_2 l_2 \rangle - \langle b_2 l_2|l_2 b_2 \rangle \left. \right] (1 + S^2)^{-1}$$

$$+ [\langle b_1 b_1|b_2 b_2 \rangle - \frac{1}{2}\langle b_1 b_2|b_2 b_1 \rangle] (1 + S^2)^{-2} \quad (5)$$

where

$$E_{\text{core}} = 2\langle 1s_{\text{O}}|-\frac{1}{2}\nabla^2 - \frac{Z_{\text{O}}}{r_{\text{O}}}|1s_{\text{O}} \rangle + \langle 1s_{\text{O}}1s_{\text{O}}|1s_{\text{O}}1s_{\text{O}} \rangle,$$

and, in general,

$$\langle \phi|V_{\text{core}}|\phi \rangle = 2\langle \phi\phi|1s_{\text{O}}1s_{\text{O}} \rangle - \langle \phi 1s_{\text{O}}|1s_{\text{O}}\phi \rangle.$$

The electrons in the orthogonalized oxygen 1s orbital, $1s_{\text{O}}$, have been included as a core potential in order to simplify Eq. (5). If S is set equal to zero we get an atomic valence state energy which will be denoted $E_{\text{vs}}^{\text{atom}}(\text{O})$.

2. Bond pair term

$$E_{bp} = (J_{b_1h_1} + K_{b_1h_1} + J_{b_2h_2} + K_{b_2h_2}) / (1 + S^2) \quad (6)$$

where

$$J_{b_1h_1} = \langle b_1 b_1 | h_1 h_1 \rangle - \langle b_1 | \frac{1}{r_{H1}} | b_1 \rangle - \langle h_1 | \frac{1}{r_O} | h_1 \rangle + \frac{1}{R_{OH}},$$

and

$$K_{b_1h_1} = \langle b_1 h_1 | h_1 b_1 \rangle + 2S \langle b_1 | -\frac{1}{2}\nabla^2 - \frac{1}{r_{H1}} - \frac{1}{r_O} | h_1 \rangle + \frac{S^2}{R_{OH}}.$$

Note that $J_{b_1h_1}$ and $K_{b_1h_1}$ are identical in form to the corresponding integrals in Eq. (4). Thus, E_{bp} is the energy of the two covalent O-H single bonds.

3. Nonbonding interaction between bond hybrid and hydrogen

$$E_{b-h} = (J_{b_1h_2} - \frac{1}{2}K_{b_1h_2} + J_{b_2h_1} - \frac{1}{2}K_{b_2h_1}) / (1 + S^2)^2. \quad (7)$$

Here $J_{b_1h_2}$ has the same form as $J_{b_1h_1}$, but $K_{b_1h_2}$ is simply equal to $\langle b_1 h_2 | h_2 b_1 \rangle$ since $S(b_1, h_2)$ is zero. A similar comment applies to the exchange contribution in all the remaining terms.

4. Lone pair-hydrogen interaction

$$E_{lp-h} = (2J_{l_1h_1} - K_{l_1h_1} + 2J_{l_1h_2} - K_{l_1h_2} + 2J_{l_2h_1} - K_{l_2h_1} + 2J_{l_2h_2} - K_{l_2h_2}) / (1 + S^2). \quad (8)$$

5. Core-hydrogen interaction

$$E_{core-h} = (2J_{1s_Oh_1} - K_{1s_Oh_1} + 2J_{1s_Oh_2} - K_{1s_Oh_2}) / (1 + S^2). \quad (9)$$

6. Hydrogen molecular valence state term

$$E_{vs}^{\text{mol}}(\text{H}) = \left[\langle h_1 | -\frac{1}{2}\nabla^2 - \frac{1}{r_{H1}} | h_1 \rangle + \langle h_2 | -\frac{1}{2}\nabla^2 - \frac{1}{r_{H2}} | h_2 \rangle \right] / (1 + S^2). \quad (10)$$

It should be remembered here that h_1 is not simply a hydrogen 1s orbital but, due to orthogonalization, it is a combination which includes oxygen orbitals and the hydrogen 1s centred on the other nucleus. For instance, for H-O-H = 105° and $\alpha = 0.9$

$$h_1 = 1.068h'_1 - 0.072h'_2 - 0.228l_1 - 0.228l_2 - 0.038b_2 \quad (11)$$

where the prime indicates the original nonorthogonal orbitals. Without orthogonalization a substantial portion of the hydrogen molecular valence state energy would serve merely to cancel extra terms in the energy expression due to overlap repulsion, particularly between the hydrogen 1s orbitals and the lone pairs.

7. Nonbonding hydrogen-hydrogen interaction

$$E_{h-h'} = (J_{h_1 h_2} - \frac{1}{2} K_{h_1 h_2}) / (1 + S^2)^2 \quad (12)$$

The five remaining contributions are due to the charge distribution $b_1 h_1$ (or $b_2 h_2$) which is associated with electron exchange between the two orbitals of the bond. Our scheme for grouping the one- and two-electron parts here is in keeping with the Mulliken approximation [11] $b_1 h_1 \sim 1/2 S [b_1 b_1 + h_1 h_1]$. Thus, we write

8. Bond pair-atomic hybrid exchange interaction

$$E_{bp-b'} = S(2J_{bp_1 b_2} - K_{bp_1 b_2} + 2J_{bp_2 b_1} - K_{bp_2 b_1}) / (1 + S^2)^2 \quad (13)$$

in which

$$J_{bp_1 b_2} = \langle b_1 h_1 | b_2 b_2 \rangle - \frac{1}{2} S \langle b_2 | \frac{1}{r_{H1}} | b_2 \rangle - \langle b_1 | \frac{1}{r_O} | h_1 \rangle + \frac{1}{2} \frac{S}{R_{OH}}$$

and $K_{bp_1 b_2} = \langle b_1 b_2 | b_2 h_1 \rangle$.

9. Bond pair-hydrogen exchange interaction

$$E_{bp-h'} = S(2J_{bp_1 h_2} - K_{bp_1 h_2} + 2J_{bp_2 h_1} - K_{bp_2 h_1}) / (1 + S^2)^2 \quad (14)$$

where

$$J_{bp_1 h_2} = \langle b_1 h_1 | h_2 h_2 \rangle - \frac{1}{2} S \langle h_2 | \frac{1}{r_O} + \frac{1}{r_{H1}} | h_2 \rangle - \langle b_1 | \frac{1}{r_{H2}} | h_1 \rangle + \frac{1}{2} S \left(\frac{1}{R_{OH}} + \frac{1}{R_{H1H2}} \right)$$

and $K_{bp_1 h_2} = \langle b_1 h_2 | h_2 h_1 \rangle$.

10. Bond pair-lone pair exchange interaction

$$E_{bp-lp} = 2S(2J_{bp_1 l_1} - K_{bp_1 l_1} + 2J_{bp_1 l_2} - K_{bp_1 l_2} + 2J_{bp_2 l_2} - K_{bp_2 l_2} + 2J_{bp_2 l_1} - K_{bp_2 l_1}) / (1 + S^2) \quad (15)$$

with

$$J_{bp_1 l_1} = \langle b_1 h_1 | l_1 l_1 \rangle - \frac{1}{2} S \langle l_1 | \frac{1}{r_{H1}} | l_1 \rangle - \langle b_1 | \frac{1}{r_O} | h_1 \rangle + \frac{1}{2} \frac{S}{R_{OH}}$$

and $K_{bp_1 l_1} = \langle b_1 l_1 | l_1 h_1 \rangle$.

11. Bond pair-bond pair exchange interaction

$$E_{bp-bp'} = S^2(4J_{bp_1 bp_2} - 2K_{bp_1 bp_2}) / (1 + S^2)^2 \quad (16)$$

where

$$J_{bp_1bp_2} = \langle b_1h_1|b_2h_2 \rangle - \frac{1}{2}S \left[\langle b_1|\frac{1}{r_O} + \frac{1}{r_{H2}}|h_1 \rangle + \langle b_2|\frac{1}{r_O} + \frac{1}{r_{H1}}|h_2 \rangle \right] \\ + \frac{1}{4}S^2 \left[\frac{1}{R_{H1H2}} + \frac{2}{R_{OH}} \right]$$

and $K_{bp_1bp_2} = \langle b_1h_2|b_2h_1 \rangle$. Finally, we have the

12. Bond pair-core exchange interaction

$$E_{bp-core} = 2S(J_{bp_1s_O} - K_{bp_1s_O} + 2J_{bp_2s_O} - K_{bp_2s_O}) / (1 + S^2) \quad (17)$$

in which

$$J_{bp_1s_O} = \langle b_1h_1|1s_O1s_O \rangle - \frac{1}{2}S \langle 1s_O|\frac{1}{r_{H1}}|1s_O \rangle - \langle b_1|\frac{1}{r_O}|h_1 \rangle + \frac{1}{2} \frac{S}{R_{OH}}$$

and $K_{bp_1s_O} = \langle b_11s_O|1s_Oh_1 \rangle$.

The total energy of the covalent structure, $E_{cov}(H_2O)$, is the sum of Eqs. (5)–(10) plus (12)–(17).

4. Discussion

For a constant O-H bond length, $E_{cov}(H_2O)$ is a function of (i) the hybrid orbital parameter α , and (ii) the H-O-H angle θ_{nuc} . The equilibrium geometry is determined by the fact that the energy is a minimum with respect to variations in both α and θ_{nuc} . By varying α with θ_{nuc} fixed at the equilibrium value one can find out what the various energy components contribute to θ_{orb} . The variation of θ_{nuc} with α fixed at the optimum value, α^{opt} , yields an analogous analysis of the internuclear angle.

We give α^{opt} (and the corresponding θ_{orb}) in Table 1 as a function of internuclear angle. Over the range from 90° to 120° the optimum hybrid angle θ_{orb} changes

Table 1. Optimum hybrid orbital angle and energy as a function of internuclear angle

Internuclear angle	α^{opt}	Optimum hybrid angle	E (Hartree)
90°	0.929	94.2	-75.8181
95°	0.918	94.9	-75.8233
100°	0.908	95.5	-75.8261
105°	0.899	96.1	-75.8269
110°	0.890	96.7	-75.8257
120°	0.871	97.9	-75.8168
150°	0.709	109.3	-75.7595
180°	0.000	180.0	-75.7087

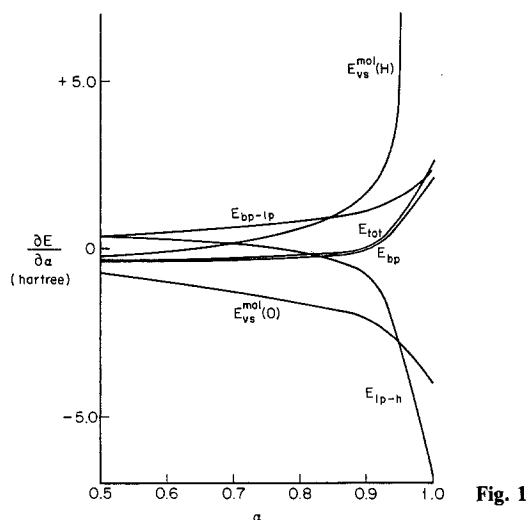


Fig. 1

by less than 4° . This is the orbital stasis phenomenon. The total energy is a minimum at $\theta_{\text{nuc}} = 104.4^\circ$ which may be compared with the observed [7] equilibrium angle of 104.5° . A quadratic fit to the energies calculated at the three angles nearest equilibrium yields a force constant that is higher than experiment [12] (0.078 vs. 0.049 a.u.) but in close agreement with other valence bond [13] and molecular orbital [14] calculations.

In Fig. 1 we have plotted $\partial E/\partial\alpha$ evaluated at the equilibrium internuclear angle (actually, for convenience, at 105°) versus α for the various energy components. As noted in an earlier paper [15] it is more appropriate to consider $\partial E/\partial\alpha$ than E because the variation condition applies particularly to the derivative. With one exception only those energy components that have large derivatives in the vicinity of α^{opt} are shown. There are four of them. The oxygen valence state energy has the largest magnitude and for it, together with the lone pair-hydrogen interaction, $\partial E/\partial\alpha < 0$. These terms lower the curve for the total energy derivative and thereby tend to increase α^{opt} or, equivalently, favor a smaller interorbital angle. The effect is opposite to that of the other two significant terms, namely the hydrogen valence state energy and the bond pair-lone pair exchange interaction.

The bond pair-lone interaction term arises because of the overlap between the two bonded orbitals (i.e. b_1 and h_1). If this overlap were reduced the interaction term would diminish and the interorbital angle would be smaller.

The large effect of the hydrogen valence state energy is due primarily to orthogonalizing the hydrogen orbitals to the lone pairs. Consequently, there is a strong tendency for this valence state term to cancel with the lone pair-hydrogen interactions. A like tendency is observed for the bond pair-lone pair and oxygen molecular valence state curves.

Over the entire range of α shown in Fig. 1 the bond-pair and total energy derivatives are remarkably close to one another. It would be inappropriate,

however, to conclude that α^{opt} is determined by bond-pair interactions since there are other much larger contributions to $\partial E/\partial\alpha$, at least in the vicinity of the energy minimum. If it turns out that the correspondence between these two curves is preserved for other molecules as well, then a more rigorous explanation for the near-cancellations will have to be found.

A similar situation exists at other internuclear angles. In fact, Fig. 1 may be taken as representative of all θ_{nuc} between 90° and 150° .

Due to the constrained form of the classical HLSP valence bond wavefunction its minimum energy is ~ 0.14 hartrees higher than that of the molecular orbital wavefunction although the calculated HLSP equilibrium internuclear angle agrees somewhat better with experiment (the molecular orbital result is 108.5°). Inclusion of the ionic O^- structure [16] lowers the valence bond energy by more than 0.14 hartrees but does not substantially affect the bending potential.

The optimum internuclear angle for a given α (or θ_{orb}) is displayed in Table 2. Over a wide range of θ_{orb} the optimum θ_{nuc} remains 7–9° larger. Hence, the nuclei follow the orbitals even though the orbitals do not follow the nuclei! In Fig. 2 we present a plot of $\partial E/\partial\theta_{\text{nuc}}$ versus θ_{nuc} for several energy components. Here $\alpha = 0.90$ which is the optimum value at equilibrium and is also very close to being optimum at all internuclear angles between 90° and 120° . Only three components are of significance in this angular region. They are the same ones mentioned previously except that, in this case, the oxygen valence state energy is unimportant. Again, the hydrogen valence state energy term and the lone pair-hydrogen interaction oppose one another. Both of them have an effect on θ_{nuc} which is opposite to their effect on θ_{orb} . The hydrogen valence state energy, for example, causes the internuclear angle to be smaller than it would otherwise be. The bond pair-lone pair exchange interaction is relatively less significant than before; it now acts in concert with the other lone pair interaction term.

We conclude that both the orbital and internuclear angles in the covalent structure of H_2O are governed by valence state energies and by lone pair interactions with either the hydrogens or the bond pairs. The bond pair interaction is due to exchange between the two bonded orbitals. Indirectly the oxygen lone pairs also

Table 2. Optimum internuclear angle as a function of hybrid orbital angle

α	Hybrid angle	Optimum internuclear angle	Energy (Hartree)	Internuclear angle – hybrid angle
1.00	90.0°	92.1°	-75.7412	2.1°
0.95	92.9°	100.1°	-75.8227	7.1°
0.90	96.0°	104.4°	-75.8269	8.4°
0.85	99.3°	108.2°	-75.8224	8.9°
0.80	102.7°	111.7°	-75.8147	9.0°
0.70	110.0°	118.6°	-75.7960	8.6°
0.60	118.1°	125.4°	-75.7769	7.4°
0.50	126.9°	132.2°	-75.7591	5.4°

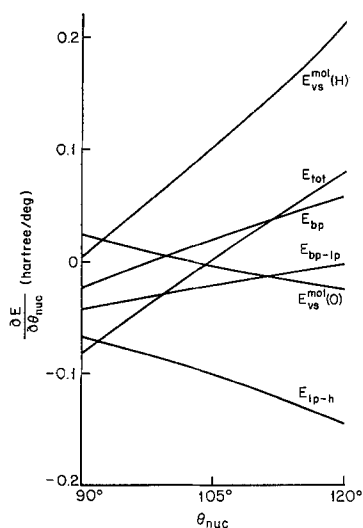


Fig. 2

play a major role in the hydrogen valence state term through the orthogonality requirement on the original hydrogen orbitals.

A similar analysis can be applied to other AH_2 molecules. We have calculated just one of the terms, namely the valence state energy of the central atom in the second row series from Be to O. Table 3 lists the hybrid orbital angle implied by the minimum in this energy component. Since ionic structures may contribute significantly in the molecule, the singly-charged species A^+ and A^- are included along with neutral A. Only in the case of the 2A_1 state of BH_2 and the 3B_1 state of CH_2 do the ionic and covalent structures give different minima. A correlation may be seen between the experimental internuclear angle and the orbital angle obtained for the covalent structure. (The relatively large difference for CH_2 between the observed angle and the angle predicted on the basis of a pure covalent molecule is probably due to the important role of the A^- structure.)

Table 3. Hybrid orbital angle corresponding to minimum in central atom valence state energy of first row AH_2 molecules

Molecule	State	Experimental internuclear angle	Hybrid orbital angle for minimum in valence state energy		
			A	A^+	A^-
BeH_2	${}^1\Sigma_g^+$	180°	180°	180°	180°
BH_2	2A_1	131°	120°	90°	180°
	2B_1	180°	180°	180°	180°
CH_2	3B_1	136°	109.5°	90°	180°
	1A_1	102.4°	90°	90°	90°
NH_2	2B_1	103.4°	90°	90°	90°
OH_2	1A_1	104.5°	90°	90°	90°

We may rationalize the observed correlation as follows. The central atom valence state energy exerts the primary influence in determining the optimum θ_{orb} . Once θ_{orb} has been found, then θ_{nuc} follows closely along as noted in our discussion of Table 2. The hydrogen valence state energy and the relevant lone pair interactions must also be taken into account but they do not alter the overall correlation.

We have identified the energy terms that govern the interorbital and internuclear angle in the classical covalent structure of H_2O . Our analysis directs attention to the primary role of the oxygen valence state energy. In addition, the lone pairs are of major significance through (i) direct interaction with the hydrogens, (ii) exchange terms involving the bond pairs, and (iii) the indirect effect on the hydrogen valence state energy due to orthogonalizing the hydrogen orbitals.

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