Theoret. Chim. Acta (Berl.) 46, 165–172 (1977)

THEORETICA CHIMICA ACTA

Valence-Bond Studies of AH_2 Molecules

II. Minimal STO Basis Set Calculations on H_2O*

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Minimal Slater basis set valence-bond calculations on the ${}^1A_1$ ground state of H_2O are reported. Determinants built up from both natural and hybrid orbitals were used. The calculations were performed at $\widehat{HOH}$ bond angles of 90°, 95°, 100°, 105° and 120°. The most important natural atomic configuration is $1s^2 2s^2 2p_x^2 2p_y 2p_z h_1 h_2$. The relative importance of the various natural atomic configurations was determined by examining configuration energies, position in a build-up study and coefficient in a "full" valence-bond wavefunction. The molecular orbital and "full" valence-bond wavefunctions were compared. The perfect pairing calculations using a set of orthogonal hybrid orbitals suggest that the bonding orbitals exhibit a "non-perfect following" behaviour as the molecule bends, continuing to point approximately in their equilibrium directions. The optimum bonding hybrid orbitals are almost pure $2p$ orbitals and the lone-pair orbitals $2s$-$2p$ hybrids, although a small hybridization of the bonding hybrids is essential to obtain an accurate description of the geometry.

Key words: Valence-bond – Water

1. Introduction

Some time ago we presented a computational scheme for performing valence-bond (VB) calculations on simple molecules making use of the Prosser-Hagstrom

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*This work is based on part of a thesis submitted by Gary W. Schnuelle in partial fulfilment of the requirements for the degree of Doctor of Philosophy, The Johns Hopkins University, 1972.

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Aided by research grants to the Johns Hopkins University from the National Science Foundation and the National Institutes of Health.

biorthogonalization technique [1] when evaluating matrix elements using Löwdin's formulae. For BeH_2 [2] it was found that with a minimal Slater basis set a valence-bond calculation neglecting ionic structures gave a lower energy than a molecular orbital calculation using the same basis set. Calculations using hybrid atomic orbitals showed that the perfect pairing valence-state gave a reasonable description of BeH_2 with a lower energy than that obtained using the molecular orbital approximation. The resonance approximation proposed by Craig and Thirunamachandran [3] was found to be a significantly poorer approximation.

In this paper we report some valence-bond calculations on H_2O using a minimal Slater basis set. As a basis for comparison we have Pitzer's and Merrifield's [4] extensive molecular orbital calculations which corrected and extended earlier work by Ellison and Shull [5]. Valence-bond calculations using more extensive basis sets have been reported by a number of workers as well as calculations using the configuration interaction approach [6]. Minimal basis set valence-bond calculations have been reported by Hamel [7], Peterson and Pfeiffer [8], Norbeck and Gallup [9], and Raimondi, Tantardini and Simonetta [10]. Chipman, Kirtman and Palke [11] have recently reported some calculations using the self-consistent DOS-VB method using a double-zeta Slater basis. Of particular relevance to our work is their study of the change in the hybrid orbital as a function of bond angle. McWeeny and Ohno [12] made use of the bond orbital and electron pair approaches in an early quantum mechanical study of the water molecule. Bishop and Randic [13] used a multi-determinantal wavefunction in their single-centre calculations on H_2O. Calculations on CH_2 along lines similar to those reported in this paper have been presented by Maclagan and Todd [14].

2. Computational Details

The coordinate system used is the same as that of Pitzer and Merrifield [4]. The z axis bisects the H–O–H angle and the y axis is in the plane of the molecule. In all calculations reported here the O–H bond distance is 1.8103 a_0. The orbital exponents used were $1s_O = 7.7$, $2s_O = 2p_O = 2.275$ and $1s_H = 1.0$. In the tables the $2p_x$, $2p_y$ and $2p_z$ orbitals are abbreviated to x, y and z respectively. Except for the bond angle of 95° all necessary integrals are given by Pitzer and Merrifield. For $\widehat{H\text{–}O\text{–}H} = 95°$ the integrals were calculated using the programs written from analytical formulae used in the calculations on CH_2 [14]. The valence-bond program has been described in an earlier paper [2].

3. Calculations Using Unhybridized Atomic Orbitals

For the water molecule, with five electrons of each spin and seven basis functions, there are a total of $(C_5^7)^2 = 441$ determinants possible. Even if the $1s$ oxygen orbital is always doubly occupied, there are still $(C_4^6)^2 = 225$ determinants. In this work we report calculations involving a total of 46 determinants from 14 configurations or structures. This set includes all configurations with $1s^2 2s^2 2p_x^2$ fixed and the structures with the $2s$ atomic orbital singly occupied.

Table 1. Valence-bond study on the ${}^1A_1$ state of H_2O: configuration energies

Charge			Configuration energies (hartrees) $\widehat{\mathrm{HOH}}$				
on O	No.	Configuration	90°	95°	100°	105°	120°
0	1	$2s^2x^2yzh_1h_2$	−75.3797	−75.3808	−75.3792	−75.3756	−75.3564
	2	$2s^2x^2z^2h_1h_2$	−74.7836	−74.7971	−74.8106	−74.8234	−74.8556
	3	$2s^2x^2y^2h_1h_2$	−74.8758	−74.8660	−74.8575	−74.8495	−74.8289
	4	$2sx^2yz^2h_1h_2$	−75.1247	−75.1452	−75.1630	−75.1790	−74.2177
	5	$2sx^2y^2zh_1h_2$	−74.3932	−74.3856	−74.3783	−74.3709	−74.3491
−1	6	$2s^2x^2yz^2h$	−75.2989	−75.3157	−75.3285	−75.3388	−75.3584
	7	$2s^2x^2y^2zh$	−75.1077	−75.0997	−75.0914	−75.0824	−75.0528
+1	8	$2s^2x^2zh_1^2h_2$	−74.8745	−74.8815	−74.8827	−74.8806	−74.8589
	9	$2s^2x^2yh_1^2h_2$	−74.8766	−74.8752	−74.8730	−74.8697	−74.8565
−2	10	$2s^2x^2y^2z^2$	−74.6949	−74.7109	−74.7250	−74.7374	−74.7666
+2	11	$2s^2x^2h_1^2h_2^2$	−74.0584	−74.0712	−74.0797	−74.0853	−74.0895
0(+ −)	12	$2s^2x^2yzh^2$	−74.6723	−74.6685	−74.6624	−74.6548	−74.6269
	13	$2s^2x^2z^2h^2$	−74.5134	−74.5151	−74.5181	−74.5217	−74.5318
	14	$2s^2x^2y^2h^2$	−74.6230	−74.5998	−74.5998	−74.5602	−74.5136

In Table 1 are listed the energies of the lowest ${}^1A_1$ state from each natural or unhybridized atomic orbital configuration as a function of bond angle. The configuration with the lowest energy is the $1s^22s^22p_x^22p_y2p_zh_1h_2$ configuration – a neutral or covalent structure. The configuration of the oxygen atom is that of the ground-state of the free atom. As would be expected with an electronegative element, configurations in which the oxygen has a negative charge have large configuration energies and hence might be expected to have a large contribution to the full valence-bond wavefunction. The angular dependence of the configuration energies differs quite markedly from configuration to configuration. With configuration 1, the optimum bond angle is 94°, compared with the experimental bond angle in H_2O of 105°. With configuration 6 in which the $2p_z$ orbital, lying along the bisector of the H–O–H angle is doubly occupied, the optimum bond angle is 126°. With configuration 7 an optimum bond angle much less than 90° is calculated. Configuration 2 has an optimum bond angle of somewhere in the vicinity of 180°. Thus in these, the four most important configurations, there is a large variation in angular dependence of the configuration energy. The bond angle is not determined by any one single structure or group of structures, but by a complicated interaction of the various structures.

A build-up study was performed. In this, configurations, starting with configuration 1, are successively added in such a way that the resultant energy is a minimum for the given number of configurations. The order determined for $\widehat{\mathrm{HOH}} = 105°$ is given in Table 3. The convergence of the energy as a function of the number of configurations can be gauged from the following set of energies obtained for $\widehat{\mathrm{HOH}} = 105°$, as successive configurations are added: −75.3756, −75.5453, −75.6025, −75.6193, −75.6396, −75.6543, −75.6679, −75.6763, −75.6847, −75.6912, −75.6944 and −75.6950 hartrees. Convergence of the value of the optimum bond angle as a function of the number of configurations is slow, the optimum bond angle being very sensitive to the inclusion of new configurations. For configuration 1 alone, the optimum bond-angle is 93.7° but for configurations 1 and 6 combined, the optimum bond angle is 102.1°. The addition of configuration 7 lowers it to 95.6°. With six configurations the optimum bond angle is 101.0°. For fourteen configurations, the bond angle is 96.5°. The build-up order is roughly the order of the configuration energies. There are exceptions to the rule e.g. configuration 9 lies sixth in the order of configuration energies but eleventh in the build-up study order, whilst configuration 13 is twelfth in energies but fifth in the build-up study. Configurations in which the oxygen atom has a positive charge have a position in the build-up study lower than that suggested by their configuration energies. Seven configurations are required to lower the energy below that obtained in a molecular orbital calculation. That the addition of further configurations is unlikely to greatly improve the energy is shown by the convergence of the build-up study. The figure of 225 or 441 determinants is thus slightly misleading as to the size of a valence-bond calculation.

In Table 2 the results of the molecular orbital calculations are compared with the various valence-bond calculations. E_{1-5} is the energy obtained using only configurations from covalent structures. Unlike the case of BeH_2 [2], it has an energy higher than the molecular orbital energy. The molecular orbital calculations predict a bond angle of 100.1° compared with the full valence-bond result of 96.5°. The calculations using only covalent structures predict a bond angle of 101°, $E_{1-3,\,6-14}$ is obtained using configurations involving $1s^2 2s^2 2p_x^2$ on the oxygen atom. It is less than the molecular orbital energy and within 0.02 a.u. of the full valence-bond energy. However, the inclusion of configurations in which the oxygen $2s$ orbital is singly occupied changes the predicted bond angle by 2.5°. The importance of these configurations can also be seen from their place in the build-up study. Raimondi *et al.* [10] have investigated the effect of neglecting excitations

Table 2. Variation of energy as a function of bond angle and orbital approximation – ${}^1A_1$ state of H_2O

	E (hartrees)				
Bond Angle	90°	95°	100°	105°	120°
MO	−75.6525	−75.6559	−75.6568	−75.6556	−75.6410
Configurations 1–5[a]	−75.5214	−75.5254	−75.5269	−75.5264	−75.5130
Configurations 1–3, 6–14[a]	−75.6890	−75.6899	−75.6878	−75.6834	−75.6581
Configurations 1–14[a]	−75.6962	−75.6984	−75.6977	−75.6950	−75.6756
Equation 2	−75.5171	−75.5219	−75.5234	−75.5232	−75.5092
(Optimum hybrid angle)	(92.5)	(92.6)	(93.1)	(93.3)	(94.3)
Equation 4	−75.4627	−75.4626	−75.4598	−75.4549	−75.4271
(Optimum hybrid angle)	(97)	(94)	(94)	(93)	(91)

[a] The configuration numbers are those of Table 1.

Table 3. Comparison of molecular orbital and valence-bond coefficients $\widehat{HOH} = 105°$

No.	Charge on O	Configuration	$\|C\|_{MO}$	$\|C\|_{VB}$	Configuration energies (hartrees)	Position in build-up study
1	0	$2s^2x^2yzh_1h_2$	0.1852	0.3547	−75.3756	1
2		$2s^2x^2z^2h_1h_2$	0.1335	0.1767	−74.8234	4
3		$2s^2x^2y^2h_1h_2$	0.0321	0.0798	−74.8495	8
4		$2sx^2yz^2h_1h_2$	0.0542	0.0701	−75.1790	6
5		$2sx^2y^2zh_1h_2$	0.0233	0.0195	−75.3709	12
6	−1	$2s^2x^2yz^2h$	0.2709	0.2522	−75.3388	2
7		$2s^2x^2y^2zh$	0.1470	0.1668	−75.0824	3
8	+1	$2s^2x^2zh_1^2h_2$	0.1433	0.0972	−74.8806	7
9		$2s^2x^2yh_1^2h_2$	0.0875	0.0616	−74.8697	11
10	−2	$2s^2x^2y^2z^2$	0.2057	0.0975	−74.7374	10
11	+2	$2s^2x^2h_1^2h_2^2$	0.4318	0.0032	−74.0853	14
12	0(+ −)	$2s^2x^2yzh_1^2$	0.0900	0.0886	−74.6548	9
13		$2s^2x^2z^2h_1^2$	0.1335	0.1214	−74.5217	5
14		$2s^2x^2y^2h_1^2$	0.0321	0.0048	−74.5602	13

from the oxygen 1*s* core. They also studied the relative importance of covalent and mono-ionic structures in the full valence-bond wavefunction. Their results are in accord with ours.

In Table 3 we compare the contributions of individual configurations to the valence-bond and to the molecular orbital wavefunction. $|C|_{VB}$ is the magnitude of the coefficient of the normalized wavefunction for the lowest $^1A_1$ state from each configuration in the full (14 configuration) wavefunction. $|C|_{MO}$ is the corresponding molecular orbital figure obtained by expanding the molecular orbital wavefunction, a single determinantal wavefunction, in terms of determinants built up from atomic orbitals. In comparing the molecular orbital and valence-bond coefficients, it is obvious that the molecular orbital approximation overemphasizes ionic structures (especially the O^{2+} structure) and underemphasizes covalent ones, e.g. the $1s^22s^22p_x^2p_y2p_zh_1h_2$ configuration. The order in $|C|_{VB}$ is roughly that in the build-up study. Peterson and Pfeiffer [8] ordered their configurations on the basis of a structure projection $v_N = C_N\Sigma_M S_{NM}$ where C_N has the same meaning as our coefficients. Their order places the O^{2-} structure higher than in our order and the O(+ −) lower. The quantity v_N takes into account the non-orthogonality of configuration wavefunctions built up from a non-orthogonal basis.

4. Calculations Using Hybrid Orbitals

Calculations were performed using the perfect pairing approximation [3]. For the covalent structure this has the form:

$$\begin{aligned}\psi_{pp} = {} & c_1[|1s\overline{1s}l_1\bar{l}_1l_2\bar{l}_2b_1\bar{h}_1b_2\bar{h}_2| + |1s\overline{1s}l_1\bar{l}_1l_2\bar{l}_2\bar{b}_1h_1\bar{b}_2h_2|] \\ & + c_2[|1s\overline{1s}l_1\bar{l}_1l_2\bar{l}_2b_1\bar{h}_1\bar{b}_2h_2| + |1s\overline{1s}l_1\bar{l}_1l_2\bar{l}_2\bar{b}_1h_1b_2\bar{h}_2|]\end{aligned} \tag{1}$$

where

$$\begin{aligned} l_1 &= 1/\sqrt{2}[p_x+\alpha s-\sqrt{1-\alpha^2}\cdot p_z] \\ l_2 &= 1/\sqrt{2}[-p_x+\alpha s-\sqrt{1-\alpha^2}\cdot p_z] \\ b_1 &= 1/\sqrt{2}[p_y+\sqrt{1-\alpha^2}\cdot s+\alpha p_z] \\ b_2 &= 1/\sqrt{2}[-p_y+\sqrt{1-\alpha^2}\cdot s+\alpha p_z] \end{aligned} \tag{2}$$

If the angle between the bonding hybrids is θ, then $\alpha=\theta/2$. l_1 and l_2 are doubly occupied lone-pair oxygen orbitals. b_1 and b_2 are the oxygen bonding orbitals where b_1 is paired with h_1 and b_2 is paired with h_2. l_1, l_2, b_1 and b_2 are mutually orthogonal. A similar set of orbitals was used by McWeeny and Ohno [12]. ψ_{pp} is not an eigenfunction of S^2. However, the determinants omitted (those in which b_1 and h_1 and b_2 and h_2 are not spin-paired) have only small contributions to the wavefunction which is an eigenfunction of S^2. If $\theta=90°$, the bond orbitals are pure p_y and p_z orbitals whilst the lone-pairs are diagonal sp_x hybrids. For $\theta=180°$ the bond orbitals are sp_y hybrids and the lone-pairs are pure p_x and p_z. At $\theta=109.5°$ the bonding and lone-pair orbitals are all sp^3 hybrids. If instead of the lone-pairs given in (2) we choose the linear combinations:

$$\begin{aligned} l_1' &= 1/\sqrt{2}[l_1+l_2]=\alpha s+\sqrt{1-\alpha^2}\cdot p_z \\ l_2' &= 1/\sqrt{2}[l_1-l_2]=p_x \end{aligned} \tag{3}$$

it is possible to form at $\theta=120°$ a set of three sp^2 hybrids. With the set given in (2) the bonding hybrids are sp^2 for $\theta=120°$ but not the lone-pairs. Since l_1 and l_2 are both doubly occupied, ψ_{pp} is the same whether we use l_1 and l_2 or l_1' and l_2'.

In Table 2 are given the results of calculations in which θ is optimised for each value of the HOH angle. The predicted bond-angle is 102°. However, as was found with configurations built up from natural aromic orbitals to describe covalent structures, the energy is poor. What was unexpected is the "non-perfect following" behaviour of the hybrid orbitals. The angle between the bonding orbitals remains at $(93\pm1)°$ while the bond angle varies over a 30° range. For this value of θ the oxygen bonding orbitals are almost pure $2p$ orbitals whilst the lone-pairs can be thought of as nearly diagonal sp_x hybrids (or as one $2p_x$ orbital and one $2s$ orbital).

It is possible to improve upon the energy in the above calculations by including configurations which describe ionic structures whilst still invoking the perfect-pairing approximation. A set of calculations was performed with the angle between the bonding orbitals set at 93° and including O^{2+}, O^{+}, O^{-} and O^{2-} as well as covalent structures. The energies obtained were: (90°) -75.6570, (95°) -75.6616, (100°) -75.6636, (105°) -75.6639 and (120°) -75.6512 hartrees. The predicted bond angle is 103° essentially unchanged from the previous result. There is a considerable improvement in the total energy which is now better than the molecular orbital result but not as good as the "full" valence-bond result involving fourteen configurations built-up from natural atomic orbitals. The bending force constant is 0.045 a.u. compared with the experimental result of 0.0489 a.u. Pitzer and Merrifield report a minimal basis set molecular orbital calculation using optimised geometry and orbital exponents which gave a bending force constant of 0.076 a.u.

Since the deviation from pure 2*p* character in the bonding orbitals is so small we investigated a perfect-pairing wavefunction in which no *s*-*p* hybridization was allowed. The oxygen valence orbitals are:

$$l_1 = 2s$$
$$l_2 = 2p_x$$
$$b_1 = \sin\beta \cdot 2p_y + \cos\beta \cdot 2p_z$$
$$b_2 = \sin\beta \cdot 2p_y + \cos\beta \cdot 2p_z$$

Here β is one half of the angle between the bonding hybrids. The bonding orbitals are not constrained to be orthogonal. The minimum energy at each bond angle was again determined by varying the hybrid angle. The results are also given in Table 2. The best energy was found at 90°. The bonding orbitals appear to move in the opposite direction to the nuclei to which they point as the molecule bends. The energies are very poor. The small *s*-*p* hybridization involved is apparently crucial. As Mulliken has noted "a little hybridisation goes a long way" [15].

Our results should be compared with those obtained by other workers using differing treatments. Bader [16] used an analysis of the charge distributions as an argument that "lone pair" orbitals (in H_2O) must possess close to *sp* hybridization and that the bonds to the hydrogen atoms must be "bent" and of almost pure 2*p* character. Edmiston and Ruedenberg have applied their energy localization procedure to the LCAO-MO wavefunction and found bonding orbitals which subtended a 90° angle [17]. Both these interpretations are in agreement with our results. On the other hand, Klessinger [18] has performed a self consistent group function calculation on H_2O which gave bonding hybrids at an angle of 102° with each other. All of the above calculations were done with the same basis set as that we have employed here. Pople, Linnett, Gillespie, and others [19] have described the hybridization in H_2O as distorted sp^3 hybrids.

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Received January 18, 1977/May 6, 1977