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Valence Bond Studies of AH_2 Molecules*

III. A Comparison of Molecular Orbital and Valence Bond Calculations on CH_2

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Minimal basis set (STO) molecular orbital and valence-bond calculations are reported for the $^3B_1$ and $^1A_1$ states of CH_2. The open-shell molecular orbital calculations used the Roothaan formulation. The valence-bond calculations used the Prosser-Hagstrom biorthogonalisation technique to evaluate the cofactors required in using Löwdin's formulae. Optimisation of geometry and orbital exponents in the molecular orbital calculation on the $^3B_1$ state gave a geometry of $R_{C-H} = 2.11$ a.u. and H–C–H = 123.2°. The energy obtained was -38.8355 a.u. The molecular orbital and valence-bond calculations are compared. In the valence-bond calculations the variation with bond-length and bond-angle of the configuration energies was studied. Valence bond "build-up" studies are also reported. Valence-bond calculations using hybrid orbitals instead of natural atomic orbitals showed that the perfect-pairing approximation is not as good for CH_2 as BeH_2. The nature of the lone-pair and bonding orbitals is found to be significantly different between the $^3B_1$ and $^1A_1$ states. In the $^3B_1$ state the 2*s* and 2*p* orbitals are fairly equally mixed between both types of orbital. However in the $^1A_1$ state the bonding orbitals have mainly 2*p* character and the lone pair orbitals have mainly 2*s* character. As was found for H_2O, the bonding hybrid orbitals do not follow the hydrogen nuclei as the bond angle varies but continue to point approximately in their equilibrium directions.

Key words: CH_2 – Valence bond calculations

1. Introduction

This is the third of a series of papers in which a comparison has been made between the valence-bond and molecular orbital descriptions of a number of AH_2 type molecules using minimal Slater basis sets. In the first paper on BeH_2 [1], the perfect-pairing and resonance approximations were investigated as well as a "full" valence-bond calculation. The perfect-pairing approximation gave an energy better than the molecular orbital method and almost as good as a "full" valence-bond calculation. In the second paper [2] on the water molecule comparison was made with calculations of Pitzer and Merrifield [3]. Particular attention was directed at the variation of various energetic terms with bond angle. In this paper we report some calculations on the $^3B_1$ and $^1A_1$ states of methylene

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molecule. Harrison and Allen [4] have also reported valence-bond-calculations on CH_2.

The methylene molecule, CH_2, is of continuing experimental and theoretical interest because of its importance as an intermediate in organic reactions and possible presence in the interstellar medium and because its relatively small size allows a sophisticated theoretical treatment.

The earliest experimental study of the structure of CH_2 was a spectroscopic study by Herzberg [5] in 1961. At that time a linear or "nearly linear" ${}^3B_1$ state was assigned as the ground state with a CH bond length of 1.946 a.u. An alternate interpretation of the data suggested a bent structure with an H–C–H angle at 140° and a bond distance of 2.024 a.u., but this was dismissed due to the absence of certain bands in the spectrum.

Early qualitative theoretical treatments of methylene predicted that the ground state be the non-linear ${}^1A_1$ state. Foster and Boys [6] in 1961 predicted a bent structure with a bond angle of 129°, a bond length of 2.11 a.u. and an energy of $E = -38.904$ a.u. However, due to approximations for integral values, they did not consider their results accurate enough to be certain that the ground state was ${}^1A_1$. In 1969, Harrison and Allen [4], using an internuclear distance of 2.0 a.u. found that the ground-state of the molecule was the ${}^3B_1$ state with a bond angle of 138° and with an energy $E = -38.9151$.

A rapid sequence of experimental developments has recently produced new evidence that the ground state of CH_2 is a bent ${}^3B_1$ state. From the zero-field-splitting parameters obtained from the EPR spectrum of CH_2, a bond angle of 136–138° for the ${}^3B_1$ state has been obtained [7]. In response to the EPR data, Herzberg and Johns [8] reinterpreted their data and concluded that CH_2 was probably bent in the ground state and that this required the assumption of predissociation in the upper state of the vacuum UV bands in order to explain the missing subbands.

The most recently published theoretical work confirms that the ground state is bent. Bender and Schaefer [9] and O'Neil, Schaefer and Bender [10] have computed the energies of seven low-lying states of CH_2 using a contracted Gaussian basis set in a CI calculation which included 408 configurations for the ${}^3B_1$ state. They found the ground state of CH_2 to have a bond-length of 2.069 a.u., a bond angle of 133.3° and an energy of -38.9826 a.u. With an enlarged GTO basis set McLaughlin, Bender and Schaefer [10] obtained an energy of -39.0121 a.u. with no substantial changes in geometry. The work of Bender and Schaefer in fact preceded the experimental realisation that triplet methylene is bent.

The right handed Cartesian coordinates used to describe the molecule were as follows: the origin is the carbon nucleus, the z-axis bisects the H–C–H angle, the y-axis would be the molecular axis for linear CH_2, and the x-axis is perpendicular to the molecular plane. The hydrogen atom along the positive y-axis is labelled H_1 and that along the negative y-axis is H_2.

The minimal Slater basis consisted of ($1s$, $2s$ and $2p$) on carbon and ($1s$) on each of the hydrogens. The unoptimised exponents for the STO's were $1s_C = 5.7$, $2s_C = 1.625$, $2p_C = 1.625$ and $1s_H = 1.0$. For the ${}^3B_1$ state the molecular geometry and the orbital exponents (except $1s_C$) were optimised. The optimum geometry was $R_{C-H} = 2.1134$ a.u. and H–C–H angle 123.2°. The optimised components were $2s_C = 1.6805$, $2p_C = 1.622$ and $1s_H = 1.217$. The integrals over the atomic basis functions were computed with programs written from analytical formulae [11–14] and the integral values were accurate to 1.0×10^{-6} a.u.

The molecular orbital calculations for the $^3B_1$ state used the Hartree-Fock-Roothaan Method [15]. In calculations on the $^3B_1$ state, convergence problems occurred due to the near degeneracy of two open-shell orbitals. They were successfully resolved by the use of a symmetry adapted basis.

Details of the valence-bond calculations have been given elsewhere [1]. Its most important feature is the use of the Prosser-Hagström biorthogonalisation technique [16] to evaluate the cofactors required in evaluating the matrix elements using Löwdin's formulae.

2. $^3B_1$ State Molecular Orbital Calculations

Calculations were performed on the $^3B_1$ state using the minimal Slater basis for $R_{C\text{-}H} = 2.10$ a.u., 2.15 a.u. and 2.20 a.u. and for HCH = 125°, 130° and 135°. The variation of the energy with bond angle and internuclear distance is indicated in Tables 1 and 2. In Table 3 are given the MO coefficients for $R_{C\text{-}H} = 2.20$ a.u. and HCH = 125°. With Slater exponents the optimum geometry has a bond angle of 121.5° and a bond length of 2.2015 a.u. The energy for this geometry was −38.8072 a.u. With $R_{C\text{-}H} = 2.2015$ a.u. and HCH = 180° the energy was −38.7704 a.u. The geometry and exponents (except $1s_C$) were optimised using an iterative parabolic fit technique. The bond angle was determined to 1° and the internuclear distance to within 0.01 a.u. The STO exponents were varied to within 0.02. For the optimum geometry of $R_{C\text{-}H} = 2.1134$ a.u. and HCH = 123.2°, the energy obtained was −38.8355 a.u. The MO coefficients are given in Table 4. O'Neil, Schaefer and Bender [10] obtained $R_{C\text{-}H} = 2.031$, HCH = 130.4° and $E = -38.9136$ a.u. from a SCF calculation and $R_{C\text{-}H} = 2.069$, HCH = 133.3° and $E = -38.9826$ a.u. from a CI calculation. Minimal Slater basis calculations by Pitzer and Merrifield [3] on H_2O predicted a bond angle in error by 4°. One-electron properties

Table 1. Valence-bond studies of the $^3B_1$ state of CH_2-variation of configuration energies with bond-length. $\widehat{HCH} = 125°$. Minimal Slater basis set

Charge on C atom	Configuration	E(hartrees)	$R_{C\text{-}H}$ (a.u.)	
		2.10	2.15	2.20
0	$1s^2 2s^2 2p_x 2p_y hh'$	−38.4473	−38.4668	−38.4840
	$1s^2 2s^2 2p_x 2p_z hh'$	−38.3362	−38.3552	−38.3728
	$1s^2 2s 2p_x 2p_y 2p_z hh'$	−38.7353	−38.7348	−38.7325
−1	$1s^2 2s^2 2p_x 2p_y 2p_z h$	−38.5889	−38.5859	−38.5811
	$1s^2 2s^2 2p_x 2p_y^2 h$	−38.1695	−38.1770	−38.1827
	$1s^2 2s 2p_x 2p_y^2 2p_z h$	−38.4103	−38.3974	−38.3832
	$1s^2 2s 2p_x 2p_y 2p_z^2 h$	−38.1661	−38.1653	−38.1628
+1	$1s^2 2s 2p_x 2p_y h^2 h'$	−38.1500	−38.1608	−38.1697
	$1s^2 2s 2p_x 2p_z h^2 h'$	−38.4498	−38.4536	−38.4554
E_{VB}		−38.8275	−38.8309	−38.8325
E_{MO}		−38.8029	−38.8059	−38.8069

Table 2. Valence-bond studies of the $^3B_1$ state of CH_2-variation of configuration energies with bond angle $R_{C\text{–}H} = 2.20$. Minimal Slater basis set

Charge on C atom	Configuration	E(hartrees)	$\mathrm{H\widehat{C}H}$	
		125°	130°	135°
0	$1s^2 2s^2 2p_x 2p_y hh'$	−38.4840	−38.4863	−38.4884
	$1s^2 2s^2 2p_x 2p_z hh'$	−38.3728	−38.3788	−38.3839
	$1s^2 2s 2p_x 2p_y 2p_z hh'$	−38.7325	−38.7365	−38.7400
−1	$1s^2 2s^2 2p_x 2p_y 2p_z h$	−38.5811	−38.5875	−38.5930
	$1s^2 2s^2 2p_x 2p_y^2 h$	−38.1827	−38.1897	−38.1965
	$1s^2 2s 2p_x 2p_y^2 2p_z h$	−38.3832	−38.3913	−38.3991
	$1s^2 2s 2p_x 2p_y 2p_z^2 h$	−38.1628	−38.1614	−38.1596
+1	$1s^2 2s 2p_x 2p_y h^2 h'$	−38.1697	−38.1667	−38.1639
	$1s^2 2s 2p_x 2p_z h^2 h'$	−38.4554	−38.4597	−38.4632
E_{VB}		−38.8325	−38.8324	−38.8317
E_{MO}		−38.8069	−38.8057	−38.8036

Table 3. Minimal Slater basis set molecular orbital calculations on the $^3B_1$ and $^1A_1$ states of $CH_2 \cdot R_{C\text{–}H} = 2.20$ a.u. $\mathrm{H\widehat{C}H} = 125°$

State	AO	MO $1a_1$	$2a_1$	$1b_2$	$3a_1$	$1b_1$
$3B_1$	$1s$	0.99667	−0.18374	0.00000	0.11871	0.00000
	$2s_c$	0.01832	0.63240	0.00000	−0.65408	0.00000
	$2p_x$	0.00000	0.00000	0.00000	0.00000	1.00000
	$2p_y$	0.00000	0.00000	0.52031	0.00000	0.00000
	$2p_z$	0.00319	0.20303	0.00000	0.79007	0.00000
	h_1	−0.00609	0.27220	0.46445	0.23649	0.00000
	h_2	−0.00609	0.27220	−0.46445	0.23649	0.00000
	ε	−11.2937	−0.8138	−0.5545	−0.5009	−0.4284
$^1A_1$	$1s_c$	0.99610	−0.19827	0.00000	0.10018	0.00000
	$2s_c$	0.02062	0.70491	0.00000	−0.57986	0.00000
	$2p_x$	0.00000	0.00000	0.00000	0.00000	1.00000
	$2p_y$	0.00000	0.00000	0.51011	0.00000	0.00000
	$2p_z$	0.00443	0.15025	0.00000	0.81629	0.00000
	h_1	−0.00581	0.23548	0.47227	0.24232	0.00000
	h_2	−0.00581	0.23548	−0.47227	0.24232	0.00000
	ε	−11.3104	−0.8516	−0.5696	−0.3465	+0.1340

Table 4. Optimised minimal basis set molecular orbital calculations on the $^3B_1$ state of $CH_2 \cdot R_{C\text{–}H} = 2.11342$ a.u., $\mathrm{H\widehat{C}H} = 123.2°$

State	AO	MO $1a_1$	$2a_1$	$1b_2$	$3a_1$	$1b_1$
$^3B_1$	$1s_c$	0.99636	−0.19230	0.00000	0.12053	0.00000
	$2s_c$	0.01832	0.63737	0.00000	−0.59247	0.00000
	$2p_x$	0.00000	0.00000	0.00000	0.00000	1.00000
	$2p_y$	0.00000	0.00000	0.55579	0.00000	0.00000
	$2p_z$	0.00323	0.20047	0.00000	0.81282	0.00000
	h_1	−0.00580	0.28338	0.41595	0.18590	0.00000
	h_2	−0.00580	0.28338	−0.41595	0.18590	0.00000
	ε	−11.2146	−0.8070	−0.5405	−0.4711	−0.3894

calculated by Aung, Pitzer and Chan [18] for H_2O, using an optimised minimal Slater basis set were generally in good agreement with experiment. This offers hope that the two electron properties which can be computed with the wavefunction reported here will also agree well with the experimental values.

3. $^3B_1$ State Valence-Bond Calculations

The work reported here complements the extensive valence-bond study of CH_2 by Harrison and Allen [4]. The basis set they used, described as "close to atomic Hartree-Fock solutions" is better than the minimal Slater basis we used. In Table 5 are given the configuration energies for the important configurations from which it is possible to form wavefunctions of $^3B_1$ symmetry. The geometry and exponents are those optimised in the MO calculations. Unlike the configurations involved in the ground-states of BeH_2 [1] and H_2O [2], it is possible to form more than one eigenfunction of S^2 with $^3B_1$ symmetry from several of these configurations. Thus coefficients of particular configurations in the "full" valence bond wavefunction are not given. The configuration of lowest energy involves the $2sp^3$ configuration on carbon, not the $2s^2p^2$ atomic ground state configuration. In Table 6 are given the results of a "build-up" study. In this configurations are successively added in such an order that the energy obtained with a given number of configurations is a minimum. The order is roughly that of the configuration energies. Five configurations are required for the energy to be lower than the molecular orbital energy. The number of determinants required to obtain an energy lower than the molecular orbital energy is larger than that found for other states we have studied. Like H_2O a configuration in which the central atom has a

Table 5. Valence bond study on the $^3B_1$ state: configuration energies. $R_{C\text{-}H} = 2.11342$ a.u. $H\hat{C}H = 123.2°$. Optimised exponents from MO calculation

Charge on C atom	No.	Configuration	Configuration energy (hartrees)
0	1	$1s^2 2s^2 2p_x 2p_y h h'$	-38.4038
	2	$1s^2 2s^2 2p_x 2p_z h h'$	-38.2979
	3	$1s^2 2s 2p_x 2p_y 2p_z h h'$	-38.7327
	4	$1s^2 2s 2p_x 2p_y^2 h h'$	-37.9560
	5	$1s^2 2s 2p_x 2p_z^2 h h'$	-37.9976
	6	$1s^2 2p_x 2p_y^2 2p_z h h'$	-37.8563
	7	$1s^2 2p_x 2p_y 2p_z^2 h h'$	-37.8975
-1	8	$1s^2 2s^2 2p_x 2p_y 2p_z h$	-38.5679
	9	$1s^2 2s^2 2p_x 2p_y^2 h$	-38.0975
	10	$1s^2 2s^2 2p_x 2p_z^2 h$	-37.6970
	11	$1s^2 2s 2p_x 2p_y^2 2p_z h$	-38.3989
	12	$1s^2 2s 2p_x 2p_y 2p_z^2 h$	-38.1617
$+1$	13	$1s^2 2s^2 2p_x h^2 h'$	-38.0426
	14	$1s^2 2s 2p_x 2p_y h^2 h'$	-37.9981
	15	$1s^2 2s 2p_x 2p_z h^2 h'$	-38.3705
$0(+-)$	16	$1s^2 2s^2 2p_x 2p_y h^2$	-37.6826
	17	$1s^2 2s^2 2p_x 2p_z h^2$	-37.8512
	18	$1s^2 2s 2p_x 2p_y 2p_z h^2$	-37.9580

Table 6. Valence-bond "build-up" study on $^3B_1$ state $R_{C-H} = 2.11342$ a.u. $H\hat{C}H = 123.2°$. Optimised exponents from MO calculation

Configurations[a] included	Position of configuration in table of increasing configuration energies	E(hartrees)
3	1	−38.7327
+ 8	2	−38.7768
+ 1	3	−38.8044
+11	4	−38.8263
+ 2	6	−38.8453
+15	5	−38.8515
+12	7	−38.8573
+14	10	−38.8594
+ 9	8	−38.8615
E_{MO}		−38.8355

[a] Numbers refer to configurations given in Table 5.

negative charge $1s^2 2s^2 2p_x 2p_y 2p_z h$ is very important. However for the $^3B_1$ state of CH_2 the configurations in which the carbon atom has a positive charge are also important. In Table 1 are shown the variations in configuration energies with internuclear distance. (In Tables 1 and 2 the calculations used a Slater basis.) The two most important configurations favour a smaller internuclear distance. The "neutral" configurations involving doubly occupied 1*s* and 2*s* carbon orbitals favour a larger internuclear distance. The optimum internuclear distance is 2.217 a.u. compared with the 2.2015 a.u. with the molecular orbital approximation. In Table 2 are shown the variation in configuration energies with bond angle. The most important configurations favour a larger bond angle that the "full" valence-bond calculation. This predicts an angle of 126.7°. The molecular orbital prediction is 121.5°. It would appear that one cannot use configuration energies in a manner similar to the way orbital energies are used in Walsh [19] diagrams to predict bond-angles. Off-diagonal terms between configurations are important in determining molecular geometry.

4. $^1A_1$ State

While our principal interest has naturally been in the $^3B_1$ ground state, some attention was also given to the $^1A_1$ state. This is the lowest singlet state, with an electronic structure similar to that of water except that there is one, not two filled lone-pair orbitals. All the calculations reported here on the $^1A_1$ state were done using integrals already available from the studies on the $^3B_1$ state. The geometry studied was found to be not close to the equilibrium geometry for the $^1A_1$ state. In Table 7 are given the energies calculated using the valence-bond and molecular orbital approximations for three internuclear distances and three bond angles. An extrapolation in both cases predicts a bond angle close to 90° and an internuclear distance greater than that for the $^3B_1$ state. O'Neil, Schaefer, and Bender [10] predicted from a configuration interaction calculation an

Table 7. Variation of energy of the $^1A_1$ state of CH_2 with $R_{\mathrm{C-H}}$ and $\mathrm{H\hat{C}H}$. Minimal Slater basis set calculations comparing MO and VB approximations

$R_{\mathrm{C-H}}$ (a.u.)	$\mathrm{H\hat{C}H}$ (degrees)	$-E$ "full" VB (hartrees)	$-E$ MO (hartrees)
2.10	125	38.7516	38.7251
	130	38.7446	38.7184
	135	38.7372	38.7113
2.15	125	38.7582	38.7300
	130	38.7509	38.7230
	135	38.7430	38.7155
2.20	125	38.7630	38.7331
	130	38.7554	38.7258
	135	38.7472	38.7179

Table 8. Variation of orbital energies with bond angle$^3B_1$ and $^1A_1$ states. $R_{\mathrm{C-H}} = 2.20$ a.u. Minimal Slater basis set

MO	$\mathrm{H\hat{C}H}$	ε(hartrees)	
	(degrees)	$^1A_1$	$^3B_1$
$1a_1$	125	−11.3104	−11.2937
	130	−11.3026	−11.2902
	135	−11.2942	−11.2862
$2a_1$	125	− 0.8516	− 0.8138
	130	− 0.8453	− 0.8113
	135	− 0.8386	− 0.8088
$1b_2$	125	− 0.5696	− 0.5545
	130	− 0.5726	− 0.5597
	135	− 0.5747	− 0.5641
$3a_1$	125	− 0.3465	− 0.5009
	130	− 0.3377	− 0.4910
	135	− 0.3291	− 0.4809
$1b_1$	125	+ 0.1340	− 0.4284
	130	+ 0.1383	− 0.4261
	135	+ 0.1429	− 0.4236

equilibrium geometry of $R_{\mathrm{C-H}} = 2.142$ a.u. and H–C–H = 104.4° and an energy of -38.9472 a.u., 0.0354 a.u. higher than that for the equilibrium geometry for the $^3B_1$ state. For $R_{\mathrm{C-H}} = 2.1$ and 2.2 a.u. and $\mathrm{H\hat{C}H} = 135°$ they quote SCF energies of -38.8452 and -38.8385 a.u. compared with -38.7113 and -38.7179 a.u. obtained with this minimal Slater basis set. In Table 3 the molecular orbitals for the $^3B_1$ and $^1A_1$ states calculated with a geometry of $R_{\mathrm{C-H}} = 2.20$ a.u. and H–C–H = 125° are compared. The basis set used was a minimal Slater basis set. While the molecular orbital coefficients do not change greatly in going from one state to another, the orbital energies, particularly the $3a_1$ and $1b_1$ are significantly different. Table 8 shows the variation in the orbital energies with bond angle for both the $^3B_1$ and $^1A_1$ states using a bond length of 2.20 a.u. and a minimal Slater basis set. All but the $1b_2$ orbital favour a bond angle less than 125°. As is

Table 9. Valence-bond study on the $^1A_1$ state: configuration energies and coefficients $R_{\text{C-H}} = 2.20$ a.u.

Charge on C	No.	Configuration	Coefficients $\widehat{HCH} = 125°$	Configuration energies (hartrees) $\widehat{HCH}$		
				125°	130°	135°
0	2	$1s^2 2s^2 2p_y 2p_z hh'$	0.3434	−38.5767	−38.5647	−38.5525
	8	$1s^2 2s^2 2p_y^2 hh'$	0.0545	−38.0908	−38.0814	−38.0725
	3	$1s^2 2s^2 2p_z^2 hh'$	0.1786	−38.2823	−38.2866	−38.2898
	12	$1s^2 2s^2 2p_x^2 hh'$	0.0265	−38.2630	−38.2690	−38.2745
	13	$1s^2 2s 2p_y^2 2p_z hh'$	0.0170	−37.9001	−37.8914	−37.8832
	1	$1s^2 2s 2p_y 2p_z^2 hh'$	0.2812	−38.5757	−38.5822	−38.5878
−1	5	$1s^2 2s^2 2p_y^2 2p_z h$	0.0740	−38.2747	−38.2645	−38.2542
	4	$1s^2 2s^2 2p_y 2p_z^2 h$	0.1459	−38.5208	−38.5200	−38.5188
	7	$1s^2 2s 2p_y^2 2p_z^2 h$	0.1005	−38.2295	−38.2415	−38.2526
+1	11	$1s^2 2s^2 2p_y h^2 h'$	0.0346	−38.2052	−38.1954	−38.1863
	6	$1s^2 2s^2 2p_y h^2 h'$	0.0906	−38.2937	−38.2792	−38.2641
0(+ −)	10	$1s^2 2s^2 2p_y 2p_z h^2$	0.0476	−37.9282	−37.9128	−37.8975
	14	$1s^2 2s^2 2p_y^2 h^2$	0.0062	−37.7213	−37.7081	−37.6962
	9	$1s^2 2s^2 2p_z^2 h^2$	0.0689	−37.9483	−37.9482	−37.9473

Table 10. Valence-bond "build-up" study on $^1A_1$ state $R_{\text{C-H}} = 2.20$ a.u.

Configurations included[a]	E (hartrees) $\widehat{HCH}$		
	125°	130°	135°
1	−38.5767	−38.5822	−38.5878
+ 2	−38.6846	−38.6785	−38.6716
+ 3	−38.7184	−38.7127	−38.7061
+ 4	−38.7315	−38.7259	−38.7195
+ 5	−38.7404	−38.7339	−38.7267
+ 6	−38.7496	−38.7422	−38.7340
+ 7	−38.7538	−38.7471	−38.7397
+ 8	−38.7570	−38.7496	−38.7417
+ 9	−38.7600	−38.7526	−38.7447
+10	−38.7619	−38.7544	−38.7462
+11	−38.7624	−38.7546	−38.7463
+12	−38.7628	−38.7551	−38.7468
+13	−38.7630	−38.7553	−38.7471
+14	−38.7630	−38.7554	−38.7472
E_{MO}	−38.7331	−38.7258	−38.7179

[a] Numbers refer to configurations given in Table 3.

found for H_2O the $3a_1$ orbital has a stronger dependence on bond angle than the other molecular orbitals, but not as strong as indicated in the diagrams in Walsh's paper [19]. In Table 9 are given the configuration energies from a valence-bond calculation on the $^1A_1$ state as a function of bond-angle. $R_{\text{C-H}}$ was 2.20 a.u. Also given for $\widehat{HCH} = 125°$ are the coefficients of the wavefunctions with $^1A_1$ symmetry built from a given configuration, in the "full" valence bond wavefunction. In Table 10 are the results of a build-up study. The optimum order of adding configurations is roughly that of decreasing coefficient or increasing configuration energy. However there are a few exceptions to this rule. Five configurations involving twenty-two determinants are required to obtain an energy lower than the molecular orbital energy. Whilst the most important configuration for the H$\widehat{C}$H = 135° favours a bond angle greater than 135°, the addition of the second most important configuration (which is actually the most important for H$\widehat{C}$H = 125°) leads to the prediction of a bond angle less than 125°.

5. Valence-Bond Calculations using Hybrid Orbitals

The valence-bond calculations described in Sections 3 and 4 used natural atomic orbitals to build up the Slater determinants from which the wavefunction is formed. It should be obvious that by using hybrid orbitals instead of atomic orbitals one should be able to reduce the number of determinants required to obtain a desired energy. Valence bond calculations were performed on both states of CH_2 using hybrid orbitals of the following form:

$$\Phi_{LP} = N_{LP}\left[\Phi_{2S} - \frac{1}{C_{SP}\cdot\cos\alpha}\,\Phi_{2P_z}\right]$$

$$\Phi_{BP} = N_{BP}[\Phi_{2S} + C_{SP}[\cos\alpha\,\Phi_{2P_z} \pm \sin\alpha\,\Phi_{2P_y}]] .$$

Φ_{LP} and Φ_{BP} are the lone-pair and bonding orbitals respectively. C_{SP} is the mixing coefficient between the 2*s* and 2*p* orbitals. Since only *s* and *p* orbitals are used in the hybrids, 2α is the angle between the two bonding orbitals. A set of calculations was performed for $R_{C-H} = 2.20$ a.u. in which the parameters C_{SP} and α were optimised. Calculations were also carried out to test the perfect-pairing approximation. The results are given in Table 11. For the $^3B_1$ state, the neutral *C* configuration perfect-pairing approximation involves the determinants: $|bp_1 bp_2\, lp 2p_x \bar{h}_1 \bar{h}_2|$, $|\overline{bp}_1 bp_2\, lp 2p_x h_1 \bar{h}_2|$, $|bp_1 \overline{bp}_2\, lp 2p_x \bar{h}_1 h_2|$, and $|\overline{bp}_1 \overline{bp}_2\, lp\, lp_x h_1 h_2|$. The non-perfect pairing determinants $|bp_1 \overline{bp}_2\, lp 2p_x h_1 \bar{h}_2|$ and $|\overline{bp}_1 bp_2\, lp 2p_x \bar{h}_1 h_2|$ were included in the VB (hybrid orbitals) calculations. The "neutral" configuration for the $^1A_1$ state was $bp_1 bp_2 2p_x p^2 h_1 h_2$. The VB (hybrid orbital) calculation involved 22 determinants compared with 72 for the $^3B_1$ "full" valence-bond calculation and 50 for the $^1A_1$ "full" valence-bond calculation using natural atomic orbitals. The energies obtained using hybrid orbitals compare quite favourably with the calculations using natural atomic orbitals. For BeH_2 [1] it was found that the

Table 11. Minimal Slater basis set valence-bond study – Use of hybrid orbitals $R_{C-H} = 2.20$ a.u.

State	H$\widehat{C}$H	Hybrid orbital parameters		Perfect pairing approximation			VB (Hybrid orbitals)	"Full" VB	MO
		C_{SP}	α	Neutral C configuration	+Negative C configuration	+Positive C configuration			
$^3B_1$	125	0.765	58.8	−38.7832	−38.8000	−38.8073	−38.8188	−38.8325	−38.8069
	130	0.727	60.6	−38.7845	−38.8017	−38.8085	−38.8201	−38.8324	−38.8057
	135	0.687	62.5	−38.7851	−38.8029	−38.8093	−38.8211	−38.8317	−38.8036
$^1A_1$	125	2.66	36.0	−38.7251	−38.7474	−38.7607	−37.7621	−38.7630	−38.7331
	130	2.36	35.2	−38.7188	−38.7414	−38.7536	−38.7549	−38.7554	−38.7258
	135	2.19	37.0	−38.7122	−38.7345	−38.7455	−38.7470	−38.7472	−38.7179

perfect-pairing approximation using a "neutral" Be configuration gave a very good approximation to the "full" valence-bond energy. This is not found here. Some ionic configurations must be included to improve on the molecular orbital energy. The transition $^3B_1 \rightarrow {}^1A_1$ is a π–n transition. However the nature of the lone-pair and bonding orbitals changes quite drastically as can be seen from the change in the parameters C_{sp} and α. In the $^3B_1$ state the $2s$ and $2p$ orbitals are roughly equally mixed between the lone-pair and bonding orbitals. In the $^1A_1$ state the bonding orbitals have more $2p$ character than the lone pair orbitals. The lone-pair orbitals have more $2s$ character than $2p$ character. The most striking result' also found for H_2O [2], is that the bonding orbitals do not strongly follow the hydrogen nuclei but continue to point approximately in their equilibrium directions. In general bonding pairs have an equilibrium angle less than the angle formed by the nuclei. This result should be of great importance in understanding the bending vibrations of molecules.

6. Conclusion

The molecular orbital calculations show that general agreement exists between these minimal Slater basis set calculations and more accurate ones such as those of O'Neil, Schaeffer, and Bender [10]. As was found for BeH_2 and H_2O a valence-bond calculation using a minimal Slater basis set gives an energy 0.03–0.04 a.u. lower than the molecular orbital calculation using the same basis set. The computational effort required is only slightly greater. The use of appropriate hybrid orbitals reduces this to less than that for the molecular orbital method. Both methods predicted molecular geometries in good agreement with those obtained using bigger basis sets. The valence-bond calculations using hybrid orbitals demonstrated several important points: Valence-bond calculations using hybrid orbitals are as accurate as molecular orbital calculations with the same basis set. They give chemically interesting information which is immediately intelligible, e.g. the direction in which orbitals point, the relative importance of neutral and ionic "structures". In addition the calculations on CH_2 and H_2O have demonstrated the "orbital non-following effect" in the angle-bending motions.

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References

1. Maclagan, R. G. A. R., Schnuelle, G. W.: J. Chem. Phys. **55**, 5431 (1971)
2. Maclagan, R. G. A. R., Schnuelle, G. W.: to be published
3. Pitzer, R. M., Merrifield, D. P.: J. Chem. Phys. **52**, 4782 (1970)
4. Harrison, J. F., Allen, L. C.: J. Am. Chem. Soc. **91**, 807 (1969)
5. Herzberg, G.: Proc. Roy. Soc. (Lond.) A **262**, 291 (1961)
   Herzberg, G., Johns, J. W. C.: Proc. Roy. Soc. (Lond.) A **295**, 107 (1966)
6. Foster, J. M., Boys, S. F.: Rev. Mod. Phys. **91**, 807 (1960)
7. Wasserman, E., Kuck, V. J., Hutton, R. S., Anderson, E. D., Jager, W. A.: J. Chem. Phys. **54**, 4120 (1971)
8. Herzberg, G., Johns, J. W. C.: J. Chem. Phys. **54**, 2276 (1971)

9. Bender, C. F., Schaefer, H. F.: J. Am. Chem. Soc. **92**, 4984 (1970)
10. O'Neil, S. V., Schaefer, H. F., Bender, C. F.: J. Chem. Phys. **55**, 162 (1971)
McLaughlin, D. R., Bender, C. F., Schaefer, H. F.: Theor. Chim. Acta (Berl.) **25**, 352 (1972)
11. Silverstone, H. J.: J. Chem. Phys. **48**, 4098 (1968)
12. Silverstone, H. J.: J. Chem. Phys. **48**, 4106 (1968)
13. Silverstone, H. J., Kay, K. G.: J. Chem. Phys. **48**, 4108 (1968)
14. Todd, H. D., Kay, K. G., Silverstone, H. J.: J. Chem. Phys. **53**, 3951 (1971)
15. Roothaan, C. C. J.: Rev. Mod. Phys. **32**, 749 (1960)
16. Prosser, F., Hagstrom, S.: Intern. J. Quantum Chem. **2**, 89 (1968)
17. Löwdin, P. O.: Phys. Rev. **97**, 1474, 1490, 1509 (1955)
18. Aung, S., Pitzer, R. M., Chan, S. I.: J. Chem. Phys. **49**, 2071 (1968)
19. Walsh, A. D.: J. Chem. Soc. (Lond.) 2260 (1953)

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