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Valence-Bond Studies of AH_2 Molecules

IV. A Comparison of Minimal Basis Set Calculations on H_2O and H_2S

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Minimal Slater basis set calculations are reported for H_2S. The calculations used both natural and hybrid atomic orbitals. The calculations were performed at H–S–H bond angles of 90°, 92.2° and 95°. The results are compared with similar calculations on H_2O and with calculations using the molecular orbital approximation. The only definite trend found in going from H_2O to H_2S is that the importance of the SH^+H^- structure decreases. Changes in the relative importance of covalent and ionic structures depend upon which measure of importance is used. Calculations using a set of orthogonal hybrid orbitals again find the hybrid orbitals exhibiting "non-perfect following" behaviour with the hybrids remaining at about the equilibrium bond angle. Localized molecular orbitals were found to move in the opposite direction to the change in the H–S–H bond angle.

Key words: Valence-bond – H_2S

1. Introduction

In this paper we present the results of some new minimal Slater basis set calculations on the $^1A_1$ ground state of H_2S and compare them with similar calculations on H_2O [1]. We have previously reported similar calculations on BeH_2 [2], CH_2 [3], H_2O [1], BH_3 [4] and CH_4 [5]. The previous calculations have allowed us to explore the trends which are exhibited as we cross the Periodic Table and increase the number of atoms around the central atom. The present calculations permit us to observe some of the trends as we go down a column of the Periodic Table. We also wish to investigate further the "non-perfect following" behaviour of the hybrid orbitals observed when we bent the H–A–H bond angle in H_2O [1] and CH_2 [3].

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One other valence-bond calculation on H_2S, by Raimondi, Tantardini and Simonetta [6], has been published. They were particularly interested in the convergence properties of the calculation and the influence of the basis set in the presence of a relatively heavy "core". As in similar studies they found that the improvement in the energy in going from a single-zeta to a double-zeta basis set is due mostly to an improved description of the core orbitals. Chemical intuition was again shown to be a valid criterion for classifying valence-bond structures according to their importance in the wavefunction. Kirtman, Chipman and Palke [7] have carried out some DOS-VB calculations on H_2S in which they also examine the questions of hybridization and non-perfect orbital following.

2. Computational Details

In the coordinate system used here, which is the same as that used in the H_2O calculations [1], the x-axis bisects the H–S–H angle and the y-axis is in the plane of the molecule. All calculations were done at the experimental [8] S–H bond distance of 1.328 Å. The calculations were performed at the experimental bond angle of 92.2° and also at 90° and 95°. The orbital exponents of the minimal Slater basis set were the best-atom values used by Boer and Lipscomb [9]: $1s_S = 15.5409$, $2s_S = 5.3144$, $2p_S = 5.9885$, $3s_S = 2.1223$, $3p_S = 1.8273$ and $1s_H = 1.2212$. In the tables the $3p_x$, $3p_y$ and $3p_z$ orbitals are abbreviated to x, y and z respectively. Where comparison is made with H_2O, x, y and z refer to the $2p_x$, $2p_y$ and $2p_z$ orbitals of oxygen. The integrals over the atomic orbitals were calculated using an integral evaluation program which used 3 Gaussians per Slater [10] in evaluating non-NDDO integrals. In this approximation the molecular orbital energy is -397.774 hartrees compared with Boer and Lipscomb's [9] exact value of -397.788 hartrees. In this approximation the H atom gross atomic population is 0.905 compared with 0.907 and the S–H overlap population is 0.645 compared with Boer and Lipscomb's value of 0.662. These comparisons show that the 3G/S approximation is satisfactory for this essentially qualitative study. The calculations on H_2O have been described in detail elsewhere [1]. The valence-bond program has been described in an earlier paper [2].

3. Results and Discussion

In Table 1 the energies from each unhybridized atomic orbital configuration with $^1A_1$ symmetry are listed as a function of bond angle. The wavefunctions here are eigenfunctions of S^2. Only configuration 1 has an energy lower than the sum of the energies of the separated atoms in their ground-states, calculated with the same basis set to be -397.5787 hartrees. Like the corresponding configuration for H_2O, configuration 1 also has the largest coefficient in the "full" valence-bond wavefunction. The right hand two columns of Table 1 compare the orders of the configuration energies for H_2O and H_2S. Previous studies [1–5] have shown this to be a useful guide to the coefficients in the "full' valence-bond calculation. The orders are very similar in H_2O and H_2S. The coefficients in the "full" valence-bond wavefunction of the covalent structure configurations are larger in H_2S and those

Table 1. Valence-bond study on the $^1A_1$ state of H_2S: configuration energies and comparison with H_2O

No.	Configuration[c]	Charge on S	Energy (hartrees) H–S–H 90°	92.2°	95°	$\|c\|_{VB}$[a]	$\|c\|_{MO}$[a]	Position in build-up study H_2O[b]	H_2S[a]	Order of configuration energies H_2O[b]	H_2S[a]
1	$3s^2x\ y\ z^2h_1h_2$	0	−397.6175	−397.6165	−397.6148	0.394	0.152	1	1	1	1
2	$3s^2x^2\ z^2h_1h_2$		−397.2069	−397.2136	−397.2212	0.139	0.068	4	4	8	6
3	$3s^2\ y^2z^2h_1h_2$		−397.1481	−397.1418	−397.1341	0.088	0.031	8	7	7	9
4	$3s\ x^2y\ z^2h_1h_2$		−397.3316	−397.3385	−397.3470	0.166	0.049	6	5	3	4
5	$3s\ x\ y^2z^2h_1h_2$		−397.0986	−397.0862	−397.0785	0.050	0.001	12	12	13	10
6	$3s^2x^2y\ z^2h_1$	−1	−397.4950	−397.4983	−397.5017	0.178	0.183	2	2	2	2
7	$3s^2x\ y^2z^2h_1$		−397.3765	−397.3733	−397.3694	0.132	0.121	3	3	4	3
8	$3s^2x\ \ z^2h_1^2h_2$	+1	−397.2596	−397.2607	−397.2609	0.083	0.118	7	6	5	5
9	$3s^2\ y\ z^2h_1^2h_2$		−397.1731	−397.1692	−397.1645	0.050	0.080	11	8	6	7
10	$3s^2x^2y^2z^2$	−2	−397.1440	−397.1492	−397.1555	0.067	0.115	10	9	9	8
11	$3s^2\ \ z^2h_1^2h_2^2$	+2	−396.7078	−396.7093	−396.7104	—	0.088	14	—	14	13
12	$3s^2x\ y\ z^2h_1^2$	0(+ −)	−396.8719	−396.8675	−396.8616	0.035	0.066	9	11	10	11
13	$3s^2x^2\ z^2h_1^2$		−396.7808	−396.7844	−396.7879	0.037	0.068	5	10	12	12
14	$3s^2\ y^2z^2h_1^2$		−396.6820	−396.6717	−396.6593	—	0.040	13	—	11	14
15	$3s\ x^2y\ z^2h_1^2$		−396.5179	−396.5252	−396.5343	—	0.017	—	—	—	15
16	$3s^2x\ y^2z^2h_1^2$		−396.4320	−396.4265	−396.4192	—	0.011	—	—	—	16

[a] The coefficients and orders given are for H–S–H = 95°.

[b] The order given is for H–O–H = 105°.

[c] Where a configuration as written involves h_1 or h_1^2, the corresponding configuration involving h_2 or h_2^2 is also included.

from ionic structures are smaller. However with the order of configuration energies, some covalent structures have a higher order and others a lower order. The next two columns to the left in the table compare the positions of the configurations in a build-up study. In a build-up study various configurations are added, one at a time, in such a way as to minimise the energy for the given number of configurations included. In H_2S the S(+ −) (or $S^0H^+H^-$) configurations are less important than in H_2O. This is presumably due to the larger H–H separation, which diminishes the importance of the S H–H structure to which these configurations contribute. Some of the other variations are in the opposite sense to those found in the order of configuration energies. The convergence of the build-up study is slow after the first three or so configurations. The relative importance to bonding may be studied in another way by the percentage contribution to the dissociation energy D_e. The calculated D_e is 76% of the experimental value [11]. In the build-up study, the cumulative $\%D_e$ with the addition of configurations 1, 6, 7, 4, 2 and 8 is 19.4%, 59%, 74%, 82%, 90% and 93% respectively of the calculated value with 12 configurations included. The S^- structure configurations are very important in determining D_e. The deletion of configurations 1, 6, 7, 4, 2 and 8 lowers the calculated D_e by 19.2%, 3.6%, 2.9%, 6.5%, 5.1% and 1.4% respectively. Also shown in Table 1 are the coefficients of each configuration in the "full" valence-bond wavefunction and in a molecular orbital wavefunction. The fact that the molecular orbital approximation overemphasizes ionic structures and underemphasizes the covalent structure is evident. The "full" valence-bond wavefunction involves 12 configurations representing 45 determinants. For H–S–H = 95°, 9 configurations were required to lower the energy below that obtained using the molecular orbital approximation. A bond angle greater than 95° is favoured. The energies from the "full" valence-bond wavefunction for H–S–H = 90°, 92.2° and 95° are −397.7736, −397.7739 and −397.7754 hartrees respectively. The corresponding molecular orbital energies are −397.7733, −397.7738 and −397.7739 hartrees.

Calculations were also carried out within the perfect-pairing approximation using orthogonal hybrid orbitals of the form:

$$b_1 = 1/\sqrt{2}[\sqrt{1-\alpha^2}\cdot 3s + 3p_y + \alpha\cdot 3p_x]$$

$$b_2 = 1/\sqrt{2}[\sqrt{1-\alpha^2}\cdot 3s - 3p_y + \alpha\cdot 3p_x]$$

$$l_1 = 1/\sqrt{2}[\alpha\cdot 3s + 3p_z - \sqrt{1-\alpha^2}\cdot 3p_x]$$

$$l_2 = 1/\sqrt{2}[\alpha\cdot 3s - 3p_z - \sqrt{1-\alpha^2}\cdot 3p_x]$$

where b_1, b_2 are bonding hybrid orbitals and l_1, l_2 the lone-pair hybrid orbitals. α is an adjustable parameter related to the angle θ between b_1 and b_2 by $\alpha = \cot\theta/2$. The covalent, S^+ and S^- structures were included with valence-shell configurations of $l_1^2\, l_2^2\, b_1\, b_2\, h_1\, h_2$ for S^0, $l_1^2\, l_2^2\, b_1\, h_1\, h_2^2$ for S^+ and $l_1^2\, l_2^2\, b_1^2\, b_2\, h_2$ for S^-. The results of the calculations are shown in Table 2. Calculations were performed including just the covalent structure configuration, those of the covalent and S^- structures and those of all three structures. In contrast to the "full" valence-bond calculation using pure unhybridized atomic orbitals, an optimum H–S–H bond

Table 2. Perfect-pairing valence-bond calculations on H_2S – variation with bond angle

Configurations	Energy (hartrees) 90°	92.2°	95°	Hybrid orbital angle 90°	92.2°	95°
S^0	−397.7220	−397.7206	−397.7204	92.28	92.15	92.64
S^0+S^-	−397.7607	−397.7593	−397.7592	91.48	91.55	91.64
$S^0+S^-+S^+$	−397.7725	−397.7709	−397.7707	91.66	91.76	91.80

angle near 90° is obtained. With just these three configurations, 98% of the value of D_e calculated from the "full" valence-bond calculation was obtained. The small difference is due to the use of the perfect-pairing approximation and the neglect of the S^{2-} and $S(+-)$ structures. In terms of determinants required, the use of hybrid orbitals required about 40% of the number of determinants to give the same energy as that obtained using pure atomic orbitals. As the bond angle varies from 90° to 95°, the hybrid bond angle scarcely changes – the non-perfect following phenomenon previously found for H_2O [1] and CH_2 [3]. The hybrid bond angle is very close to the experimental bond angle. Like the bonding orbitals in H_2O, those in H_2S are almost pure *p* orbitals and the lone-pairs are very close to *s-p* hybrids. By contrast, with localized molecular orbitals calculated using the criterion of Foster and Boys [12], the angle between the bond pairs is 97.5°, 96.9° and 96.4° for 90°, 92.2° and 95° respectively – a decrease in the angle between the bond pairs with an increase in the bond angle. Some of the difference between the behaviour of the valence-bond hybrid orbitals and the localized molecular orbitals could arise because the latter include contributions from core orbitals.

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