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Ab initio Computations on H_2S: LCAOSCF Wave Functions without *d* Orbitals

B. CADIOLI and U. PINCELLI
Istituto di Chimica Fisica, Università di Modena, Via Campi 183, I-41100 Modena
G. L. BENDAZZOLI and P. PALMIERI
Istituto di Chimica Fisica e Spettroscopia, Università di Bologna
Viale Risorgimento 4, I-40136 Bologna

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Ab initio MO-SCF wave functions are derived for H_2S for different bond angles by using a double-zeta type set of gaussian *s* and *p* orbitals. The predicted equilibrium bond angle is 95.5°. The computed value of the total electronic energy is expected to be near the Hartree-Fock limit for the molecule. The predicted value of the dipole moment does not show significant improvement with respect to similar computations not including polarisation functions.

Ab initio-Funktionen aus Doppel-ζ-Gaussfunktionen werden für H_2S bei verschiedenen Valenzwinkeln angegeben. Die tiefste Energie (95.5°) dürfte nahe beim Hartree-Fock-Wert liegen. Die Einführung von polarisierenden Funktionen liefert hinsichtlich des Dipolmomentes keine Verbesserung.

Des calculs non empiriques pour plusieurs valeurs de l'angle de liaison ont été effectués pour H_2S avec une base étendue de fonctions gaussiennes *s* et *p*. L'angle d'équilibre prévu est de 95.5°. L'énergie électronique totale est estimée très proche de la limite Hartree-Fock pour la molécule. La valeur du moment dipolaire calculé est pareille à celle qui a été trouvée par d'autres calculs n'incluant pas des fonctions de polarisation.

Attempts for a quantitative discussion of bonding properties of sulphur have been recently made in the framework of non empirical SCFLCAO theory [1, 2, 3]. The molecule which received most attention is one of the simplest sulphur derivatives: H_2S. Orbital basis of different size with and without inclusion of *d* orbitals were adopted and a large number of wave functions are now available for H_2S molecule [1, 3, 4, 5, 6, 7]. Evidence has been given [1, 3] that the rôle played by *d* orbitals in the theoretical description of the molecule may be considerably affected by the type and the size of the orbital basis. The aim of this note is to ascertain how accurate an SCF molecular wave function for H_2S can be if *d* orbitals or other polarisation functions are not included in the basis set.

Computational Procedure and Results

The Roothaan's SCF-LCAO-MO method was applied. The IBMOL program [8] adapted for the CDC 6600 computer by D-J. David [9] was used. The basis set (12*s*, 9*p* gaussian orbitals for sulphur and 5*s* for hydrogen, contracted respectively to 6*s*, 4*p*, 2*s*) has been given by Veillard [10], and Huzinaga [11]. As far as molecular geometry is concerned the only parameter adopted is the SH bond length (2.521 a. u.) [12] and computations were performed for a set of bond angles (75°, 90°, 95°, 100°, 105°). Total energies are given in Table 1. The orbital energies when the bond angle is 95° are given in Table 2. A Mulliken population analysis is reported in Table 3. The computed physical properties for the molecule are collected in Table 4 while a comparison with *ab initio* results by other authors is made in Table 5.

Table 1. *Computed total energies (a. u.) of* H_2S *for different bond angles*[a]

75°	90°	95°	100°	105°
-398.60595	-398.61886	-398.62029	—398.61950	-398.61712

[a] A four-point Lagrange interpolation gives an equilibrium bond angle of 95.5° and -398.62030 and 398.58391 for the total and the kinetic energy, respectively.

Table 2. *Orbital energies (a. u.) for* H_2S *at 95°*

	1	2	3	4	5	6	7
a_1	-91.9992	-8.9895	-6.6773	-1.0167	-0.4978	0.2043	0.7686
b_2	- 6.6797	-0.6039	0.2014				
b_1	- 6.6735	-0.4065	1.2139				

Table 3. *Gross atomic and overlap populations*

	Gross atomic populations					Overlap populations	
	s_S	$(x, y)_S$	z_S	s_H	d_S	H—H	S—H
present work	5.872	6.340	4.	0.893	–	0.089	0.667
Ref. [6] *s, p*	5.805	6.381	4.	0.907	–	–	0.662
Ref. [6] *s, p, d*	5.785	6.421	3.998	0.824	0.147	–	0.719

Table 4. *Experimental and computed physical properties of* H_2S. *All values in a. u.*

	theor.	exp.	Ref.
r_{SH}	2.521 (ass.)	2.521	[12]
$\widehat{HSH}$	95.5°	92.2°	[12]
D_e	0.1388	0.2584	[14]
μ	0.6748	0.3856	[19]
1st IP	0.4065 ($2b_1$)	0.3785	[16]
2nd IP	0.4978 ($5a_1$)	0.4851	[16]
3rd IP	0.6039 ($2b_2$)	0.5549	[16]
S_{2p} IP	6.6735 ($1b_1$)	6.2879	[16]
S_{2s} IP	8.9895 ($2a_1$)	8.6178	[16]

Table 5. *Summary of ab initio computations on* H_2S *(bond lenght and bond angles when assumed are quoted in brackets). All values in a. u.*

References	r_{SH}	$\widehat{HSH}$	E	D_e	1st IP	μ
[4]	2.509	89.4°	−397.5891		0.351	0.6789
[5]	2.525	(93.05°)	−394.6794			
[1]	(2.5228)	99.9°	−379.6395		0.1247	
		98.8°^{a}	−381.0404^a		0.1196^a	0.6885^a
[6]	(2.5096)	(92.2°)	−397.8415	0.2139	0.346	
[7]	(2.5427)	(93.3°)	−397.905	0.2771	0.3660	0.021
[3]	(2.5096)	(92.2°)	−394.463		0.356	0.6846
			−394.516^a		0.343^a	0.2597^a
present work	(2.521)	95.5°	−398.6203	0.1389	0.4068	0.6748
experimental	2.521	92.2°	−400.80^b	0.2584	0.3785	0.3856

[a] *d* orbitals included

[b] Estimated by Moccia [4].

Discussion

The Hartree-Fock energy of separated atoms in H_2S is estimated −398.5048 [13]. The total molecular energies here computed are the only ones in the literature below this limit[1]. If one keeps in mind the experimental value of atomisation energy (0.26 a. u.) [14], the SH bond correlation energy (0.04 a. u.) [15] and pays attention to the fact that the charge distribution of inner electrons in the sulphur atom and in the molecule should not greatly differ, our computed energy for the equilibrium bond angle is expected to be no more than 0.06 a. u. above the Hartree-Fock limit of the molecule. This estimate corresponds to a complete neglect of the bond-bond and bond-core correlation energies, which are expected to reduce significantly the above quoted value.

The equilibrium bond angle obtained in the present work is in better agreement with experiment than the value in Ref. [1] although we did not include *d* orbitals. On the other hand the same kind of accuracy has been achieved by Moccia with a simpler wave function (OCE) [4]. An approximation to the first ionization potential obtained by assuming the validity of Koopman's theorem compares favourably with the results by other authors [6, 7]: *d* orbitals have small effects on this property, the electron being removed essentially from the $3p_\pi$ orbital of sulphur, whose energy in the molecule is practically the same as in the atom. The accuracy of ionization potentials as predicted by orbital energies decreases significantly for inner electrons. For instance, the ionisation potential of $2p$ sulphur electron (S_{2p} IP) is −180.7 eV. to be compared with an experimental value of −171.7 eV. [16]. Relativistic effects, although not negligible [17], cannot account for such a difference. Therefore a more careful analysis of the limits of the Koopman's approximation when inner electrons are involved in transitions seems necessary.

Using the orbital energies in Table 2 the first excited state is predicted of $^1A_2$ symmetry, 0.2835 a. u. above the ground state, in agreement with Polezzo

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[1] *Note Added in Proof:* A recent calculation by B. Roos and P. Siegbahn: Theoret. chim. Acta (Berl.) **17**, 199 (1970), with polarisation functions on all atoms implementing the same basis set used here, gives −398.682 a.u. for the total energy (geometrical parameters not reported).

et al. results [7]. On the other hand virtual orbitals in Table 2 differ considerably from those given in [7]: $3b_2, 6a_1, 7a_1$ orbital energies, for example, are 1.5 and 5.7. eV. lower and 7.0 eV. higher, respectively. Even larger differences are observed when comparison is made with semiempirical values [18]. This makes the previous assignment [18] of UV transitions in H_2S rather doubtful.

The computed atomization energy for the molecule ($D_e = 0.1389$ a. u.) is about 50% the experimental value, as it is usually found in many accurate LCAO-SCF computations, the difference being mainly due to the extra-correlation bond energy. Some authors [6, 7] by using more limited orbital basis but inclusive of *d* orbitals report values in fair agreement with experiment. By accepting the previous estimate of the Hartree-Fock energy of the molecule, the addition of *d* orbitals to the basis set we used is expected to cause only a small change in the computed binding energy (a value less than 0.19 a. u. should be obtained).

The analysis of the total electronic density in terms of gross atomic and gross overlap populations provides a simple way of comparing different wave functions. If comparison is made with Boer-Lipscomp [6] *s*, *p* wave function, our populations do not show significant changes (Table 3). All computations not including polarisation functions lead practically to the same electron distribution and the computed dipole moments do not change with the size of the orbital basis, all values being in the range 0.67 – 0.69 a. u.[2], to be compared with an experimental value 0.38 a. u. [19]. With *d* orbitals included, larger gross atomic charge separations and SH overlap populations have been predicted (Table 3) and the computed dipole moments are below the experimental value (a value as low as 0.021 a.u. is quoted [7]). Judging from these results, *d* orbitals are very effective in changing the electron distribution within the molecule even if different polarisation functions (*p* orbitals over hydrogen atoms, for example) could in principle be suitable to this purpose.

Theoretical values of the binding energy and dipole moment of H_2S suggest that *d* orbital contribution to the bonding has been somewhat overestimated when incomplete *s*, *p* basis sets have been used.

In a following paper a more quantitative discussion of these problems will be presented.

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[2] The computed dipole moment increases slightly with the bond angle in the range considered and a value of 0.702 a. u. is found when $\widehat{HSH}$ is 105°.

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Dr. Beniamino Cadioli
Istituto di Chimica Fisica
Università di Modena
Via Campi 183
I-41100 Modena, Italy