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MO-SCF-LCAO Studies of Sulphur Compounds

I. H_2S and SO_2

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Results from approximate Hartree-Fock calculations on the molecules H_2S and SO_2 are reported. The calculations employ two contracted Gaussian functions per atomic orbital. Polarization functions have been added on all atomic centres. 3*d* functions on sulphur are found to be of importance for the description of the SO bond in SO_2, especially through d-π backbonding. A number of molecular properties have been computed. Good agreement with experiment is obtained in all cases, where such data are available. An electron density map for the molecule SO_2 is shown, together with an electron density difference map showing the detailed effect of the 3*d* functions on the electron distribution.

Für H_2S und SO_2 werden die Ergebnisse näherungsweiser Hartree-Fock-Rechnungen, die auf kontrahierten Sätzen von Gaußfunktionen und zusätzlichen Polarisierungsfunktionen beruhen, mitgeteilt. Es zeigt sich, daß die 3*d*-Funktionen für die SO-Bindung in SO_2 (d-π-Rückbindung) von Wichtigkeit sind. Eine Reihe molekularer Eigenschaften wurde mit gutem Erfolg — soweit Vergleichsmaterial vorliegt — berechnet und der Einfluß der 3*d*-Funktionen auf die SO-Bindung mittels Elektronendichte- und -dichtedifferenz-Diagrammen veranschaulicht.

Introduction

This paper is the first in a series, which will present results from *ab initio* MO–SCF calculations with Gassian type wave functions for the molecules H_2S, SO_2, SCO, CS_2, SOF_2, SF_6, C_4H_4S and also the ion SO_4^{-2}. Chemical shifts of S(2*p*) ionization potentials for these molecules were reported in a previous paper [1], where the correlation between the chemical shifts and the charge on the sulphur atom was discussed.

In the present paper we present the details of the calculations on H_2S and SO_2 together with a number of molecular properties. These molecules are the smallest in the series and were therefore used to test the basis sets used in the subsequent calculations, and the importance of polarization functions on different centres. Some of the results obtained in the study of the polarization functions have been reported in an earlier paper [2]. Energy optimizied values were obtained for 3*d* exponents for S and O in H_2S and H_2O, and for the 2*p* exponent for H in H_2O. These orbital exponents have been used in the present work. Another part of the calculations, reported in [2], was concerned with the relative importance of polarization functions for first and second row atoms. 3*d* functions on sulphur in H_2S were found to be more important than 2*p* functions on the hydrogens. The 2*p* functions were on the other hand found to be more important in H_2O than 3*d* functions on oxygen, which had only a small effect on the charge distribution. The subsequent calculations on the other sulphur compounds will include polarization functions for sulphur and hydrogen but not for first row atoms.

All calculations have been made by means of the program system IBMOL, version 4 [3] on an IBM 360/75 computer.

H_2S

Method

A number of *ab initio* calculations on this molecule have been reported [4–9]. Recently Rothenberg, Young and Schaefer presented a Gaussian type wave function for this molecule very similiar to the present calculation with the larger basis set [10].

All calculation were performed at the experimental geometry, with an S–H distance of 1.335 Å and a bond angle of 92°12 [11].

We have previously reported Gaussian basis sets for first and second row atoms [12]. These basis sets are of medium size, including 10*s*-type and 6*p*-type functions. The number of basis functions is large enough to be contracted to a split shell set (i.e. with two contracted functions per atomic shell). The contractions used here is for *s*-type functions (4, 2, 1, 1, 1, 1) and for *p*-type functions (2, 2, 1, 1). In addition to this basis one set of 3*d* functions with exponent 0.54 [2] was included. For hydrogen we use the 4*s*-type functions given by Huzinaga [13] with the contraction (3, 1) and augmented with one set of *p*-type functions with exponent 0.8 [2].

The basis set for sulphur discussed above will be used in all calculations in this series. It is therefore of interest to compare the results obtained with this basis to a near Hartree-Fock calculation for the smallest molecule H_2S. We have therefore also made a calculation with the large (12, 9) basis set of Veillard [14]. The contraction was for *s*-type functions (6, 2, 1, 1, 1, 1) and for *p*-type functions (5, 1, 2, 1). Two sets of 3*d*-functions with exponents 0.54 and 2.00 were added. The same basis set as mentioned above was used for hydrogen. This large basis set is comparable to that ot Rothenberg *et al.* They used a somewhat different contraction for the sulphur *p*-type functions and 5*s*-type functions on the hydrogens. The different calculations will be labelled as follows:

I. (S/10, 6) (H/4) contracted to $\langle S/6, 4\rangle$ $\langle H/2\rangle$,
II. (S/10, 6, 1) (H/4, 1) contracted to $\langle S/6, 4, 1\rangle$ $\langle H/2, 1\rangle$,
III. (S/12, 9) (H/4) contracted to $\langle S/6, 4\rangle$ $\langle H/2\rangle$,
IV. (S/12, 9, 2) (H/4, 1) contracted to $\langle S/6, 4, 2\rangle$ $\langle H/2, 1\rangle$.

Results

The total and orbital energies obtained in the different calculations are presented in Table 1. Comparison is made to the one-center calculation of Moccia [4], the minimal STO basis calculation by Boer and Lipscomb [8] and to the large basis GTO calculation by Rothenberg *et al.* [10].

Table 1. *Total and orbital energies for* H_2S *(in atomic units)*

	I	II	III	IV	OC[a]	STO[b]	*A*[c]	Exp.
T.E.	−398.513	−398.562	−398.631	−398.682	−397.589	−397.842	−398.686	−400.420[e]
MO:								
$1a_1$	− 91.957	− 91.950	− 91.986	− 91.976	− 92.479	− 91.902	− 91.974	—
$2a_1$	− 8.962	− 8.949	− 8.971	− 8.959	− 9.080	− 8.775	− 8.962	8.618[d]
$1b_2$	− 6.654	− 6.642	− 6.660	− 6.647	− 6.636	− 6.447	− 6.652	
$3a_1$	− 6.652	− 6.641	− 6.658	− 6.646	− 6.635	− 6.446	− 6.651	6.281
$1b_1$	− 6.649	− 6.638	− 6.656	− 6.644	− 6.632	− 6.442	− 6.649	
$4a_1$	− 0.997	− 0.975	− 1.003	− 0.982	− 0.940	− 0.935	− 0.986	0.809
$2b_2$	− 0.586	− 0.582	− 0.593	− 0.592	− 0.531	− 0.561	− 0.594	0.550
$5a_1$	− 0.486	− 0.491	− 0.493	− 0.500	− 0.454	− 0.466	− 0.501	0.485
$2b_1$	− 0.385	− 0.376	− 0.391	− 0.382	− 0.351	− 0.346	− 0.383	0.379

[a] One-center approximation, Ref. [4].

[b] Minimal basis STO calculation, Ref. [8].

[c] Rothenberg *et al.*, Ref. [10].

[d] Experimental ionization-potentials, Ref. [17].

[e] Calculated from the experimental energies of the free atoms and the dissociation energy of H_2S [16].

Summing up the experimental energies for sulphur and hydrogen and the dissociation energy of H_2S, 7.54 eV [15], gives a total experimental energy of −400.421 a.u. The dissociation energy D_e can be decomposed into three terms if we assume, that relativistic energy is unchanged compared to the free atoms.

$$D_e = D_{HF} - \Delta E_{corr} - E_{zp},$$

where D_{HF} is the dissociation energy in the HF approximation, ΔE_{corr} the molecular extra correlation energy and E_{zp} the zero-point energy. An upper limit of −2.0 eV for ΔE_{corr} seems reasonable, since two extra electron pairs are formed in H_2S. With an experimental value of 7.54 eV for D_e and 0.40 eV for E_{zp} [16], this gives D_{HF} less than 5.94 eV, and a lower limit for the Hartree-Fock energy for H_2S of −398.72 a.u. Rothenberg *et al.* estimates the HF energy to be −398.73 a.u. The lowest energy obtained in the present work is −398.68 a.u. and is thus 0.04 a.u. above the HF limit. Calculations on the sulphur atom shows that 0.03 a.u. of this discrepancy is due to an inadequate description of the inner shells.

The total energy, obtained with the medium size basis, including polarization functions, is 0.17 a.u. above the HF-limit. The same energy difference, 0.17 a.u. is obtained for the free atoms. The molecular formation therefore appears to be equally well described with this basis set as with the large set. This point will be further discussed below.

The experimental ionization potentials given in the last column of Table 1 have been measured with the ESCA technique [17]. Koopmans' theorem gives good agreement between outer shell orbital energies and the ionization potentials. The agreement is less good for the inner shells, where the reorganization energy becomes larger.

Results from the population analysis and calculated dipole moments are given in Table 2. It is of interest to note that the results obtained with the

Table 2. *Population analysis and dipole moment for* H_2S

	I	II	III	IV	Ref. [10]
$q(S)$[a]	16.21	16.16	16.18	16.16	16.10
$q(H)$	0.89	0.92	0.91	0.92	0.95
$o(S\text{–}H)$[b]	0.58	0.67	0.57	0.67	0.68
$o(H\text{–}H)$	−0.07	−0.04	−0.08	−0.05	−0.03
$q(S3d)$[c]		0.07		0.08	0.06
μ[d]	1.82	1.27	1.87	1.28	1.33

[a] Gross atomic population.

[b] Overlap population.

[c] 3*d* population on sulphur.

[d] Dipole moment in Debye (experimental value 1.02 *D* [23]).

Table 3. *The Hellmann-Feynman forces on the nuclei in* H_2S[a]

	I	II	III	IV	Ref. [10]
$F_z(S)$	1.37	0.39	1.63	0.43	0.68
$F_x(H)$	0.11	0.01	0.10	0.01	0.02
$F_z(H)$	−0.09	−0.01	−0.08	−0.00	−0.01

[a] In atomic units (1 a.u. of force = 8.2378×10^{-3} dyn).

medium size basis is almost identical to the large basis results. Also the 3*d* populations are similar. Rothenberg *et al.* have pointed out that a minimal basis set calculation such as that of Boer and Lipscomb [8], or Simonetta *et al.* [7] tend to overestimate the 3*d* participation in the bonding. It is therefore gratifying to see, that the 3*d* functions also in the medium size basis play the role of polarization functions rather than that of improving inadequacies in the *sp*-basis.

The present calculation gives a 3*d* population on only 0.08 electrons. A similar result was obtained by Rothenberg *et al.* A discussion of the fact that 3*d* functions are of relatively little importance in H_2S, as compared to SO_2, will be given below.

A further confirmation of the similarity of the two basis sets for the description of the chemical bond in H_2S can be found from a study of the Hellmann-Feynman forces on the nuclei. These forces will, according to the Hellmann-Feynman theorem, coincide with the actual forces at the Hartree-Fock limit. The actual calculations give, of course, a total force different from zero. It is, however, of interest to notice, that the two basis sets give almost identical results. The total force is dominated by the force on the sulphur nucleus. Since inner shell orbitals will give only small contributions to this force, it appears that the outer molecular orbitals are equally well described by the medium size basis as by the larger basis set. A large reduction of the forces is obtained, when polarization functions are included. The individual forces are reduced mainly by the inclusion of polarization functions on the appropriate centre. Thus the inclusion of 2*p* functions on hydrogen reduces $F_z(S)$ from 1.63 to 1.33 a.u., but $F_x(H)$ from 0.10 to 0.02 and $F_z(H)$ from

−0.08 to −0.01 a.u. The three forces are further reduced to 0.43, 0.01 and 0.00 a.u. when $3d$-functions on sulphur are added to the basis set. It should be noted that the individual forces will not go to zero, when the wavefunction approaches the HF-limit, since the calculations have not been done at the HF-equilibrium geometry.

Another sensitive measure of the details of the charge distribution is given by the quadrupole moment tensor. Computed values are given in Table 4. The larger basis set gives larger values for all components and also for $\langle r^2 \rangle_{\mathrm{CM}}$. This is probably due to the fact that the valence orbital exponents are generally smaller in a larger basis. The use of the same contraction (two contracted functions per valence orbital) therefore gives more diffuse basis functions in this case. It is not clear whether these functions are optimal in the molecule, than the more compressed ones obtained with the medium size basis. For SO_2 this smaller basis set actually gives better agreement with observed values of the quadrupole moment tensor, than the larger basis calculation of Rothenberg

Table 4. *Molecular properties for* H_2S

	I	II	III	IV	Ref. [10]	Obs[a]
Quadrupole moment (10^{-26} esu · cm^2):						
θ_{xx}	2.38	2.52	2.83	2.94	2.89	
θ_{yy}	− 3.03	− 3.41	− 3.55	− 3.94	− 3.88	
θ_{zz}	0.65	0.89	0.72	0.94	0.99	
Diamagnetic susceptibility (10^{-6} erg/G^2 · mole):						
χ^d_{xx}	−32.94	−32.46	−33.72	−33.31	−33.27	
χ^d_{yy}	−37.61	−36.83	−37.82	−37.12	−37.05	
χ^d_{zz}	−33.15	−32.72	−33.70	−33.39	−33.38	
χ^d_{av}	−34.57	−34.00	−35.08	−34.61	−34.58	
Potential at the nucleus (a.u.):						
ϕ(S)	−59.24	−59.24	−59.19	−59.20	−59.20	
ϕ(H)	− 0.98	− 1.02	− 0.98	− 1.01	− 1.01	
Electric field gradient at the sulphur nucleus (a.u.):						
q_{xx}(S)	− 2.201	− 2.254	− 2.454	− 2.398	− 2.168	
q_{yy}(S)	2.824	2.779	3.072	2.817	2.558	
q_{zz}(S)	− 0.624	− 0.328	− 0.618	− 0.419	− 0.389	
Quadrupole coupling constants, assuming $Q(S^{33}) = -0.062$ barns (MHz):						
$eq_{xx}Q$	32.1	32.8	35.7	35.0	31.6	32
$eq_{yy}Q$	41.2	40.5	44.8	41.1	37.2	40
$eq_{zz}Q$	9.1	7.7	9.0	6.1	5.6	8
Other expectation values (a.u.):						
$\langle 1/r_{\mathrm{S}} \rangle$	−60.03	−60.04	−59.98	−59.99	−60.00	
$\langle 1/r_{\mathrm{H}} \rangle$	− 7.60	− 7.63	− 7.59	− 7.63	− 7.67	
$\langle r^2 \rangle_{\mathrm{CM}}$	43.65	42.93	44.29	43.70	43.67	
$\delta(\bar{r} - \bar{r}_{\mathrm{S}})$	2522.3	2522.2	2598.8	2598.5	2598.5	
$\delta(\bar{r} - \bar{r}_{\mathrm{H}})$	0.386	0.368	0.378	0.363	0.427	

[a] Ref. [19].

and Schaefer [18] (*vide supra*). It should also be noted that the addition of polarization functions has almost the same effect on the quadrupole moments in both calculations.

A number of other expectation values are reported in Table 4. The difference between the results obtained with the two basis sets are in all cases small.

Only for the nuclear quadrupole constants do we have the possibility to make a comparison with observed values [9]. Rothenberg and Schaefer have from their studies of H_2S and SO_2 and from the wavefunction for OCS by McLean and Yoshimine [20] concluded, that -0.062 barns is the most reliable value for the nuclear quadrupole moment of S^{33}. Agreement between predicted and observed values are equally good, or even better, for the medium size basis calculation.

SO_2

Method

Two *ab initio* calculations on this molecule have been reported in the literature. Hillier and Saunders [21] have discussed the importance of 3*d* functions on sulphur from an approximate STO calculation.

Recently Rothenberg and Schaefer performed a calculation with two contracted gaussian functions per valence shell [18]. For sulphur 12*s*-type functions were grouped (6, 2, 1, 1, 1, 1) and 9*p*-type functions (6, 1, 1, 1). A set of 3*d* functions with exponent 0.6 was added to the basis set. For oxygen 10*s*-type and 5*p*-type functions were contracted to (3, 4, 2, 1) and (4, 1) respectively. In addition a set of 3*d* functions with exponent 0.8 was used.

The calculation reported here utilized the medium size basis described in the previous section for sulphur. For oxygen we have used a set of 7*s*-type and 3*p*-type primitive gaussians, contracted to (4, 1, 1, 1) and (2, 1) respectively [12]. A set of 3*d* functions with exponent 1.33 was added. This exponent had been optimized in a previous calculation on the water molecule [2]. The number of contracted functions is thus the same in both calculations. Rothenberg and Schaefer, however, used a larger set of primitive gaussians. Their wave function will therefore give a better description, especially of the inner shell orbitals. It is of great value to be able to compare the results obtained in the present calculation to the result obtained with this near Hartree-Fock wave function for SO_2. It will be possible to draw conclusions about the reliability of the results obtained for the larger sulphur compounds, where large basis calculations are unfeasible, from such a comparison. The calculations were performed at the experimental geometry, with an S–O distance of 1.432 Å and an O–S–O angle of 119°54 [26].

Results

The total energies are presented in Table 5. The difference between our best result and the lowest energy given by Rothenberg and Schaefer is 0.38 a.u. Inspection of corresponding calculations on the free atoms shows, that 0.30 a.u. is due to a less good description of the inner shell orbitals. The improve-

Table 5. *Total energies, virial theorem and dissociation energies for* SO_2

	TE (a.u.)	$-V/T$	D_e (eV)
no $3d$	-546.629	1.9963	0.27
$3d$ on S only	-546.788	1.9974	4.60
$3d$ on O only	-546.696	1.9969	2.10
$3d$ on S and O	-546.831	1.9978	5.77
Ref. [18]	-547.209	2.0003	3.85
Exp.	-549.775	—	11.18[a]

[a] Ref. [18].

Table 6. *Orbital energies and sulphur 3d orbital populations in* SO_2 *(energies in a.u.)*

	no $3d$	With $3d$	Ref. [18]	IP(obs.)	$q(3d\mathrm{S})$
$1a_1$	-92.193	-92.159	-92.196		—
$2a_1$, $1b_2$	-20.635	-20.618	-20.613		—
$3a_1$	-9.198	-9.145	-9.163		—
$2b_2$	-6.891	-6.838	-6.853		—
$4a_1$	-6.884	-6.836	-6.850	6.457[a]	—
$1b_1$	-6.884	-6.835	-6.852		—
$5a_1$	-1.550	-1.498	-1.510		0.02
$3b_2$	-1.428	-1.393	-1.404		0.06
$6a_1$	-0.873	-0.856	-0.870		0.01
$7a_1$	-0.694	-0.677	-0.696	0.613[b]	0.02
$4b_2$	-0.671	-0.676	-0.699	—	0.00
$2b_1$	-0.673	-0.649	-0.667	0.609	0.03
$5b_2$	-0.525	-0.516	-0.540	0.496	0.09
$1a_2$	-0.480	-0.491	-0.516	0.485	0.18
$8a_1$	-0.468	-0.466	-0.491	0.460	0.16

[a] Ref. [17]. — [b] Ref. [22].

ment in total energy due to the inclusion of $3d$ functions on all centres is 0.20 a.u., which is somewhat less than the 0.26 a.u. obtained in [18].

Orbital energies are presented in Table 6. The $3d$ populations on sulphur for the different molecular orbitals is also given. When $3d$ functions are included, the energy level order differs from that in [18] only in the relative positions of the orbitals $7a_1$ and $4b_2$. These two orbitals are, however, almost degenerate in both calculations. The energies for the outer orbitals can be compared to the ionization potentials obtained from the photoelectron spectrum for SO_2 reported by Eland and Danby [22].

The first band was found to be due to ionization from a lone-pair electron. The corresponding molecular orbital $8a_1$ can, however, not be characterized as a lone-pair. It extends over all three atoms and is antibonding with a large negative overlap population between the sulphur and oxygen atoms.

The second band includes two progressions corresponding to the two closely spaced orbitals $1a_2$ and $5b_2$, both of which are antibonding between the oxygens. Analysis of the vibrational structure also indicates that one of these orbitals is S–O bonding. The π-orbital $1a_2$ is non-bonding in the sp-approximation. This is,

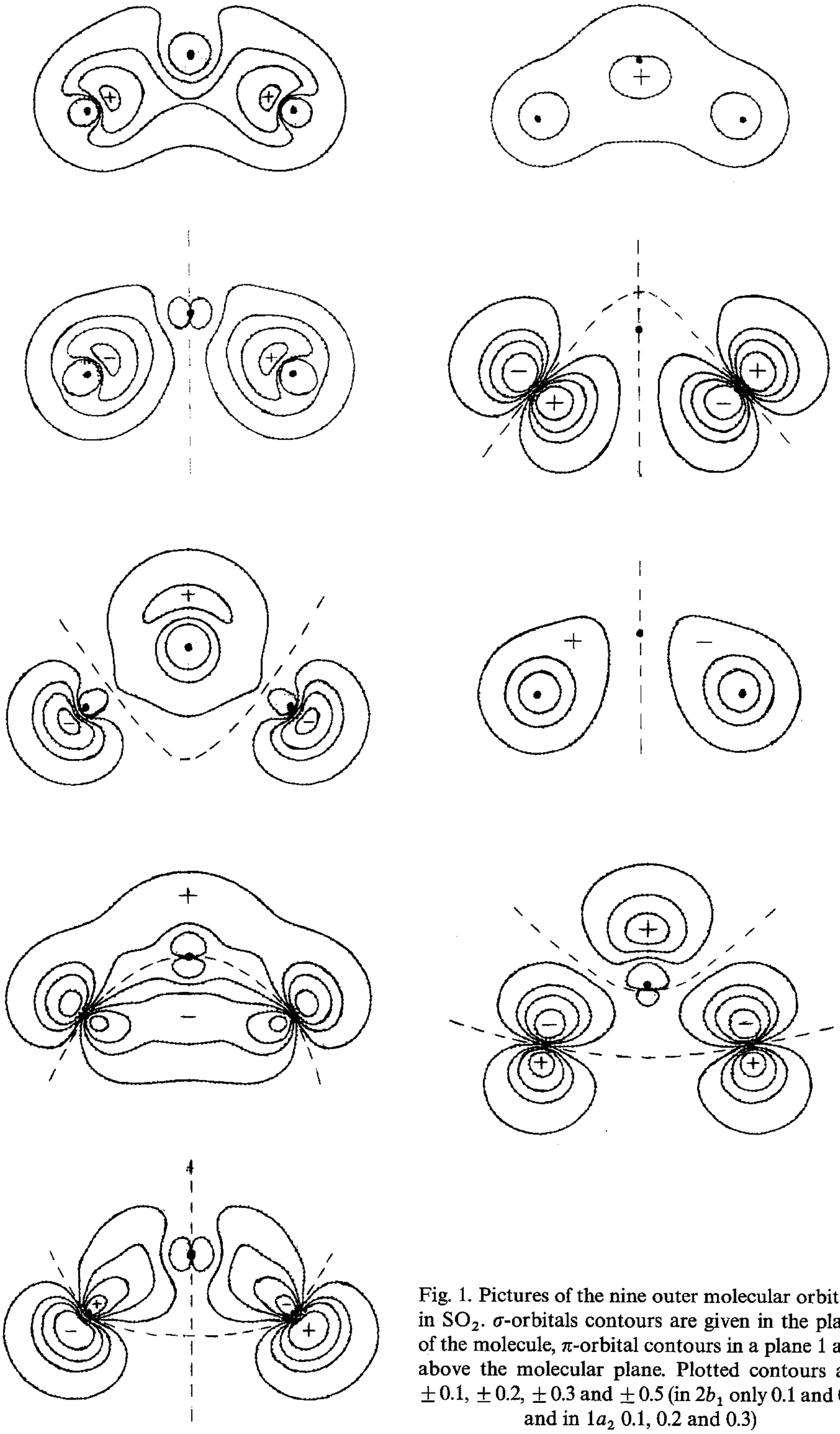

Fig. 1. Pictures of the nine outer molecular orbitals in SO_2. σ-orbitals contours are given in the plane of the molecule, π-orbital contours in a plane 1 a.u. above the molecular plane. Plotted contours are ±0.1, ±0.2, ±0.3 and ±0.5 (in $2b_1$ only 0.1 and 0.2 and in $1a_2$ 0.1, 0.2 and 0.3)

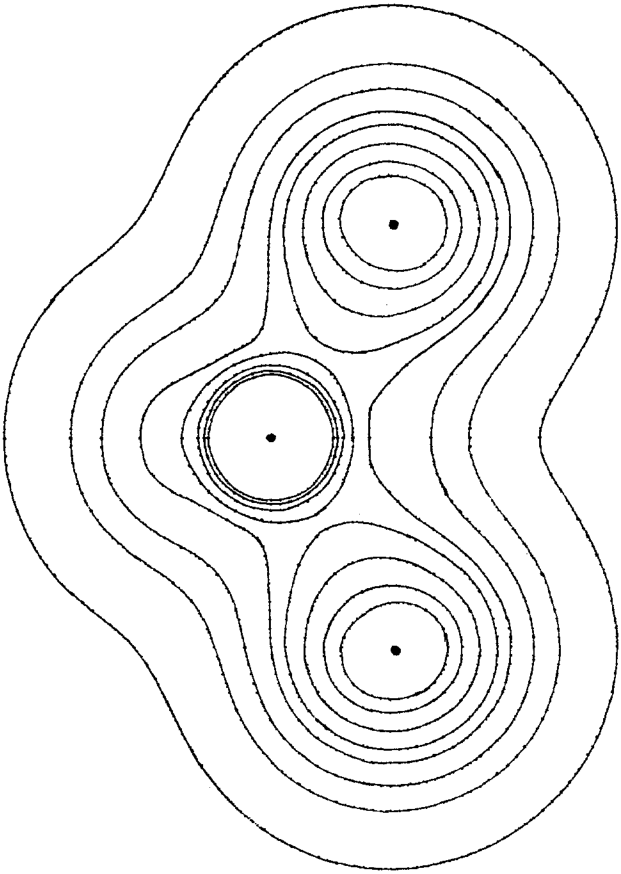

Fig. 2. Total electron density contours for SO_2. Plotted contours are 0.01, 0.05, 0.10, 0.20, 0.30, 0.50 and 1.00

however, the orbital, which has the largest $3d$ population on sulphur (cf. Table 6). The calculations thus give an effective d-π backbonding in this orbital.

Eland and Danby found two progressions in the third band system. These could be assigned to two of the three molecular orbitals $7a_1$, $2b_1$ and $4b_2$, presumably the two bonding orbitals $7a_1$ and $2b_1$. The orbital $7a_1$ and the non-bonding orbital $4b_2$ have in all calculations been found to be almost degenerate. It is therefore surprising that the photoelectronspectrum does not contain a progression corresponding to ionization of a $4b_2$ electron, at least not in the range below 18 eV.

Contour diagrams for the nine outer molecular orbitals in SO_2 are given in Fig. 1. The σ-orbitals are shown in the molecular plane and the π-orbitals in a plane one atomic unit from and parallel to the molecular plane.

Table 7 gives the gross atomic and overlap populations. The total number of $3d$ electrons on sulphur was found to be 0.55, which should be compared to the 0.43 electrons obtained in [18]. The minimal basis calculation of Hillier and Saunders [21] gives a $3d$ population of 1.17 electrons. That $3d$-electrons are important for the description of the bonding in SO_2 is evident from the overlap population, which increases from 0.08 to 0.78 when 3*d* functions are added. 13% of this (0.10 electrons) is due to *d*-π backbonding in $1a_2$. The total electron density distribution is shown in Fig. 2, which gives the density contours in the molecular plane. In Fig. 3 we show the electron density difference obtained when the polarization functions are added to the basis set. The effect of the 3*d* functions on sulphur is to increase the density in the bonding region and also in the lone-pair region at the sulphur atom. The 3*d* functions will, quite naturally have their largest effect on the most loosely bound electrons. The main effect will therefore not be to increase the bond strength of already bonding orbitals, but to make non-bonding orbitals bonding and diminish the anti-bonding character of others. It was noted above that the π-orbital $1a_2$, which is non-bonding, without 3*d* functions, shows an effective *d*-π backbonding, when these functions are included, with 0.18 electrons in the 3*d* sulphur orbital. The next largest effect is on the antibonding orbital $8a_1$. The negative S–O overlap population in this orbital increases from -0.46 to -0.24 with the inclusions of the 3*d* functions. The orbital also becomes more localized at the sulphur atom, thus increasing its lone-pair character. The effect of the 3*d* functions on other orbitals is less pronounced. The orbital $5b_2$ has a sulphur 3*d* population of 0.09 and becomes weakly S–O bonding and less O–O anti-bonding.

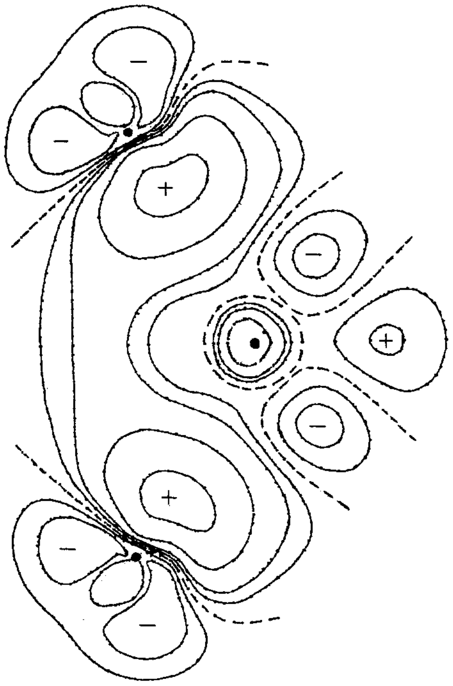

Fig. 3. Electron density difference contours for SO_2 showing the effect of 3*d* functions. Plotted contours are 0.0, ±0.01, ±0.02, ±0.05 and ±0.10

Table 7. *Population analysis for* SO_2

	no 3*d*	3*d* on S	3*d* on S and O	Ref. [18]
q(S)	14.49	15.08	14.95	14.87
q(O)	8.76	8.46	8.52	8.56
$q(3d\text{S})$	—	0.59	0.55	0.43
$q(3d\text{O})$	—	—	0.07	0.06
o(S–O)	0.08	0.74	0.78	0.69

Table 8. *Molecular properties for* SO_2

	no 3*d*	With 3*d*	Ref. [18]	Obs.
Dipole moment (Debye)				
μ	2.60	2.17	2.28	1.63[a]
Quadrupole moment (10^{-26} esu · cm^2)				
θ_{xx}	− 8.71	− 6.56	− 6.88	− 5.3 ± 0.4[b]
θ_{yy}	6.46	4.99	5.17	4.0 ± 0.6
θ_{zz}	2.27	1.57	1.71	1.3 ± 0.3
Diamagnetic susceptibility (10^{-6} erg/G^2 mole)				
χ^d_{xx}	− 55.8	− 54.8	− 55.8	− 54.9[b]
χ^d_{yy}	−168.6	−165.6	−166.8	−164.3
χ^d_{zz}	−148.5	−145.9	−147.1	−145.1
χ^d_{av}	−124.3	−122.1	−123.2	−121.4
Potential at nucleus (a.u.)				
ϕ(S)	− 59.01	− 59.04	− 58.98	—
ϕ(O)	− 22.28	− 22.29	− 22.30	—
Hellmann-Feynman force (a.u.)				
F_z(S)	1.45	0.57	0.95	—
F_x(O)	2.38	0.89	0.76	—
F_z(O)	− 1.27	− 0.47	− 0.40	
Electric field gradient at the sulphur nucleus (a.u.)				
q_{xx}(S)	− 0.203	− 0.134	− 0.046	—
q_{yy}(S)	− 1.895	− 1.930	− 2.112	
q_{zz}(S)	2.098	2.064	2.159	
Quadrupole coupling constants, assuming $Q(S^{33}) = -0.062$ barns (MHz)				
$eq_{xx}Q$	2.95	1.95	0.71	1.7 ± 0.2[c]
$eq_{yy}Q$	27.61	28.12	32.25	24.0 ± 0.2
$eq_{zz}Q$	− 30.57	− 30.07	− 32.97	− 25.71 ± 0.03
Other expectation values (a.u.)				
$\langle 1/r_S \rangle$	64.92	64.95	64.89	—
$\langle 1/r_O \rangle$	29.90	29.91	29.93	—
$\langle r^2 \rangle_{CM}$	156.97	154.18	155.56	153.3[b]
$\delta(\bar{r} - \bar{r}_S)$	2523.6	2523.1	2599.6	—
$\delta(\bar{r} - \bar{r}_O)$	284.7	284.4	287.5	—

[a] Ref. [23]. — [b] Ref. [24]. — [c] Ref. [25].

The discussion above refers to the calculation with 3*d* functions on all centres. It is, however, evident from the number given in Table 7, that the dominant effect is from the sulphur 3*d* functions. Polarization functions on the oxygens will only result in minor changes in calculated quantities.

A number of molecular properties have been calculated. Table 8 gives the results obtained in the calculations, without 3*d* functions and with 3*d* functions on both centres. A comparison is made to the results obtained by Rothenberg and Schaefer [18] and to experiment, where such data are available. A thorough discussion of the properties has been given in [18]. This will therefore not be repeated here. It is somewhat surprising to see, that agreement with experiment is in all cases slightly better for the calculation with the medium size basis.

Conclusions

MO–SCF calculations on the molecules H_2S and SO_2 using a medium size, split shell, basis of contracted gaussian functions have been reported. It was for both molecules possible to compare the results with calculations using a large set of primitive gaussians, but with the same number of contracted functions. The over all agreement with observed values for a number of molecular properties was found to be better with the medium size basis. There is one possible explanation to this. The orbital exponents for the valence orbitals become smaller when the number of basic functions is increased. It is therefore quite possible that the orbital exponents from the medium size basis are closer to exponents which would be optimal in the molecules. The conclusion would be, that a larger basis set is not always going to give better results, if not also the number of contracted functions in increased.

The 3*d* functions were found to be of much larger importance for SO_2 than for H_2S. One of the major reasons for this is the possibility of d-π backbonding in the former molecule. The 3*d* functions also have a large effect on strongly anti-bonding orbitals.

It seems possible to make the general conclusion that 3*d* functions will be of importance for a given molecular orbital, if the loss in energy due to the population of the 3*d* function is compensated by a corresponding increase in bond strength.

It is with this in mind easy to understand why 3*d* functions will be relatively unimportant in H_2S. The most loosely bond orbitals $5a_1$ and $2b_1$ are almost completely localized at the sulphur atom. There is then nothing to be gainded by a 3*d* population in these orbitals. The bonding orbitals are on the other hand too low in energy to interact effectively with the 3*d* functions. Actually the major part of the 3*d* population in H_2S (0.06 out of a total population of 0.08 electrons) is found in the bonding orbital $2b_2$, where the effect is a slight increase in bond strength.

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