

MO–SCF–LCAO Studies of Sulphur Compounds

II. The Sulphate Ion

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Received March 19, 1971

Results from an MO–SCF–LCAO study of the electronic structure of the sulphate ion is reported. An extended *sp* basis set of contracted Gaussian functions has been used together with *3d* polarization functions on the sulphur atom. The effect of these functions has been found to be significant, but not as large as has been suggested from previous calculations made with a minimal *sp*-basis. The effect of the *3d* functions on a number of expectation values of one-electron operators has been studied.

Es wird über die Ergebnisse einer MO–SCF–LCAO-Studie der Elektronenstruktur des Sulfations berichtet. Es wurde ein erweiterter *sp*-Basissatz von kontrahierten Gaußfunktionen zusammen mit *3d*-Polarisationsfunktionen am Schwefelatom benutzt. Der Einfluß dieser Funktionen ist bedeutend, aber nicht so groß wie in früheren Rechnungen mit minimalen *sp*-Basissätzen vermutet wurde. Der Effekt der *3d*-Funktionen auf eine Anzahl von Erwartungswerten von Einelektronen-Operatoren wurde untersucht.

Résultats d'un calcul MO SCF LCGO sur la structure électronique de l'ion sulfate. On a utilisé une base *sp* étendue de fonctions gaussiennes contractées avec des fonctions de polarisation *3d* sur l'atome de soufre. L'effet de ces fonctions s'avère significatif, mais cependant moins important que ne le laissaient prévoir des calculs antérieurs en base *sp* minimale. Etude de l'effet des fonctions *3d* sur les valeurs moyennes des opérateurs monoélectroniques.

1. Introduction

We report, in this series of papers the theoretical electronic structure and molecular properties of a number of sulphur compounds. The first paper in the series (hereafter referred to as I) presented the results obtained for the molecules H_2S and SO_2 [11]. Here the corresponding results for the sulphate ion, SO_4^{2-} , will be reported. The calculations are made within the MO–SCF–LCAO approximation, using an extended basis of contracted Gaussian functions, including also *3d* polarization functions on sulphur.

A number of approximate molecular orbital studies of the sulphate ion have appeared in the literature. The first seem to have been a series of Wolfsberg-Helmholtz calculations by Bishop *et al.* [1–2]. The outcome of these calculations were somewhat uncertain, since the results for the molecular orbital order were dependent on the parameter choice. It could, however, be concluded, that the highest filled orbital should be triply degenerate, and that sulphur *3d* orbitals are important for the description of sulphur oxygen bonds.

CNDO calculations on a number of molecules with second row atoms have been reported by Santry and Segal [3]. For the sulphate ion they obtained the molecular orbital order 1 below, if the basis set did not include $3d$ functions.

1. $(4a_1)^2 (3t_2)^6 (5a_1)^2 (4t_2)^6 (1e)^4 (1t_1)^6 (5t_2)^6$,
2. $(4a_1)^2 (3t_2)^6 (5a_1)^2 (4t_2)^6 (1e)^4 (5t_2)^6 (1t_1)^6$.

The ordering of the molecular orbitals $1t_1$ and $5t_2$ was reversed and order 2 obtained, when these functions were added to the basis set. The inclusion of $3d$ functions was thus found to have a significant effect. The gross atomic charge on sulphur was +1.15 with the sp -basis, but only +0.41 with the spd -basis. The explanation for this large reduction in charge was that backbonding and back-donation of charge through the molecular orbital $1e$ is made possible by the inclusion of the $3d$ functions. In the absence of these functions this orbital is completely localized on the oxygens. A large $3d$ population was also found in the orbital $5t_2$, which explained the stabilization of this orbital relative to the non-bonding orbital $1t_1$. The total $3d$ population obtained in this work was 2.19 electrons.

Approximate MO-SCF calculations for several sulphur and chlorine oxy-anions have been reported by Manne [4]. For the sulphate ion he obtained the order 2 for the molecular orbitals even without the inclusion of $3d$ functions. This is a noticeable deviation from results obtained in other calculations using similar methods.

Brown and Roby tested different CNDO schemes on the sulphate ion and obtained sulphur charges in the range +0.76 – +0.13 [5].

Hillier has reported on approximate MO-LCAO-SCF calculations, which give results similar to those obtained with the CNDO scheme [6]. The order of the molecular orbitals $1t_1$ and $5t_2$ were found to depend on the $3d$ functions. The sulphur charge was found to be +2.2 without and +1.2 with these functions. A total $3d$ population of 1.53 was reported.

Ab initio calculations on the sulphate ion have been reported by Hillier and Saunders [7–8] and also by Keeton and Santry [9]. Both these calculations utilize a minimal spd -basis of Slater orbitals, expanded in Gaussian functions by a least square procedure. Hillier and Saunders used a three term expansion and a $3d$ exponent of 1.2 (the three GTO exponents were 0.07, 0.17 and 0.54). Keeton and Santry used between three and six terms in their expansion and optimized the $3d$ exponent, obtaining the value 1.46 (STO).

The results of Hillier and Saunders show the same general features as the approximate calculations. Thus, without the $3d$ -functions order 1 was obtained, but with these functions the $5t_2$ orbital was strongly stabilized and order 2 obtained. Further the sulphur gross atomic charge changed from +1.55 to –0.55. The total population of the $3d$ -functions was found to be 2.57. However, the orbital exponent used, 1.2, corresponds to a very diffuse orbital which makes it difficult to assign the populations to the different atoms.

In summary then, previous calculations indicate that the $3d$ functions are of significant importance for the explanation of the chemical bond in the sulphate ion. These functions have a large stabilizing effect on the orbitals $1e$ and $5t_2$, and reverse the order of the orbitals $5t_2$ and $1t_1$. The sp approximation gives a very

polar S-O bond with a sulphur charge of around +2. On the other hand the *spd* calculations give an almost neutral sulphur atom, which results from back-bonding in the $1e$ orbital and *pd* hybridization in the $1t_2$ orbital.

These calculations have all been done with a minimal *sp* basis set. It is known, that calculations in this approximation tend to overestimate the importance of the $3d$ functions [11, 15]. Therefore one of the reasons for undertaking the present study was to investigate the effect of using a more extended *sp* basis. In addition we have calculated a number of molecular properties and investigated the importance of $3d$ functions for these properties.

2. Details of the Calculation

A tetrahedral configuration of SO_4^{-2} was used with an S-O distance of 1.50 Å. This is the average distance in a number of sulphates [10]. It is somewhat longer than the distance 1.44 Å used in previous studies.

The *sp* Gaussian basis set is the same as that used in the calculation on SO_2 [11, 12]. It consists of 10*s*-type and 6*p*-type primitive Gaussians for sulphur. This basis was augmented with one set of $3d$ functions with exponent 0.5, which is slightly less than the optimal value, 0.54, found for H_2S [13]. Keeton and Santry optimized the $3d$ exponent for a Slater type orbital expanded in three Gaussians by a least square procedure [9]. They obtained the values 1.78 and 1.46 for H_2S and SO_4^{-2} , respectively. Gaussian functions with the same radial density maxima have the exponents 0.53 and 0.36. The calculations were, however, done with a minimal *sp* basis. Their optimal exponent for the $3d$ functions is therefore probably smaller than the optimal exponent one would obtain with an extended *sp* basis. However, it is doubtful that using an extended *sp* basis would increase the optimal value as much as to 0.5. Hillier and Saunders used the STO exponent 1.2, which corresponds to a GTO exponent of 0.24 [8]. This certainly gives a too diffuse $3d$ function.

The Gaussian basis set for oxygen consists of 7*s*-type and 3*p*-type functions. The primitive Gaussian functions were contracted to give a final basis set consisting of two basis functions per atomic shell. The total number of contracted functions in the basis set was thus 64.

All calculations have been performed at an IBM 360/91 computer with the program system IBMOL IV [14].

3. Results and Discussion

The total and orbital energies are presented in Table 1. The total energy compares favourably with the results obtained from the minimal basis calculations of Hillier and Saunders [8]. Keeton and Santry, who used a more extended number of primitive Gaussians, but the same number of contracted functions, obtained a total energy of -692.608 a.u.

The addition of the $3d$ functions to the basis set gave an energy improvement of -0.232 a.u. Hillier and Saunders obtained an improvement of -0.837 a.u. with one set of $3d$ functions. An additional improvement of -0.102 a.u. was obtained

Table 1. Total and orbital energies for SO_4^{2-} (in atomic units)

	This calc. ^a		Hillier and Saunders [8] ^b		
	no 3d(S)	with 3d(S)	s, p	s, p, d	s, p, split d
T.E.	-695.910	-696.142	-687.489	-688.326	-688.428
-V/T	1.995	1.997	1.997	2.009	2.010
$\epsilon(1a_1)$	-91.771	-91.723	-90.590	-90.677	-90.670
$\epsilon(2a_1)$	-20.068	-20.050	-19.438	-19.757	-19.779
$\epsilon(1t_2)$	-20.068	-20.050	-19.438	-19.758	-19.780
$\epsilon(3a_1)$	-8.765	-8.692	-8.545	-8.586	-8.572
$\epsilon(2t_2)$	-6.457	-6.387	-6.224	-6.271	-6.258
$\epsilon(4a_1)$	-1.066	-1.014	-0.933	-1.003	-0.998
$\epsilon(3t_2)$	-0.863	-0.834	-0.684	-0.792	-0.796
$\epsilon(5a_1)$	-0.344	-0.317	-0.123	-0.230	-0.228
$\epsilon(4t_2)$	-0.208	-0.184	-0.029	-0.137	-0.138
$\epsilon(1e)$	-0.051	-0.053	+0.204	+0.004	-0.001
$\epsilon(5t_2)$	-0.012	-0.012	+0.270	+0.097	-0.079
$\epsilon(1t_1)$	+0.024	+0.051	+0.266	+0.177	+0.169

^a "Double zeta" GTO basis with one set of 3d functions.

^b Minimal sp STO basis, with one or two sets of 3d functions.

when this set was split in two. Our results clearly demonstrates that the importance of the polarization functions will decrease when the number of basis functions of *s*- and *p*-type is increased. A somewhat larger energy improvement would be obtained in the present work, if the 3d exponent was optimized, or more 3d functions were added, but it would certainly still be far from the value -0.939 obtained in the minimal basis calculation using two sets of 3d functions.

The ordering of the molecular orbitals is found to be unaffected by including the 3d functions. These functions do, however, affect the energies of the levels raising them for all orbitals except $1e$ and $5t_2$, in which the 3d population is concentrated. The reason for this is the balance between the one- and two-electron energies. The polarization functions tend to concentrate the electron density to the bonding regions (cf. Fig. 2). This results in an increased electron repulsion energy. However, this increase is more than compensated for in the total energy by a corresponding decrease in the kinetic energy and an increase in the absolute value of the nuclear attraction energy of the electrons. The sum of the orbital energies contains, however, the repulsion term twice. An increase in the Coulomb repulsion energy will therefore have a larger effect on the orbital energies. The calculations show that this effect dominates with a net increase in the orbital energies. The orbitals $1e$ and $5t_2$ do not follow this pattern since they are directly stabilized by the polarization functions. In this case we find almost no change in the orbital energies. The same effect of the polarization functions on the orbital energies has been found in previous calculations on H_2S and SO_2 [11, 15-16].

Population analysis data are presented in Table 2. Comparison is made with the results of Hillier and Saunders. The results, obtained here, without the polarization functions give a bonding picture in which the sulphur atom has a charge close to $+2$ and the S-O bonds are formed by means of sp^3 hybridized sulphur valence orbitals. The actual number of electrons in $3s$ is 1.09 and in $3p$, 2.67. This

Table 2. Population analysis

	no 3d	with 3d	sp ^a	spd ^a
Gross atomic populations				
S (s-orb.)	5.091	5.052	5.355	5.196
S (p-orb.)	8.672	8.663	9.227	8.778
S (3d(e))	—	0.320	—	1.262
S (3d(t ₂))	—	0.625	—	1.313
S (total)	13.763	14.659	14.582	16.549
O(s-orb.)	3.987	3.892	3.917	3.823
O(p-orb.)	5.073	4.943	4.938	4.540
O(total)	9.060	8.835	8.855	8.363
Overlap populations				
S-O	0.355	0.862		
O-O	-0.115	-0.064		

^a Calculations by Hillier and Saunders [8].

Table 3. Calculated properties of SO₄²⁻

	no 3d	with 3d
Diamagnetic susceptibility (10 ⁻⁶ erg/G ² mole)		
χ_{av}^d	-288.8	-285.7
Diamagnetic shielding (ppm)		
$\sigma_{av}^d(\text{S})$	-418.3	-418.6
$\sigma_{av}^d(\text{O})$	-199.1	-199.2
Potential at the sulphur nucleus (a.u.)		
$\Phi(\text{S})$	-59.42	-59.46
Electrical field at an oxygen nucleus (a.u.) ^a		
$E_z(\text{O})$	0.276	0.215
Electrical field gradient at an oxygen nucleus (a.u.) ^a		
$q_{xx}(\text{O})$	0.999	0.769
$q_{yy}(\text{O})$	0.999	0.769
$q_{zz}(\text{O})$	-1.997	-1.538
Quadrupole coupling constant for O ¹⁷ , assuming $Q(\text{O}^{17}) = -0.0256$ barns (MHz) ^a		
$e q_{xx} Q(\text{O}^{17})$	6.01	4.63
$e q_{yy} Q(\text{O}^{17})$	6.01	4.63
$e q_{zz} Q(\text{O}^{17})$	12.02	9.25
Other expectation values (a.u.)		
$\langle 1/r_s \rangle$	-70.70	-70.74
$\langle 1/r_o \rangle$	-33.66	-33.67
$\langle r^2 \rangle_{\text{C.M.}}$	364.64	360.78

^a The coordinate system has sulphur in origo and the oxygen nucleus, referred to, on the positive z-axis.

picture is modified somewhat, but not drastically, when the $3d$ functions are included. Additional bonding is achieved through backbonding in the $1e$ orbitals, which get a total $3d$ population of 0.32 electrons. The bonds in $5t_2$ are strengthened through pd hybridization with a $3d$ population of 0.45 electrons. The rest of the $3d$ population comes from the $3t_2$ orbitals, which contain 0.18 electrons. The total number of $3d$ electrons is thus 0.95. It is of interest to note, that each of the orbitals in $1e$ and $5t_2$ contains around 0.15 $3d$ electrons. This number is close to the values 0.18 and 0.16 obtained for the $3d$ population in the two outermost orbitals $1a_2$ and $8a_1$ in SO_2 , as obtained in I.

The total charge on the sulphur atom decreases from +2.24 to +1.34 when $3d$ functions are included. This decrease is entirely attributable to the population of the $3d$ functions. The number of electrons in $3s$ and $3p$ is hardly affected at all. This result is in contrast to the results obtained with a minimal sp basis. Here a large $3d$ population is partly compensated for by a decrease in $3s$ and $3p$ populations. This might be taken to indicate that the $3d$ functions in that case compensate for the inadequacy of the minimal sp basis.

Fig. 1 shows the overall electron density distribution in a plane containing sulphur and two of the oxygens. It is obtained from the calculation including the $3d$ functions. This picture is similar to the corresponding electron density map for SO_2 shown in I. The electron density distribution on the outer side of the oxygen atoms is in fact almost the same in SO_2 and SO_4^{2-} . The excess charge in the sulphate ion is thus concentrated in the interior of the ion. This modifies somewhat

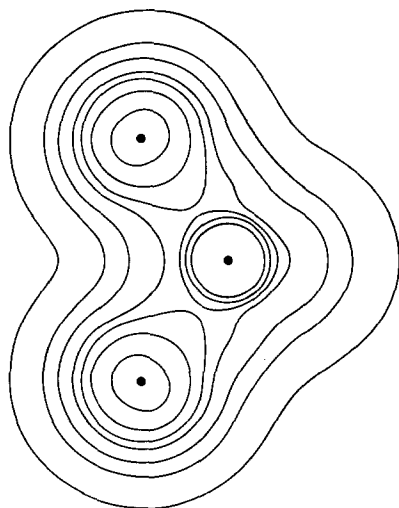


Fig. 1

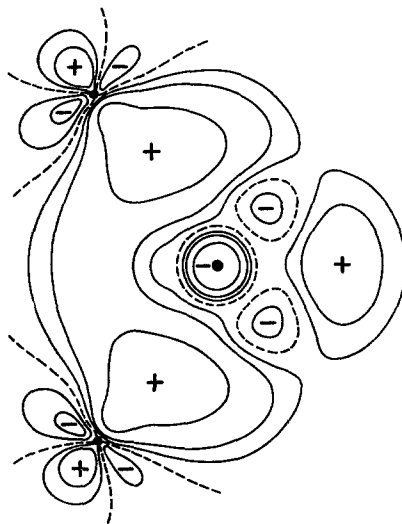


Fig. 2

Fig. 1. Total electron density contours for SO_4^{2-} in a plane through the sulphur atom and two oxygen atoms. Plotted contours are: 0.01, 0.05, 0.10, 0.20, 0.30, 0.50 and 1.00

Fig. 2. Electron density difference contours for SO_4^{2-} (in the same plane as in Fig. 1) showing the effect of $3d$ functions. The picture shows the difference in total electron density between the calculations with and without $3d$ functions in the basis set. Plotted contours are ± 0.01 , ± 0.02 and ± 0.05 . Broken lines give the zero contours

the picture obtained from the population analysis data which gives the oxygen atoms a charge of -0.84 in SO_4^{-2} which is to be compared to the value -0.46 obtained for SO_2 .

The effect of the $3d$ functions upon the charge distribution is shown in Fig. 2. Again SO_4^{-2} shows the same features as SO_2 . The number of electrons in the bonding regions increases while a decrease is found in the nonbonding regions around the atoms.

It appears, however, that a large part of the electron density increase in the S-O bonds comes from a region close to the sulphur nucleus. This region has a small volume, but the decrease in electron density is large compared to the increase in the outer regions. The reduction goes from zero at a distance of around 0.5 a.u. from the nucleus to -1.1 at the nuclear site. One should note that the largest density increase occurs rather close to the oxygen atoms. This suggests that one should not rely solely on population analysis data to study the effects of polarization functions on atomic charges.

A number of molecular properties have been computed. The results are collected in Table 2. There exists no adequate experimental data for comparison with the computed values. The effect of the $3d$ functions on these expectation values is rather limited and of the same order of magnitude as in SO_2 .

4. Conclusions

Based on the present calculations on the sulphate ion we have concluded that the S-O bonds are highly polar with a sulphur charge of $+1.34$ and an oxygen charge of -0.84 . Qualitatively we can describe the bonds as being formed between sp^3 hybrids on a dipositive sulphur atom and the $2p$ orbitals on negatively charged oxygen atoms. A certain amount of double bond character is introduced through backbonding from the π orbitals of the oxygen atoms to $3d$ orbitals on the sulphur. An increased bond strength is also obtained by means of a polarization of the sulphur $3p$ orbitals giving the sp^3 hybrids a certain amount of d character.

The results obtained in the present work are in some aspects in disagreement with the previous studies [1-9]. The $3d$ functions also in our calculations have an important influence on the results. However, this influence has been reduced and is now essentially of a quantitative nature. Thus, the molecular orbital order 2 is still obtained in the calculations with the $3d$ functions deleted. The polarity of the S-O bond is weakened somewhat, but not drastically, and the sulphur atom still has a large positive charge, when the $3d$ functions are included in the basis set.

A number of expectation values have been calculated. There is no experimental data with which to compare these results. However, corresponding results for SO_2 [11] and for $\text{C}_4\text{H}_4\text{S}$, CS_2 , SOF_2 and SF_6 , which will be the subjects of further reports in this series, obtained with similar basis sets, are in good agreement with available experimental information.

Acknowledgements. We are greatly indebted to IBM World Trade Corporation and to the Swedish IBM Corporation for granting a fellowship to one of us (U.G.) that made it possible to perform the larger part of the calculations at IBM Research Laboratory in San José. Part of this work has been supported by a grant from the Swedish Board for Technical Development and the Swedish Natural Science Research Council.

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