The Electronic Structure of the Octa-Sulphur Molecule: An ab Initio Configuration Interaction Study

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An *ab initio* SCF calculation of better than double zeta quality (192 basic functions) acted as a starting point for a configuration interaction (CI) study. The final CI with 3408 configurations showed that the 3d orbital density was reduced further than the initial value of 0.1 e; the SCF configuration was dominant, but an element of in – out correlation occurred, with incorporation of the orbital 1 a_2 in replacement for 1 b_1 being notable in many configurations.

Semi-empirical molecular orbital calculations [1, 2] of S_8 at the known crystal (D_{4d}) structure [3, 4] (Figure 1 a) showed only a very low level of 3 d_S character in the ground state single configuration calculation; thus several other authors have not included the 3 d orbitals in their studies [5–7]. We now report a large sp-basis set *ab initio* calculation, both with and without d-orbitals, and including configuration interaction, in order to provide a more rigorous base-line for subsequent studies of electronically excited and ionised states. The *ab initio* basis consisted of a (12s 9p 1d) gaussian orbital basis contracted to [7s 4p 1d], i.e. one better than double zeta in the sp-part [8–11] as in previous work; this yields a free S atom energy of −397.49655 a.u. ($^3P_{3/2}$) to be compared with the Hartree-Fock limiting value of −397.505 a.u. The Cartezian Gaussian basis (3 d^6) set was combined into the usual 3 d^5 set of xy, xz, yz, (x^2-y^2) and $(3z^2-r^2)$. Thus a total of 192 basis functions were used; the computer program was ATMOL-III (integrals and SCF) and SPLICE (CI study) implemented on the Daresbury Laboratory/ULCC Cray-1 Computer. The integrals evaluation took 1430 secs and the SCF iterations 51 seconds each.

Table 1. Single configuration SCF results for S_8.

	sp-Basis	spd-Basis
(a) Total energy (a.u.)	−3179.9211 [a]	−3180.2840 [b]
(b) Valence shell orbitals		

CI Sequence No.	Symmetry	Energy (eV)	Atomic populations s	p	d
2	3 a_1	10.23	4.80	92.96	2.24
16, 17	3 e_3	10.36	2.96	93.68	3.44
12, 13	3 e_2	10.81	−0.90	99.40	1.50
8, 9	3 e_1	11.03	4.26	93.16	2.58
5	2 b_2	13.02	5.81	91.25	2.94
10, 11	2 e_2	14.06	10.48	88.40	1.12
6, 7	2 e_1	14.12	4.16	93.38	2.46
1	2 a_1	15.46	4.43	94.10	1.47
14, 15	2 e_3	16.26	8.78	89.45	1.77
3	1 b_1	16.78	0.00	94.88	5.12
4	1 b_2	20.67	82.95	16.69	0.36
–	1 e_3	23.28	76.87	21.70	1.93
–	1 e_2	27.42	83.94	13.86	2.20
–	1 e_1	30.46	91.60	7.28	1.12
–	1 a_1	31.61	92.40	6.88	0.72
Total population (e)	–		5.8862	10.0038	0.1099

[a] Previous total energies: −3173.5500 a.u. [12]; −3145.45970 a.u. [6].
[b] Previous total energies: −3174.5755 a.u. [12].

a) *The SCF Wave-function.* The present energies (Table 1) are markedly lower than any previous calculation; while the effect of the 3 d-orbitals is still quite large on an energy basis (0.36 a.u., 1 a.u. = 2626 kJ · mol^{-1}), it is much smaller than in the only previous calculation, where a minimal AO basis was used (1.02 a.u.) [12]. The low total atomic 3 d^5 population (0.11 e), is derived from the atomic s-population rather than the p-orbital one. Mulliken analysis of the occupied orbitals (Table 1) shows that the 3 d orbitals (generally around 2 ~ 3%) reach a maximum of 5% in the 1 b_1 orbital, the only orbital of that symmetry in the valence state and one where s-orbital participation is zero by symmetry. The 3 d orbitals have an effect upon the Aufbau ordering,

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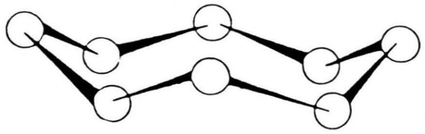
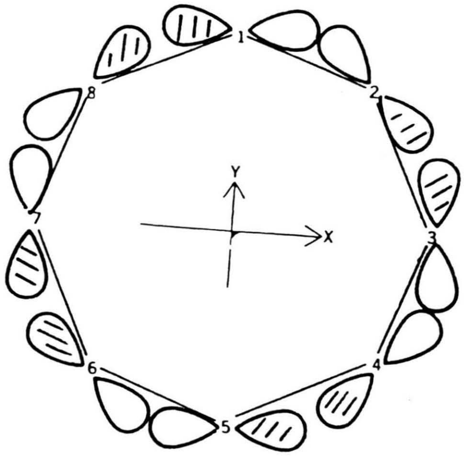
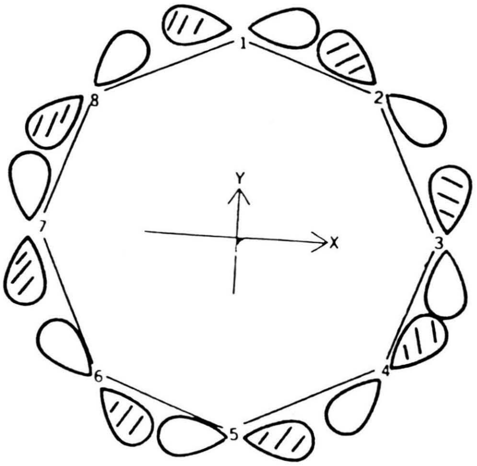
1 a



1 b



1 c



for example in the order of 3 e_1 and 3 e_2, but the effect is an indirect one, since the inclusion of 3d orbitals leads to a differing proportion of 3s and 3p functions in what are basically lone pair orbitals (LP). The *ab initio* calculations lead to the HOMO being 3 a_1 in contrast to the semi-empirical results, which lead to 3 e_3 (EH) [5] or 3 e_1 (CNDO, Xα) [1, 2, 7].

b) *The CI Study.* The high symmetry of the molecule means that a large number of configurations are generated for each state symmetry largely through the three degenerate products:

$$E_1 \times E_1 = A_1 + A_2 + E_2,$$

$$E_2 \times E_2 = A_1 + A_2 + B_1 + B_2,$$

$$E_3 \times E_3 = A_1 + A_2 + E_2.$$

In the first phase of CI (Table 2), two sets of active electrons were used (16 and 32) in the sp-basis; the SCF wave-function was extremely dominant, but 30 configurations had eigenvectors > 0.02. It was clear that a larger CI involving the 3d orbitals was required. The spd-basis SCF orbitals from the highest occupied orbital (HOMO) down to 5 b_2 [13] were used, a total of 34 active electrons; the virtual set, into which all double and single replacements were allowed, consisted of the first vacant orbital (LUMO) upwards (in aufbau order) for a total of 26 additional orbitals, yielding an active space of 43 orbitals. A total of 83004 configurations were generated for the ground state, which were reduced in number by perturbation selection [14], with varying thresholds (10^{-4}, 5×10^{-5} and 2.5×10^{-5} Hartree). The principal contributors to the ground state are the same at each level of selection (Table 3).

Table 2. Configuration interaction energy results for S_8 using both sp- and spd-basis.

Active Set		Configurations		Selection level (μH)	Final CI energy (a.u.)
Electrons	Virtuals	Total	Selected		
(a) spd-Basis					
34	27	83 004	3408	25	−3180.46288
34	27	83 004	1455	50	−3180.47038
34	27	83 004	538	100	−3180.47623
(b) sp-Basis					
32	18	35 759	1391	50	−3180.06487
16	18	9 077	899	15	−3179.95785
16	18	9 077	326	50	−3179.95913

Table 3. Principal configurations of the S_8 ground state.

(a) Wave-function

Eigenvector	Orbitals occupied
0.9552	1^2-17^2
−0.0299	$1^2, 3^2-10^2, 12^2-17^2$, (11, 20), (2, 33)
+0.0223	$1^2, 3^2-9^2, 11^2-17^2$, (10, 20), (2, 32)
+0.0216	$1^2, 2^2, 4^2, 5^2, 7^2-17^2$, (3, 20), (5, 26)
−0.0211	$2^2, 4^2-17^2$, (3, 20), (1, 23)

(b) Sequence number of orbitals

A1	1	2	18	19						
B1	3	22								
B2	4	5	23	24	25					
E1	6	7	8	9	26	27	28	29	30	31
E2	10	11	12	13	32	33	34	35	36	37
E3	14	15	16	17	38	39	40	41	42	43
A2	20	21								

The CI energy lowering relative to the spd-SCF function was about double that for the sp basis, and amounted to 0.18 a.u. Again the SCF wave-function was dominant, but the convergence of the contributing configurations was sharper; only 7 configurations had eigenvectors > 0.02 (Table 3 shows the leading terms). In both cases however, the most commonly vacated orbital from the SCF wave function was $1\,b_1$ (see above). In the sp-basis calculation the major replacement was $1\,b_1 \rightarrow 2\,b_1$, always accompanied by another (variable) replacement. In the spd calculation the dominance of configurations in which $1\,b_1^2$ has been vacated is even more evident. Of the first eight excited configurations, six were $1\,b_1 \rightarrow 1\,a_2$ with other orbital products of B_2 symmetry: all eight of these configurations involved $1\,a_2$, a symmetry species which is not occupied in the SCF ground state calculation. Both $1\,b_1$ and $1\,a_2$ orbitals have a common feature – the absence of s-orbital components, and neither are rich in 3d orbitals ($1\,b_1$, 5.12%; $1\,a_2$, 8.39%). In the case of $1\,b_1$ (Fig. 1b) the orbital is almost entirely made up of 3p orbitals (exponent = 0.2918) largely tangential at the S atoms and bonding between pairs of adjacent atoms; in contrast, $1\,a_2$ (Fig. 1c) is completely antibonding between neighbouring pairs of atoms, but is confined almost exclusively to the $3p'$ orbitals (exponent = 0.1029). Thus the interplay of $1\,b_1$ and $1\,a_2$ yields an "in-out" correlation, i.e. an element of long range antibonding character is introduced into the correlated wave-function [15]. Calculations with the present atomic basis set on the free S atom showed the values of $\langle r^2 \rangle$ for the inner (3p) and outer ($3p'$) components are 1.032 and 2.164 (Å) respectively; given the S–S bond length of 2.046 Å, the inner function has a value of $\langle r \rangle$ (in each lobe) near to the S–S bond midpoint, whilst the outer function has its maximum nearer the neighbouring S atom. Thus the effect of the replacement $1\,b_1 \rightarrow 1\,a_2$ is to concentrate electron density near the S–S bond midpoint.

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[13] In D_{4D} the full set of electrons occupy orbitals $1\,a_1-7\,a_1$, $1\,b_2-6\,b_2$, $1\,b_1$, $2\,b_1$ and $1\,e_i-8\,e_i$ (i = 1, 2, 3); here a valence shell only numbering system is used [5], the highest members being $3\,a_1$, $3\,e_i$ (i = 1, 2, 3), $2\,b_2$ and $1\,b_1$.
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