ELECTRONIC ENERGY LEVELS OF THE S_8 MOLECULE

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ABSTRACT: The electronic energy levels of the molecule S_8 calculated by
the molecular orbital method, assuming simple bounds between
neighbour sulfur atoms and two lone pairs per atom. Tetrahedral
hybrids are used for all the atoms and the numerical values of
the integrals are estimated by semi-empirical methods. Two
different approximations are used and it is found that the energy
levels are practically independent of the approximation used,
especially for the occupied levels in the ground state of the
molecule.

INTRODUCTION

Although the S_8 molecule has been known for many years and in particular, its geometry is well established,[1,2] there are no calculations of its electronic energy levels. The only theoretical papers[3,4,5] on S_8 refer to the calculation of torsional energy and prediction of the dihedral angle, as well as of the vibrational spectra[6]. Apart from the intrinsic interest in this molecule, it offers particular interest because the molecular crystal of orthorhombic sulfur is made up of S_8 molecules. Therefore, it is to be expected that any information about the S_8 molecule will be useful as a starting point for theoretical studies of the crystal.

METHOD

The S_8 molecule is cyclic, with the shape of a regular crown, bond angle S-S-S of $107.8°$, dihedral angle S-S-S-S of $99.3°$ and bond length of $2.037 Å^2$ (Fig. 1).

The ground state configuration for the S atom is: $(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^4$. Considering that the electrons on the closed shells $(1s)^2 (2s)^2 (2p)^6$ are not modified by molecular bonding, we are left with a problem of 48 electrons (6 per atom). These electrons can be arranged in a variety of ways, and some suggestions have been given by Schmidt[7]. In particular, one could think of double bonds between all pairs of neighbour atoms, or in alternate simple and triple bonds, with one lone pair per atom in both cases. But for any of these configurations, one would expect the possibility of addition reactions, similar to those of non-saturated, and aromatic hydrocarbons, and these reactions have not been found for the S_8 molecule. Furthermore, the S_8 molecule is not planar so that the $\pi - \sigma$ separation adecuate for aromatic hydrocarbons, should not apply here. Therefore, the double and triple bonds would be rather different than those for hydrocarbons.

Following a suggestion by Pauling[3], we have considered a simpler configuration: namely, that with single bonds between all pairs of neighbour atoms, and two lone pairs per atom. As the bond angle in S_8 ($107.8°$) is almost the tetrahedral angle ($109° 28'$) we have considered the formation of four tetrahedral hybrids, of the sp^3 type, in each sulfur atom. Of these four hybrids, the two that are directed towards the neighbour atoms contribute to the bonds, while the other two are the two lone pairs. In this way the problem reduces now to 16 orbitals (2 hybrids per atom) and 16 electrons (2 per atom).
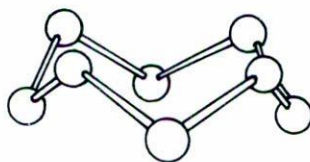
FIGURE 1

We call $h_{i,j}$ the hybrid centered on atom i and directed towards atom j, and we number the sulfur atoms sequentially from 1 to 8. We shall consider two different approximations:

(i)   In the first approximation we consider different from zero only the following integrals:

$$\alpha = <h_{i,i+1}|H|h_{i,i+1}> ; \quad \beta_0 = <h_{i,i+1}|H|h_{i,i+1,i}> ;$$

$$\gamma = <h_{i,i+1}|H|h_{i,i-1}>$$

and

$$S_0 = <h_{i,i+1}|h_{i+1,i}>$$

and we call this, the approximation of "nearest first neighbours".

(ii)   In the second approximation we consider different from zero, apart from the above integrals, also the following:

$$\beta_1 = <h_{i+1,i}|H|h_{i,i-1}> ; \quad \beta_2 = <h_{i,i-1}|H|h_{i+1,i+2}>$$

$$S_1 = <h_{i+1,i}|h_{i,i-1}> \quad ; \quad S_2 = <h_{i,i-1}|h_{i+1,i+2}>$$

and we call this, the approximation of "complete first neighbours".

Slater orbitals and screening constants were used in all the calculations and the overlap integrals S_0, S_1 and S_2 were obtained from interpolation in Mulliken's tables[8]. For the other integrals semi-empirical procedures were used. For the integrals β_0, β_1 and β_2 we used Mulliken's approximation[9], which amounts to make the resonance integrals proportional to the overlap integrals, namely

$$\beta_0 = \lambda S_0 \quad ; \quad \beta_1 = \lambda S_1 \quad ; \quad \beta_2 = \lambda S_2 .$$

The parameter λ was obtained from the experimental data of the energy of the S–S bond. This energy, ΔE, varies from 51 Kcal/mole for the S_2 molecule to 63 Kcal/mole for the S_8 molecule. For S_2, ΔE is approximately[10].

$$\Delta E = 2\alpha - 2\,\frac{\alpha + \beta_0}{1 + S_0}$$

from which we obtain $\lambda = -0.581$ (we explain below the procedure for the calculation of α needed, of course, to obtain β_0 and λ, from the above equation).

A similar interpretation of the energy per S–S bond in the S_8 molecule is, obviously, impossible. Only if we neglect all interactions except β_0, we get an expression similar to the above, but this is equivalent to replace S_8 by $4S_2$, which does not seem very convincing. (Anyhow if $\Delta E = 63$ Kcal/mole is used, we obtain $\lambda = -0.608$ which is not too different from the previous value). Obviously, the atomic orbitals (hybrids) in S_2 and S_8 need not be the same, so that the value for β_0 (and for λ therefore) in S_2 need not be the same as that in S_8. Anyhow, as the S–S bond energies in S_2 and in S_8 differ in only 20% we expect that the values of β_0 in S_2 and in S_8 will not differ greatly.

The integral α, after expanding the hybrids, becomes

$$\alpha = \frac{1}{4}\left[< s_i | H | s_i > + 3 < p_{i,\,i+1} | H | p_{i,\,i+1} > + 2\sqrt{3} < s_i | H | p_{i,\,i+1} > \right]$$

If we neglect the term $< s_i | H | p_{i,\,i+1} >$, we have inside the bracket the energy of a 3s electron plus three times the energy of a 3p electron in the effective field H, of the S_8 molecule.

The integral γ becomes

$$\gamma = \frac{1}{4} \left[<s_i \mid H \mid s_i> + 3 \cos(p_{i,i-1}, p_{i,i+1}) <p_{i,i-1} \mid H \mid p_{i,i+1}> \right.$$

$$\left. + 2\sqrt{3} <s_i \mid H \mid p_{i,i+1}> \right]$$

where $(p_{i,i-1}, p_{i,i+1})$ is the tetrahedral angle. In the calculation of this integral we shall also neglect the last term. We assume that the quantities $<s_i \mid H \mid s_i>$ and $<p_{i,i+1} \mid H \mid p_{i,i+1}>$ are not too different from the corresponding values in the free atom and so we have used for them the experimental values for the free atom. In order to check this method we have proceeded in a similar way in diamond, for which there are rather precise calculations of the α integral, using also tetrahedral hybrids [12], and the error is of 28%, which we consider acceptable compared with the probable errors introduced in the other approximations used by us. It is impossible to know that part of this error is due to the neglect of the integral $<s_i \mid H \mid p_{i,i+1}>$.

Finally, the values of the integrals used are:

$$\alpha = -0.47 \qquad \beta_0 = -0.3342 \qquad \beta_1 = -0.03781 \qquad \beta_2 = 0.00574$$

$$\gamma = -0.09002 \qquad S_0 = 0.5748 \qquad S_1 = 0.06504 \qquad S_2 = 0.00988$$

As usual in this type of calculations, group theory was used to factorize the secular determinant, taking into account the fact that the S_8 molecule belongs to the D_{4d} group.

RESULTS

The symmetry of the molecular orbitals, their degeneracies and the corresponding energies in the first and second approximations are given in Table 1, in order of increasing energies, in e.v. It is interesting to note that there appear molecular orbitals belonging to all of the irreducible representations of the group. The ground state molecular orbital belongs to the totally symmetric representation a_1, as expected. In the ground state of

the molecule the 16 electrons that we have considered as contributing to the chemical bonds occupy the lowest five molecular orbitals, giving a singlet state for the molecule.

TABLE 1

Representation	Degree of degeneracy	Energy, in e.v., in the first approximation.	Energy, in e.v., in the second approximation.
a_1	1	-15.5	-15.5
e_1	2	-15.4	-15.4
e_2	2	-15.3	-15.3
e_3	2	-14.9	-14.8
b_2	1	-14.5	-13.9
b_1	1	-12.3	-12.0
e_3	2	-10.7	- 9.7
e_2	2	- 7.3	- 8.1
e_1	2	- 4.2	- 6.3
a_2	1	- 2.9	- 6.1

The first and second approximations give very similar results, thus indicating that the first approximation, of "nearest first neighbours" is acceptable. This result indicates that the interactions that dominate the spectra of molecular orbitals are β_0 and γ. Obviously, this conclusion is conditioned to the goodness of the approximations used in the calculation of the integrals, which were obtained by rather crude semi-empirical methods.

It should be noticed that the occupied levels in the ground state of the molecule extend only from -15.5 e.v. to -13.9 e.v. (or 14.6 e.v.). If we make $\gamma = \beta_1 = \beta_2 = 0$, there appears great accidental degeneracy of the energy levels, and only two different levels appear, namely the occupied level $(\alpha + \beta_0)/(1 + S_0) = -13.9$ e.v. and the empty one $(\alpha - \beta_0)/(1 - S_0) = -8.7$ e.v. We see, therefore, that although the integral γ (and also β_1 and β_2) removes completely the degeneracy, it produces a rather small splitting

of the energy levels. Again, we cannot decide if this effect is a real one, or is due to the approximations used in the calculations of the integrals.

In short, in this paper a first attempt is made to classify and order the electronic energy levels of the S$_8$ molecule for the molecular orbitals associated with single covalent bonds between neighbour-sulfur atoms.

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RESUMEN

Se calculan los niveles de energía electrónicos de la molécula S$_8$ por el método de los orbitales moleculares, suponiendo que existen uniones simples entre los átomos de azufre vecinos y dos pares aislados (lone pairs) por átomo. Se usaron híbridos tetraédricos en cada átomo y los valores numéricos de las integrales se estimaron por métodos semi-empíricos.

Se usaron dos aproximaciones diferentes y se encontró que los niveles de energía obtenidos son prácticamente independientes de la aproximación usada, sobre todo para los niveles que resultan ocupados en el estado base de la molécula.