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Molecular Orbital Energy Levels for the Sulfate Ion

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A series of semiempirical molecular orbital calculations for the SO_4^{2-} ion is described. These calculations show the effect on the order of the molecular orbital energy levels of a) using the Wolfsberg-Helmholz approximation, b) using the Cusachs approximation, c) variation of the proportionality constant, F, in the Wolfsberg-Helmholz approximation, d) inclusion of d-orbitals in the basis set, and e) variation of ζ_d when d-orbitals are included. It is found that the highest filled level is t_1 for all the Wolfsberg-Helmholz calculations when d-orbitals are included and is $3t_2$ for all the other calculations.

Es wird eine Reihe von semiempirischen MO-Rechnungen für das Sulfatanion beschrieben, und zwar werden a) das Wolfsberg-Helmholz-Modell mit verschiedenen Proportionalitätskonstanten, b) die Cusachs-Näherung und c) solche Modelle bei Einschluß von d-Funktionen mit unterschiedlichen ζ_d-Werten auf ihre Termfolge hin untersucht. Dabei zeigt sich, daß bei allen Wolfsberg-Helmholz-Rechnungen mit d-Zuständen der oberste besetzte Zustand t_1 ist, in allen anderen Fällen dagegen $3t_2$.

Description d'une série de calculs de l'ion SO_4^{2-} par la méthode des orbitales moléculaires semi-empirique. Ces calculs montrent l'effet sur l'ordre des niveaux d'énergie des orbitales moléculaires des facteurs suivants: a) approximation de Wolfsberg-Helmholz, b) approximation de Cusachs, c) variation de la constante de proportionnalité dans l'approximation de Wolfsberg-Helmholz, d) inclusion d'orbitales d dans la base, e) variation de d. On trouve que le plus haut niveau occupé est t_1 pour tous les calculs Wolfsberg-Helmholz avec orbitales d et $3t_2$ pour tous les autres calculs.

1. Introduction

Recently there has been a revival of interest in the calculation of molecular orbitals by the Wolfsberg-Helmholz method [1—4], a method first introduced in 1952. Though the method suffers from a number of well known defects, it owes its popularity to its simplicity. The present paper investigates the method for the sulfate ion (SO_4^{2-}) with three main questions in mind: a) do the relative positions of the energy levels depend radically on the parameters involved, b) does inclusion of d-orbitals in the basis set effect the ordering of the levels, c) what is the effect of the Cusachs modification [5]?

2. Method

The sulfate ion was assumed to be tetrahedral and the S — O bond distance was taken to be 1.44 Å [6], the O — O distance was then necessarily 2.35 Å. The basis functions, ϕ_i, are given in Tab. 1 along with the appropriate normalization constants, N_i. The axes which were chosen for the ion are shown in Fig. 1. The diagonal H matrix elements, $H_{ii} = \int \phi_i^* \mathscr{H} \phi_i \, d\tau$, with one exception, were taken as the negative of the valence orbital ionization potentials (VOIPs) given by

Basch et al. [7]. The one exception was the matrix element for the sulfur $3d$-orbital, for which no data is available. It was therefore estimated from the calculated values of H_{ss}, H_{pp} and H_{dd} for sulfur given by Craig and Zauli [8] and from the values of H_{ss} and H_{pp} given by Basch et al. [7]. A plot of one set of H_{ii} against

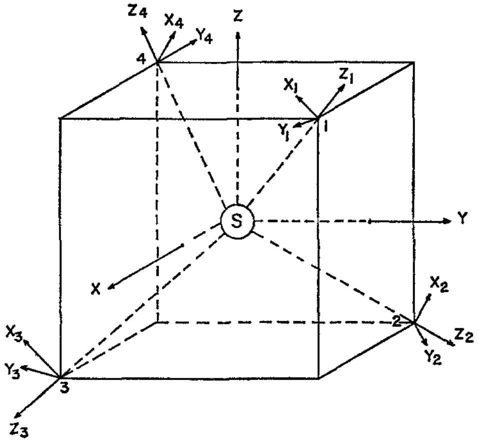

Fig. 1. Orientation of the coordinates

Table 1. *Basis functions, normalization constants and uncorrected diagonal H matrix elements*

Representation	i	ϕ_i[a]	N_i[b]	H_{ii}[c]
A_1	1	s	1	h_1
A_1	2	$\frac{1}{2}(s_1 + s_2 + s_3 + s_4)$	$(1 + 3S_1)^{-1/2}$	h_4
A_1	3	$\frac{1}{2}(z_1 + z_2 + z_3 + z_4)$	$(1 + 2S_2 + S_3)^{-1/2}$	h_5
E	4	d_{z^2}	1	h_3
E	5	$\frac{1}{2}(x_1 - x_2 - x_3 + x_4)$	$(1 + S_2/2 - S_3/2)^{-1/2}$	h_5
T_2	6	p_z	1	h_2
T_2	7	d_{xy}	1	h_3
T_2	8	$\frac{1}{2}(z_1 - z_2 - z_3 + z_4)$	$(1 - 2S_2/3 - S_3/3)^{-1/2}$	h_5
T_2	9	$\frac{1}{2}(s_1 - s_2 - s_3 + s_4)$	$(1 - S_1)^{-1/2}$	h_4
T_2	10	$-\frac{1}{2}(x_1 + x_2 + x_3 + x_4)$	$(1 + S_2/6 + 11S_3/6)^{-1/2}$	h_5
T_1	11	$\frac{1}{2}(y_1 + y_2 + y_3 + y_4)$	$(1 - S_2/2 - 3S_3/2)^{-1/2}$	h_5

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[a] The orientation of the axes is shown in Fig. 1. The orbitals s, p_z, d_{z_1} and d_{xy} are on the sulfur atom and s_1, x_1, y_1, z_1, are s- and p-type orbitals on oxygen atom 1 etc. It should be noted that only one set of basis functions is shown for each of the degenerate representations.

[b] S_1, S_2, and S_3 are the atomic overlap integrals (s, s), $(p, p)\sigma$ and $(p, p)\pi$ respectively.

[c] $h_1 = -12.23q_s^2 \quad -124.0q_s \quad -166.7$
$h_2 = -13.17q_s^2 \quad -98.5q_s \quad -93.4$
$h_3 = -12.7q_s^2 \quad -111.25q_s \quad -0$
$h_4 = -27.95q_0^2 \quad -184.6q_o \quad -260.8$
$h_5 = -27.94q_0^2 \quad -149.75q_o \quad -127.4$

These matrix elements are in units of 1000 cm^{-1} and with the exception of h_3 (see text) are taken from Ref. [7]. q_s and q_0 are the charges on the sulfur and each oxygen atom, respectively.

the corresponding values of the other set gave an approximate H_{dd} for an atomic charge of zero. The slope and curvature of the dependance of H_{dd} on charge were assumed to be the average of these quantities for H_{ss} and H_{pp}, which between themselves were not very different. In this way

$$H_{dd} = h_3 = -12.7q_s^2 - 111.25q_s - 40.0$$

was obtained [9], where q_s is the charge on the sulfur atom. However, in order to determine the effect of changes in this matrix element, the more general expression:

$$h_3 = -12.7q_s^2 - 111.25q_s - D$$

was used in the calculations, with $D = 15{,}40$.

In the Wolfsberg-Helmholz method these diagonal terms were then corrected for ligand-ligand overlap by multiplying them by the factor $[N_i^2 + F(1 - N_i^2)]$, where F is the Wolfsberg-Helmholz proportionality factor. This correction is not neccessary in the Cusachs-type calculation.

In the Wolfsberg-Helmholz calculation, the off-diagonal H matrix elements were taken as

$$H_{ij} = F(H_{ii} + H_{jj})\, S_{ij}/2$$

where F, the proportionality factor, was given a series of values: 1.6, 1.8, 2.0, 2.2, and H_{ii} and H_{jj} are the uncorrected diagonal terms and S_{ij} is the overlap matrix element, $S_{ij} = \int \phi_i^* \phi_j \, d\tau$. In the Cusachs-type calculation, the off-diagonal H matrix elements were taken as

$$H_{ij} = (H_{ii} + H_{jj})\, S_{ij}\, (2 - |S_{ij}|)/2\, .^*$$

The diagonal overlap matrix elements were all unity and the off-diagonal ones were evaluated from the atomic overlap integrals by use of the formulae given by Ballhausen and Gray [10]. The atomic overlap integrals were evaluated by using the atomic orbitals of the double-zeta type published by Clementi [11]. The $3d$ sulfur orbital, not given by Clementi, was taken as a Slater-type orbital with ζ_d equal to either 1.2 or 1.34; the first value has been suggested by Craig et al. [8] and the second by Cruickshank et al. [12]. The atomic overlap integrals for the chosen geometry were then:

oxygen-oxygen

$(s, s) = 0.029493$

$(p, p)_\sigma = 0.091616$

$(p, p)_\pi = 0.021837$

$(s, p)_\sigma = 0.058762$

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* Only if one formally assumes that $(2 - |S_{ij}|)S_{ij}$ transforms like S_{ij} are the molecular orbitals found by the Cusachs' method invariant to rotation of the molecular axes. For a discussion of this point see Pople, J. A., D. P. Santry, and G. A. Segal: J. chem. Physics **43**, 5129 (1965); Newton, M. D., F. P. Boer, and W. N. Lipscomb: J. Amer. chem. Soc. 88, 2353 (1966); Newton, M. D.: J. chem. Physics **45**, 2716 (1966); Cusachs, L. C.: J. chem. Physics **45**, 2717 (1966); Ruttink, P. J. A.: Theoret. chim. Acta **6**, 83 (1966); Carroll, D. G., and S. P. McGlynn: J. chem. Physics **45**, 3827 (1966).

sulfur-oxygen

$$\begin{array}{lll}
(s,\ s) & = & 0.30145\\
(s,\ p)_\sigma & = & 0.31241\\
(p,\ p)_\sigma & = & 0.25876\\
(p,\ s)_\sigma & = & 0.45583\\
(p,\ p)_\pi & = & 0.23829
\end{array}$$

$$\left.\begin{array}{lll}
(d,\ s) & = & 0.46340\\
(d,\ p)_\sigma & = & 0.00911\\
(d,\ p)_\pi & = & 0.40297
\end{array}\right\}\ \zeta_d = 1.2$$

$$\left.\begin{array}{lll}
(d,\ s) & = & 0.45591\\
(d,\ p)_\sigma & = & 0.05046\\
(d,\ p)_\pi & = & 0.39347
\end{array}\right\}\ \zeta_d = 1.34$$

The energy levels were found as the eigenvalues of the secular equation

$$|\, H_{ij} - S_{ij}\, E \,| = 0\,,$$

and the eigenvectors of this equation determined the coefficients of the basis functions in the molecular orbitals. The 32 valence electrons were then fed into the lowest energy levels and the charge on the sulfur atom, q_s, determined by a Mulliken population analysis [13]. The H matrix elements themselves depended upon q_s and so a self-consistent procedure was used to determine q_s. The charge on each oxygen atom, q_0, was taken to be $(-2 - q_s)/4$. Two other possibilities were also considered for q_0, namely zero and -0.1775. The former value is equivalent to saying that the oxygen VOIPs are independent of atomic charge and the latter value is equivalent to fixing the VOIP for the oxygen $2p$ orbital at 101.7 [9], the ionization potential of H_2O [14].

In all, 75 calculations were made, corresponding to the four values of F, two values of ζ_d, two values of D, three possible choices for q_0, inclusion or exclusion of sulfur d-orbitals, and the two methods: Wolfsberg-Helmholz and Cusachs.

3. Results and Discussion

In Tab. 2 and 3 the results are presented for calculations without and with the inclusion of d-orbitals, respectively. The results of calculations with $\zeta_d = 1.34$ are not presented as they were almost exactly the same as those with $\zeta_d = 1.2$. Altogether, five different electronic energy level orders were found, they are:

$$1a_1^2 < 1t_2^6 < 2a_1^2 < 2t_2^6 < 1e^4 < t_1^6 < 3t_2^6 \tag{1}$$

$$1a_1^2 < 1t_2^6 < 2t_2^6 < 2a_1^2 < t_1^6 < 1e^4 < 3t_2^6 \tag{2}$$

$$1a_1^2 < 1t_2^6 < 2a_1^2 < 2t_2^6 < t_1^6 < 1e^4 < 3t_2^6 \tag{3}$$

$$1a_1^2 < 1t_2^6 < 2a_1^2 < 2t_2^6 < 1e^4 < 3t_2^6 < t_1^6 \tag{4}$$

$$1a_1^2 < 1t_2^6 < 2t_2^6 < 2a_1^2 < 1e^4 < 3t_2^6 < t_1^6 \tag{5}$$

where the superscripts denote the number of valence electrons in each level.

Discussion of these results will be restricted to simply the order of the energy levels; there seems little point in a method as approximate as this one, in giving

Table 2. *Electronic populations for the sulfate ion using s and p basis functions*

Input			Output			
F	q_0	q_s	q_s	Q_s[a]	Q_p[a]	order[b]
		Wolfsberg-Helmholz method				
1.6	0	1.100	1.091	1.469	3.44	1
	− 0.1775	0.890	0.883	1.533	3.585	1
	− 0.5875	0.350	0.376	1.684	3.941	1
1.8	0	1.210	1.205	1.362	3.432	1
	− 0.1775	1.020	1.009	1.421	3.570	1
	− 0.6200	0.480	0.491	1.574	3.934	1
2.0	0	1.299	1.298	1.291	3.411	1
	− 0.1775	1.110	1.124	1.343	3.533	1
	− 0.6475	0.590	0.581	1.499	3.920	1
2.2	0	1.360	1.364	1.241	3.395	1
	− 0.1775	1.200	1.192	1.292	3.517	1
	− 0.6700	0.680	0.670	1.441	3.889	1
		Cusachs' method				
	0	1.000	1.014	1.647	3.339	2
	− 0.1775	0.790	0.767	1.723	3.510	2
	− 0.5650	0.260	0.274	1.874	3.852	3

[a] Q_s and Q_p are the sulfur s- and p-orbital populations, respectively.

[b] See text.

a quantitative discussion of the results. The essential conclusions may then be summarized as follows:

a) the highest occupied level in all cases is triply degenerate,

b) in the Cusachs-type calculation the energy level order is independent of the inclusion of d-orbitals but, depending on the value of q_0, is either of type (2) or (3). These two orders, however, are very much the same, differing only by a reversal in order of the $2a_1$ and $2t_2$ levels. In both orders $3t_2$ is the highest occupied level.

c) In the Wolfsberg-Helmholz calculation without the inclusion of d-orbitals, energy level order (1) is obtained and the highest occupied level is again $3t_2$. However, when d-orbitals are included, the highest and next to highest levels, $3t_2$ and t_1, reverse their order and order (4) is obtained, or, in a few cases, depending on the value of q_0, order (5), where the $2a_1$ and $2t_2$ levels are in reverse order as well. In either order (4) or (5) the highest occupied level is t_1.

One must conclude therefore that calculations of this type are not yet at the stage where one can definitely predict energy level orders. There are nonetheless three fairly concrete results from this work: a) the inclusion of d-orbitals is important, b) in the Wolfsberg-Helmholz calculation the order of the energy levels is independent of F, the proportionality constant, c) the order is independent of small changes in ζ_d, d) the highest occupied level in the sulfate ion (SO_4^{2-}) is triply degenerate*.

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* This result is different from that in Ref. 2. The energy levels in Ref. 2. were calculated on the basis of incorrect overlap matrix elements, an error caused by the misprints mentioned in Ref. 10. The results of Ref. 2. should therefore be disregarded.

Table 3. *Electronic populations for the sulfate ion using s, p and d basis functions with* $\zeta_d = 1.2$

Input				Output				
F	D	q_0	q_s	q_s	Q_s[a]	Q_p[a]	Q_d[a]	order[b]
				Wolfsberg-Helmholz method				
1.6	15	0	0.540	0.515	1.144	2.453	1.888	4
		− 0.1775	0.380	0.426	1.236	2.645	1.694	4
		− 0.5225	0.090	0.171	1.465	3.217	1.147	4
	40	0	0.420	0.437	1.056	2.182	2.326	4
		− 0.1775	0.260	0.245	1.145	2.360	2.250	4
		− 0.4925	−0.030	0.026	1.335	2.770	1.870	4
1.8	15	0	0.460	0.500	1.012	2.393	2.095	4
		− 0.1775	0.330	0.291	1.096	2.594	2.019	4
		− 0.5175	0.070	0.085	1.285	3.064	1.567	4
	40	0	0.350	0.318	0.946	2.197	2.539	4
		− 0.1775	0.200	0.191	1.015	2.338	2.456	4
		− 0.4850	− 0.060	0.023	1.164	2.668	2.145	4
2.0	15	0	0.390	0.430	0.940	2.375	2.255	4
		− 0.1775	0.270	0.274	1.011	2.546	2.169	4
		− 0.5100	0.040	0.108	1.170	2.954	1.768	4
	40	0	0.280	0.248	0.884	2.205	2.664	5
		− 0.1775	0.140	0.155	0.941	2.326	2.577	4
		− 0.4800	−0.080	−0.146	1.075	2.656	2.415	4
2.2	15	0	0.330	0.336	0.896	2.374	2.394	5
		− 0.1775	0.220	0.203	0.958	2.530	2.309	5
		− 0.5050	0.020	−0.005	1.101	2.912	1.991	4
	40	0	0.210	0.214	0.842	2.206	2.739	5
		− 0.1775	0.090	0.073	0.897	2.334	2.696	5
		− 0.4725	−0.110	−0.161	1.011	2.620	2.530	4
				Cusachs' method				
	15	0	0.580	0.553	1.350	2.417	1.681	2
		− 0.1775	0.420	0.395	1.474	2.647	1.484	2
		− 0.5275	0.110	0.182	1.745	3.288	0.785	3
	40	0	0.460	0.439	1.238	2.116	2.207	2
		− 0.1775	0.290	0.291	1.357	2.291	2.061	2
		− 0.4975	−0.010	0.039	1.610	2.769	1.582	3

[a] Q_s, Q_p and Q_d are the sulfur *s*-, *p*- and *d*-orbital populations, respectively.
[b] See text.

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References

1. Wolfsberg, M., and L. Helmholz: J. chem. Physics **20**, 837 (1952).
2. Bishop, D. M., M. Randič, and J. R. Morton: J. chem. Phys. **45**, 1880 (1966).
3. Basch, H., A. Viste, and H. B. Gray: J. chem. Physics **44**, 10 (1966).
4. Oakland, R. L., and G. F. Duffey: J. chem. Physics **46**, 19 (1967).
5. Cusachs, L. C.: J. chem. Physics **43**, S 157 (1965).
6. Tables of Interatomic Distances and Configurations in Molecules and Ions, Special Publication No. 11 (Chemical Society, London, 1958).
7. Basch, H., A. Viste, and H. B. Gray: Theoret. chim. Acta **3**, 458 (1965).
8. Craig, D. P., and C. Zauli: J. chem. Physics **37**, 601 (1962).
9. In units of 1000 cm^{-1}.

10. BALLHAUSEN, C. J., and H. B. GRAY: Molecular Orbital Theory (W. A. Benjamin, Inc., New York, 1964) p. 114. There is a mitsprint in the integral $G_{T_2}(\sigma_p, \pi)$, the numerator should read $2\sqrt{2}[S(p\sigma_L, p\sigma_L) - S(p\pi_L, p\pi_L)]$, and in the integral $G_{T_2}(p, \sigma_s)$, the numerator should read $2\sqrt{3}\,S\,(p\sigma_M, s_L)$.
11. CLEMENTI, E.: A supplement to IBM. J. Res. Develop. **9**, 2 (1965), Tables 45 – 1 and 45 – 4 in this supplement.
12. CRUICKSHANK, D. W. J., B. C. WEBSTER, and D. F. MAYERS: J. chem. Physics **40**, 3733 (1964).
13. MULLIKEN, R. S.: J. chem. Physics **23**, 1833 (1955).
14. Reference 10, p. 124.

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