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SCF LCAO MO Calculations for the Iso-Electronic Series ClO_4^-, SO_4^{2-}, and PO_4^{3-}

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Ab initio SCF LCAO MO calculations have been performed for the ground states of the perchlorate, sulphate and phosphate ions. The basis sets used consisted of contracted gaussian-type orbitals having 12*s*, 10*p* and 2*d*-type primitive functions on the central atoms and 10*s* and 6*p*-type functions on the oxygens. The results are thought to be nearly at the Hartree-Fock limit.

Key words: Phosphate – Sulphate – Perchlorate

1. Introduction

The work reported here has been undertaken to investigate the influence of charge upon molecular orbital calculations on ions and also as a preliminary to an investigation of the influence of crystalline surroundings in such calculations.

Ab initio calculations have been performed both on ClO_4^- and SO_4^{2-} by earlier workers [1–4], but no such calculations for PO_4^{3-} have so far been reported. It was decided to perform calculations using the same basis set for the complete iso-electronic series so that meaningful comparisons could be made between the results for each member and to facilitate future discussions when crystalline potentials and so on are included. It was further felt that a more accurate description was needed for these important ions.

2. Details of Calculations

For chlorine, sulphur and phosphorous the (X/12, 9), X = Cl, S and P, basis sets reported by Veillard [5] were augmented by another *p*-function and with two *d*-functions to (X/12, 10, 2). For oxygen the basis set was the same as the one applied in the similar MnO_4^- calculation [6], (O/10, 6) [7]. The basis sets were contracted ⟨X/6, 6, 2⟩ (or rather ⟨X/8, 6, 2⟩ when the two extra *s*-orbitals produced by the totally symmetric components of the two *d*-orbitals are included)

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Table 1. Orbital exponents for the two outermost p-functions and for the two d-functions

Exponent	Cl	S	P
α_p^9	0.17	0.14	0.11
α_p^{10}	0.08	0.065	0.05
α_d^1	0.90	0.71	0.57
α_d^2	0.40	0.32	0.25

and $\langle O/5, 3\rangle$ respectively. The functions were grouped in the following way:

X s: (1 2 3 4 5 6) (7 8) (9) (10) (11) (12)
p: (1 2 3 4 5) (6) (7) (8) (9) (10)
d: (1) (2)
O s: (1 2 3 4 5) (6 7) (8) (9) (10)
p: (1 2 3 4) (5) (6).

The valence orbitals are, therefore, as in the MnO_4^- calculation [6] described by approximately three contracted functions as well as some polarization functions. The d-orbital exponents chosen are shown in Table 1; the functions are grouped around the values suggested by Roos and Siegbahn [8], and the exponents have a ratio close to 2.25. The outermost p-orbital from the (X/12, 9) set was modified, and a further p-orbital added, Table 1. As might be seen from the corresponding radial maxima, these functions are spanning the space more adequately for the description of the valence electrons of the ions without deteriorating the description of the atoms. This part of the basis set is not to be considered as "atomic", and it has, therefore, not been energy optimized as such.

The total energies for the contracted sets, $(X/12, 10)\rightarrow\langle X/6, 6\rangle$, are: Cl($^2P$) −459.4554 a.u., S($^3P$) −397.4816 a.u. and P($^4S$) −340.6962 a.u., which means differences to the near Hartree-Fock results [9] of 0.026, 0.023, and 0.023 a.u. respectively. The same figure for the oxygen basis set, $\langle O/5, 3\rangle$, is 0.009, and adding up for all atoms in an XO_4-ion we get a total difference of 0.06 a.u.

Tetrahedral geometry was assumed for the ions, and interatomic distances were for ClO_4^- taken as 1.4625 Å [10], for SO_4^{2-} as 1.488 Å [11] and for PO_4^{3-} as 1.555 Å [12]; where all values were taken as average bond distances from the crystal structure determinations. A slightly modified version of the program REFLECT [13] was used, and the systems were solved in C_2 symmetry. The CPU-time needed for calculating integrals and building up supermatrices was for each system 2 h and 30 min on an IBM 360/195 computer.

3. Results and Discussion

Total energies for the systems are presented in Table 2, and the values fall for ClO_4^- and SO_4^{2-} approximately 0.70 a.u. lower than the best previous results [1, 4]. This should be compared with the sum of deviations from Hartree-

Fock values for the atomic basis sets of 0.06 a.u. as opposed to a deviation of around 0.63 a.u. in the other calculations. If we form the differences between the energies of the ions and the constituent atoms as it is discussed in [6], we see that only a very small binding in this sense is found for SO_4^{2-} and that the two other ions show negative values for this figure as it was also the case for MnO_4^-. There is, however, a further stabilization of the ions of around 0.1 a.u. if we compare with the results from the smaller calculations. Thus, most of the energy gain is made on the atomic level (inner shells in particular) and only a smaller fraction in the binding. From these figures we might expect to be within 0.1 a.u. of the Hartree-Fock energies, and we have to conclude, as with the permanganate ion [6, 14], that the stability cannot be fully explained at the Hartree-Fock level, but both the cohesive energy from the crystal and the correlation energy in forming the new electron pairs have to be considered explicitly.

The populations, Table 2, show the same trends as in the case of MnO_4^- [6]. The larger basis sets tend to even out gross charges on the atoms; and, taking chlorine as an example, we find in calculations with (Cl/10, 6), (Cl/10, 6, 1) and (Cl/12, 10, 2) the gross charge to be +2.37, +1.54, and +0.778 respectively. The same pattern is found for sulphur, but it is somewhat surprising that the formal positive gross charge on the central atom is increasing slightly with increasing negative charge of the ion. As reported in earlier investigations [1, 4] the change in gross charge for the first step is reflected directly in the *d*-orbital participation, whereas the further decrease in charge with the second improvement

Table 2. Total energies, gross charges (q) and overlap populations (o) for the iso-electronic series (X = Cl, S, P)

	ClO_4^-	SO_4^{2-}	PO_4^{3-}
Total energy (a.u.)	−758.6189	−696.8543	−639.8409
$E_X + 4E_O - E_{XO_4^{n-}}$	− 0.0380	+ 0.1712	− 0.0568
X gross charge	+ 0.778	+ 0.964	+ 1.194
$q\,(Xs)$	5.488	5.226	4.896
$q\,(Xp)$	9.599	8.788	8.094
$q\,(Xd)$	1.135	1.022	0.816
O gross charge	− 0.444	− 0.741	− 1.048
$q\,(Os)$	3.877	3.831	3.810
$q\,(Op)$	4.567	4.910	5.239
$o\,(X–O)$	0.865	1.118	1.117
$o\,(O–O)$	− 0.148	− 0.151	− 0.116

Table 3. Overlap populations (o) in different calculations for ClO_4^- and SO_4^{2-} (X = Cl, S)

$o\,(X–O)$	(O/7, 3) (X/10, 6)	(O/7, 3) (X/10, 6, 1)	(O/10, 6) (X/12, 10, 2)
ClO_4^-	0.153	0.618	0.865
SO_4^{2-}	0.355	0.862	1.118

of the basis set is counterbalanced very evenly in the populations of the *s*, *p* and *d* orbitals (0.23, 0.28, and 0.25, respectively, in the case of ClO_4^-). Also the overlap populations in Table 3 behave as found previously [1, 4, 6], such that increasing basis sets give rise to increasing overlap populations between the binding atoms. It should, however, again be stressed that conventional population analysis partly loses its significance in calculations with large basis sets, where many of the functions have only minor importance in the description of the corresponding atomic systems.

The orbital energies are shown in Fig. 1 and Table 4, and there is so far full agreement as to the order of the filled levels both in the calculations [1–4, 15, 16] and in the experiments [17, 18]. It can be seen from the figure and from Tables 4 and 5 that there is a great similarity in these levels for the three ions. The main difference is a uniform shift to higher energy of about 0.25 a.u. for each charge unit, which arises because no account has been taken of the crystalline surroundings. The virtual orbitals are on the other hand, more unsystematically distributed, and it remains to be seen whether or not this will show up in the excited states as well, and also which role the crystal will play in this respect. It seems, however, very likely that the gap between the $1t_1$ and $6t_2$ levels

Table 4. Orbital energies (a.u.) for the iso-electronic series

	ClO_4^-	SO_4^{2-}	PO_4^{3-}
$1a_1$	−105.0803	−91.8074	−79.4281
$1t_2$	− 20.3978	−20.1104	−19.8640
$2a_1$	− 20.3977	−20.1103	−19.8640
$3a_1$	− 10.7424	− 8.7586	− 6.9310
$2t_2$	− 8.2214	− 6.4523	− 4.8379
$4a_1$	− 1.4918	− 1.0851	− 0.7216
$3t_2$	− 1.2154	− 0.8998	− 0.6110
$5a_1$	− 0.7124	− 0.3707	− 0.0626
$4t_2$	− 0.5684	− 0.2489	0.0428
$1e$	− 0.4045	− 0.1270	0.1311
$5t_2$	− 0.3546	− 0.0882	0.1593
$1t_1$	− 0.2814	− 0.0137	0.2230

Table 5. Population analysis for the valence electrons of the iso-electronic series

	ClO_4^-					SO_4^{2-}					PO_4^{3-}				
	Cl			O		S			O		P			O	
	s	*p*	*d*	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*s*	*p*	*d*	*s*	*p*
$4a_1$	1.02	—	—	0.81	0.16	0.77	—	—	1.09	0.14	0.51	—	—	1.40	0.09
$3t_2$	—	1.27	0.16	4.27	0.30	—	0.90	0.13	4.74	0.23	—	0.66	0.12	5.10	0.13
$5a_1$	0.47	—	—	1.07	0.47	0.46	—	—	0.70	0.84	0.38	—	—	0.38	1.24
$4t_2$	—	1.91	—	1.28	2.81	—	1.47	0.02	0.76	3.75	—	0.99	0.06	0.35	4.60
$1e$	—	—	0.46	—	3.54	—	—	0.41	—	3.59	—	—	0.29	—	3.71
$5t_2$	—	0.42	0.52	0.08	4.98	—	0.42	0.45	0.03	5.09	—	0.45	0.35	0.01	5.19
$1t_1$	—	—	—	—	6.00	—	—	—	—	6.00	—	—	—	—	6.00

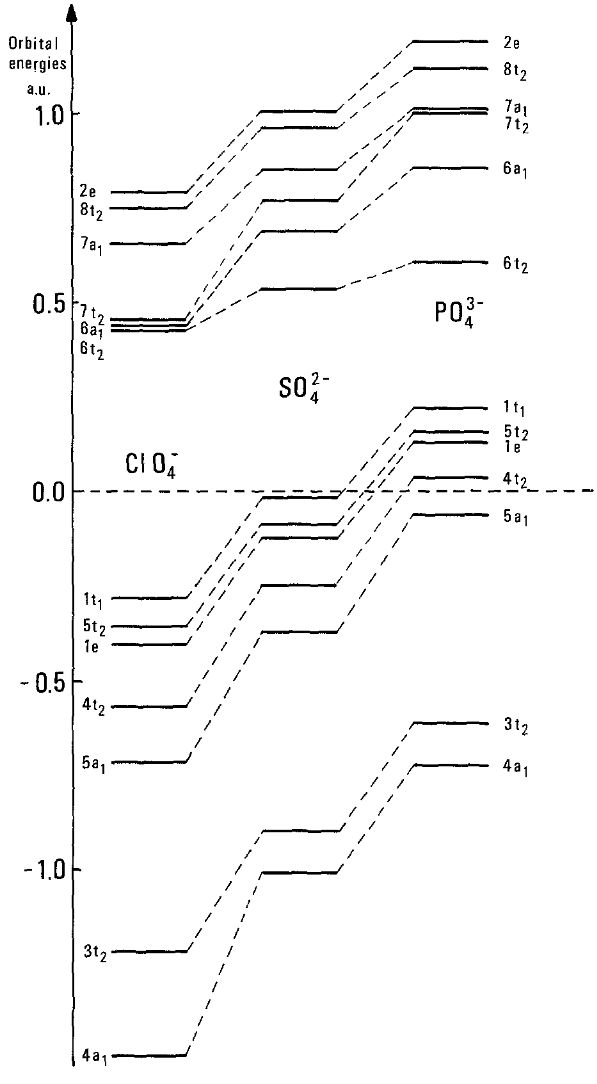

Fig. 1. Orbital energy diagram for the iso-electronic series: ClO_4^-, SO_4^{2-}, and PO_4^{3-}

will also diminish through the series ClO_4^-, SO_4^{2-} and PO_4^{3-} when the crystalline potential is introduced.

A comparison of the results of Hartree-Fock type calculations for ClO_4^- and SO_4^{2-}, obtained using the basis set (X/10, 6, 1) (O/7, 3), and corresponding results found by the scattered-wave method [16] has already been given [1]. A similar comparison using the present more accurate calculations shows the same trends. The discrepancy discussed in [1] was not found in the MnO_4^- study, and it is most probably due to an inaccurate choice of the α-parameter for the intersphere region in the scattered-wave calculations [19]. This region is given a constant potential, and it is for these systems taking up about 80% of the volume inside the Watson sphere and it contains about one third of the valence electrons. So even in these very spherical ions we may expect the absolute positions of orbital energies to be rather sensitive to variations in the exchange parameter.

On the whole, however, it seems that the two methods complement each other quite well.

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References

1. Johansen, H.: Chem. Phys. Letters **11**, 466 (1971)
2. Keeton, M., Santry, D. P.: Chem. Phys. Letters **7**, 105 (1970)
3. Hillier, I. H., Saunders, V. R.: Intern. J. Quant. Chem. **4**, 203 (1970); — Chem. Commun. 1181 (1969)
4. Gelius, U., Roos, B., Siegbahn, P.: Theoret. Chim. Acta (Berl.) **23**, 59 (1971)
5. Veillard, A.: Theoret. Chim. Acta (Berl.) **12**, 405 (1968)
6. Johansen, H.: Chem. Phys. Letters **17**, 569 (1972)
7. Clementi, E., Mehl, J.: IBM Research Report RJ 813 (1971)
8. Roos, B., Siegbahn, P.: Theoret. Chim. Acta (Berl.) **17**, 199 (1970)
9. Clementi, E.: IBM J. Res. Develop. **9**, 2 (1965)
10. Structure Reports for 1957, Vol. **21**, p. 357. Utrecht: Oosthoek 1957
11. Structure Reports for 1958, Vol. **22**, p. 449. Utrecht: Oosthoek 1958
12. Structure Reports for 1960, Vol. **24**, p. 397. Utrecht: Oosthoek 1960
13. Siegbahn, P.: Chem. Phys. Letters **8**, 245 (1971)
14. Johansen, H.: Proceedings of the second seminar on computational problems in quantum chemistry, p. 48. Straßburg, 1972 (Max-Planck-Institut, München 1973)
15. Manne, R.: J. Chem. Phys. **46**, 4645 (1967)
16. Johnson, K. H., Smith, F. C., Jr.: Chem. Phys. Letters **7**, 541 (1970)
17. Prins, R., Novakov, T.: Chem. Phys. Letters **9**, 593 (1971)
18. Manne, R., Karras, M., Suoninen, E.: Chem. Phys. Letters **15**, 34 (1972)
19. Wahlgren, U.: private communication 1972

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