Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam
Printed in the Netherlands.

SEMI-EMPIRICAL MOLECULAR ORBITAL THEORY APPLIED TO THE CHROMATE(VI) ION

G. DE MICHELIS, L. OLEARI AND L. DI SIPIO

Istituto di Chimica Generale, Università di Padova, Consiglio Nazionale delle Ricerche, Roma (Italy)

1. INTRODUCTION

It is our intention to calculate the energies and the molecular orbital coefficients for $(XO_4)^{n-}$ ions of the first row transition elements by using a semi-empirical molecular orbital theory according to the S.C.F.–L.C.A.O. approach.

The choice of this particular class of compound depended upon two considerations:

a) In 1952, Wolfsberg and Helmholz[1] first attempted to apply a semi-empirical M.O.–L.C.A.O. calculation to inorganic complexes. The complexes involved were the $(CrO_4)^{2-}$ and $(MnO_4)^-$ ions. It is possible to make a direct comparison between their calculation and that used in the present work.

b) The experimental data existing for these complexes offers the greatest possible number of cross-checks to control the validity of our calculation.

The first ion we chose to study was the $(CrO_4)^{2-}$ ion; this communication presents the results of our preliminary calculations.

2. METHOD OF CALCULATION

As already mentioned, we have used the molecular orbital (M.O.) approximation in the L.C.A.O. form.

We suppose that the bonding electrons on the chromium and on the oxygen do not influence the non-bonding electrons, and that those nearer the nuclei of the chromium and of the oxygen form an "effective core", in whose field the valence electrons are considered to move. Thus we need only concern ourselves with the 3*d*, 4*s* and 4*p* atomic orbitals of the central ion, and the 2*p* atomic orbitals of the oxygen atoms. With these we construct the molecular orbitals into which the twenty four valence electrons of the chromate ion are arranged. Although we should in fact include the 2*s* orbitals of the oxygen atom, in order to simplify the calculation, and because the 2*s*–2*p* energy separation is large, such electrons are considered part of the "central core".

Moreover to simplify the calculation further, the chromate ion is assumed to have a regular tetrahedral structure (with a chromium oxygen distance of 1.6 Å), even though the experimental evidence[2,3] favours a distorted tetrahedron. The molecule therefore belongs to the point group T_d and the atomic orbital combinations so obtained are those already reported by Wolfsberg and Helmholz[1].

The molecular orbital energies and the atomic orbital coefficients have been calculated with an electronic computer (ELEA 6001). The Roothaan[4] self-consistent field procedure has been applied with the "zero differential overlap" approximation[5,9]. In order to estimate the electron transition energies more accurately, a configuration interaction calculation has been performed. This has been extended to all the more important singly-excited configurations belonging to the irreducible representation T_2, remembering that for the group T_d, only transitions of the type $A_1 \rightarrow T_2$ are permitted.

TABLE I

THE ELECTRON DISTRIBUTION IN THE CHROMATE(VI) ION

Atomic orbitals	*Wolfsberg–Helmholz**	*This work**
Chromium		
s	0.189	0.397
$p_x = p_y = p_z$	0.040	0.075
$d_{z^2} = d_{x^2-y^2}$	0.828	0.725
$d_{xy} = d_{zy} = d_{zx}$	0.545	0.351
Oxygen		
p_σ	2.[illegible]82	1.821
$p_{\pi x} = p_{\pi y}$	1.478	1.698
Charge on the Chromium	3.600	3.125
Loss of charge from Chromium**	−2.396	−2.875
Charge on each Ligand	5.100	5.219
Increase in charge on each Ligand**	+1.098	+1.219

* These values have been calculated according to Mulliken[13].

** By taking as reference, the neutral atoms.

One obtains in this way 15 possible transitions (Fig. 1) which through further considerations of symmetry may be divided into two configuration subgroups which do not interact with each other.

3. EVALUATION OF THE ONE AND TWO-CENTRE INTEGRALS NECESSARY FOR THE S.C.F. CALCULATION

a) *One-centre coulomb repulsion integrals (ii|jj)*

These are calculated semi-empirically by using the method illustrated earlier[6], and by considering the valence states corresponding to the oxidation numbers −1,

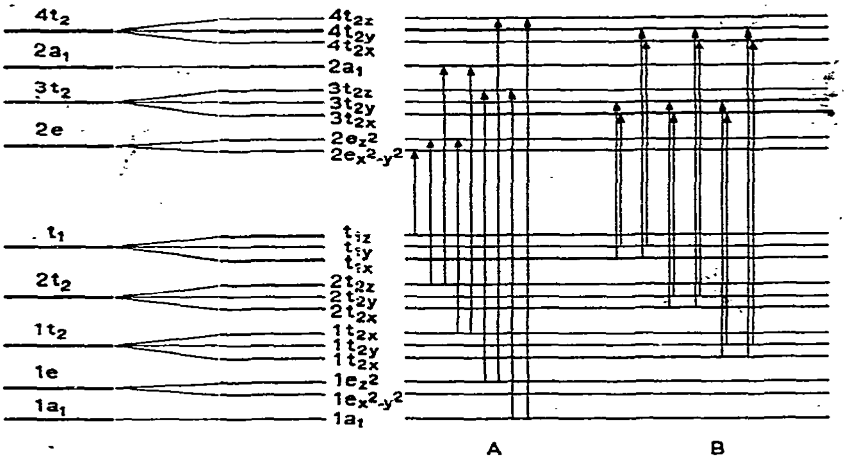

Fig. 1. Monoexcited configurations considered in the C.I. calculation. The vector of the electric dipole transitions is oriented along the z axis. For each pair of group B excitations only the linear combination of symmetry T_2 has to be considered.

0 and +1 for both chromium and oxygen. The experimental valence state energies are calculated by using the Slater-Condon parameters as given by Hinze and Jaffe for chromium[7], and by Skinner and Pritchard for oxygen[8].

The values obtained are quite satisfactory. They reproduce the experimental valence state energies with a deviation of ±0.5 eV.

b) *Two-centre coulomb repulsion integrals* (ii/jj)

In analogy with the "uniformly charged sphere approximation" suggested by Pariser and Parr[9], the charge distribution of each orbital has been approximated to the charge distribution obtained by associating to each lobe a uniformly charged sphere. The radii of the spheres are chosen in such a way that the electrostatic repulsion energy, interaction of the charge cloud on each orbital with itself, reproduces the value of the corresponding one centre Coulomb integral, estimated semi-empirically. The two-centre coulomb repulsion integrals have then been estimated by considering the electrostatic repulsion energy derived from such a distribution of charge.

c) *Penetration integrals* $(r:ii)$

It is necessary to consider such integrals in the evaluation of the diagonal elements of the energy matrix. We have given values to these integrals such that they reproduce, using a self-consistent calculation, the experimental dissociation energy of CrO (equal to 3.8 eV)[10].

d) *Integrals of the type* $H_{ij} = \beta_{ij}$

As already indicated by Wolfsberg and Helmholz[1], such integrals are approximated by assuming that they are proportional to the corresponding overlap integrals $S(i,j)$, according to the following relation

$$H_{ij} = F_x \cdot S(i,j) \cdot (I_i + I_j)/2$$

where F_x is a constant (assumed equal to 1) and I_i and I_j are the valence state ionisation potentials of the *i*th and *j*th atomic orbitals respectively. In this first calculation we have deliberately used values for the overlap integrals as given by Wolfsberg and Helmholz[1]. However a much more exact evaluation of these integrals may be obtained by using S.C.F. atomic orbitals in place of the Slater orbitals.

This has been done in order to have a direct comparison of the two systems of calculation.

4. RESULTS OF THE CALCULATION AND DISCUSSION

Although the present calculations are rather approximate, particularly in that the overlap integrals have been calculated on the basis of Slater atomic orbitals, some interesting points can be made:

a) The molecular energy level order (Fig. 2) corresponds substantially with that postulated by Ballhausen and Liehr[11] and differs from that of Wolfsberg and Helmholz[1]. We have shown that it is possible by using a molecular orbital calculation to obtain agreement both with the predictions of the crystal field theory ($E_{3t_2} > E_{2e}$) and with predictions based on experimental data (intensities of spectral transitions, e.s.r. etc.).

b) The S.C.F. molecular orbitals obtained, though confirming the covalency of the complex, do not seem too satisfactory, when we consider the charge distribution which is derived therefrom.

There appears to be an excessive transfer of charge from the chromium to the oxygens in disagreement with the Pauling Electroneutrality principle.

We consider that this is due, in the estimation of the one centre integrals, to the choice of the baricentre in the valence state energy polynomial expansion[6]. In the present calculation, the baricentre is the state of oxidation number zero, whilst in the complex there is very probably a partial transfer of charge towards the ligands.

If we calculate the one centre integrals of chromium by assuming the baricentre is Cr^+, we will obtain a better charge distribution. In fact, as a result of doing this, the values of the chromium diagonal elements of the energy matrix will increase. This will have the effect of moving charge back from the ligands towards the central ion, precisely as one desires.

c) With regard to the values of the transition energies obtained by carrying out a

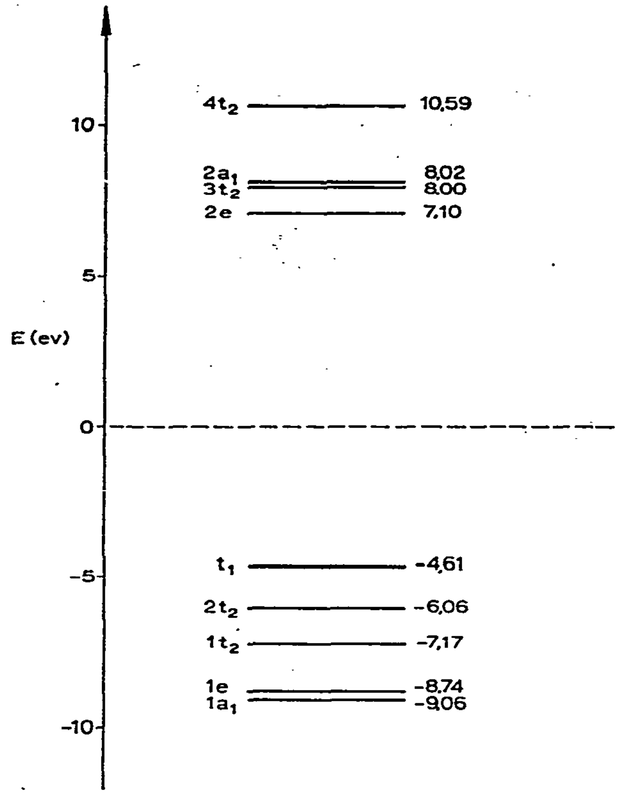

Fig. 2. Molecular orbital energy levels for CrO_4^{2-} ion.

configuration interaction calculation, they differ remarkably from the values obtained from the differences of the molecular orbital energies.

Therefore we think that it is not a correct procedure to interpret spectra by considering the difference in orbital energies, as other authors have done. In Tables II and III, we compare the experimental values of the transition energies with those calculated, as well as with the differences in the orbital energies: without wishing to make a detailed analysis of the spectra which will be done later on the basis of more precise calculations, we believe that there is moderate agreement between the calculated and experimental values.

TABLE II

ELECTRONIC TRANSITION ENERGIES

Transition	*Difference between the orbital energies (eV)*	*Values from C.I. calculation (eV)*
$t_1 \rightarrow 2e$	11.715	5.074
$t_1 \rightarrow 3t_2$	12.613	5.678
$2t_2'' \rightarrow 2e$	13.160	5.624

TABLE III

EXPERIMENTAL ELECTRONIC TRANSITION ENERGIES

Energy, eV	*Molar extinction coefficient*
2.84	very weak
3.25	4,700
4.59	3,900

5. CONCLUSIONS

Although our studies are in a preliminary stage, we can say that the semi-empirical calculation gives sufficiently accurate results for it to be useful in the theoretical study of inorganic complexes.

We cannot say just how useful the theory will be until we have the results of further calculations on the $(CrO_4)^{2-}$ and $(MnO_4)^{-}$ ions and also on the $(MnO_4)^{2-}$ and $(MnO_4)^{3-}$ ions, with the following modifications:

a) New values for the overlap integrals will be obtained by using S.C.F. atomic orbitals.

b) New values for the one centre integrals will be obtained by varying the baricentre of the valence state energy polynomial expansion

c) A more accurate evaluation of the two centre integrals will be attempted.

In this way we hope to be able to satisfactorily explain the principal molecular properties of tetrahedral complexes of the first row transition metals.

REFERENCES

1 M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, 20 (1952) 837.
2 H. W. Smith and M. Y. Colby, *Z. Krist.*, 101 (1940) 90.
3 D. I. Bujor, *Z. Krist.*, 105 (1944) 364.
4 C. C. J. Roothaan, *Rev. Mod. Phys.*, 23 (1951) 69.
5 J. A. Pople, *Trans. Faraday Soc.*, 49 (1953) 1375.
6 L. Oleari, L. Di Sipio and G. De Michelis, *This Volume*, p. 13.
7 J. Hinze and H. H. Jaffe, *J. Chem. Phys.*, 38 (1963) 1834.
8 H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, 49 (1953) 1254.
9 R. Pariser and R. G. Parr, *J. Chem. Phys.*, 21 (1953) 466, 767.
10 G. Herzberg, *Spectra of Diatomic Molecules*, Van Nostrand, New York, 1950, p. 523.
11 C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectry.*, 2 (1958) 342.
12 D. S. Schonland, *Proc. Roy. Soc. (London)*, *Ser. A*, 254 (1960) 111.
13 R. S. Mulliken, *J. Chem. Phys.*, 23 (1955) 1833.