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CONSIDERATIONS ON THE SEMI-EMPIRICAL MOLECULAR ORBITAL THEORY FOR COORDINATION COMPOUNDS*

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1. INTRODUCTION

In the last two years there has been renewed interest in the semi-empirical molecular orbital method for the determination of the electronic structure and the excitation energies of transition metal complexes[1-4].

Generally the method suggested by Wolfsberg and Helmholz[5] and subsequently modified by Ballhausen and Gray[1] has been applied. However a critical analysis of the procedure[6] and of the results[3,7] has pointed out certain ambiguities and limitations.

Recently, in order to avoid such ambiguities, we have applied to some tetroxo-ions[8] a semi-empirical molecular orbital method. This method was obtained by proper elaboration from the Pople-Pariser-Parr scheme[9-11] which works rather well for the unsaturated hydrocarbons.

The purpose of this paper is to examine the limitations and the advantages of this method, especially with respect to the Wolfsberg-Helmholz scheme.

2. THE APPROXIMATIONS OF THE SEMI-EMPIRICAL MOLECULAR ORBITAL METHOD

The Wolfsberg-Helmholz method is analogous to the Hückel method for unsaturated hydrocarbons: the diagonal elements of the secular equation are approximated as the valence state ionization energies and the electron transition energies are given as the difference of the molecular orbital energies.

Now in a coordination compound the situation is very different from that of an unsaturated hydrocarbon and the above approximations are rather rough, as appears from the following considerations:
i) In a coordination compound atomic orbitals with quite different electronegativities are usually involved in the bonding, and, as a consequence the electron distribution is very seldom strictly covalent. The atomic orbital coefficients in a

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given molecular orbital strongly depend upon the field of the other occupied molecular orbitals. Therefore, the diagonal elements of the secular equation must completely take into account the field due to the other atomic orbitals and cannot be approximated as the valence-state ionization potentials.

ii) Frequently in a coordination compound the following two situations occur: a) The wave function of the ground state cannot be expressed by a single Slater determinant. b) There are many excited configurations of the same symmetry, with close energies, which interact rather strongly. In this way one cannot make any assignment of the observed bands on the basis of the order of the energy levels.

It is clear that, in order to take into account both of these facts, a configuration-interaction calculation needs to be performed.

From these considerations it is evident that the molecular orbital calculations for the ground state and for the excited states must be performed in the most complete manner.

Today the molecular orbital theory according to the S.C.F.–L.C.A.O. scheme is the method with the least restrictive approximations and, therefore, the most suitable for describing systems like transition metal complexes.

From a chemical point of view, it is convenient to apply the molecular orbital theory in a semi-empirical way by evaluating some of the integrals from known experimental quantities, *e.g.* spectroscopic data, which already take into account the electron correlation[12].

The Pople-Pariser-Parr scheme substantially fulfils the above requirements. Therefore the problem consists in ascertaining whether the approximations of the method can be applied to inorganic complexes and which variations have to be introduced.

Therefore, hereafter, the approximations used in the evaluation of the integrals and the rôle of the various features in the calculation will be discussed separately.

3. DISCUSSION OF THE APPROXIMATIONS USED IN THE EVALUATION OF THE INTEGRALS

a. Zero differential overlap

This approximation consists in neglecting all the two-electron integrals in which the product $\chi_r(1)\chi_s(1)$ appears (χ_r and χ_s are atomic orbitals on different atoms).

At a first glance this approximation is rather rough. However, after careful examination Ruedenberg[13] has shown that "the neglect of differential overlap represents a valid and effective approximation if the atomic orbitals satisfy Mulliken's approximation[14] and if the molecular orbitals are simultaneously eigenvectors of the overlap matrix".

We wish to point out here that when the second condition is not exactly fulfilled, but the overlap between the involved atomic orbitals is not larger than 0.3–0.35 as it is in many coordination molecules, the "zero differential overlap" is still a good approximation. Therefore, we will discuss the effect of the "zero differential overlap" on the values of the molecular integrals. If

$$\phi_i = \sum_r c_{ir}\chi_r$$

represents a molecular orbital without "zero differential overlap", the coulomb and exchange integrals between two molecular orbitals Φ_i and Φ_j,

$$\mathrm{J}_{ij} = \sum_{p,q,r,s} c_{ip}c_{iq}c_{jr}c_{js}\,(pq \mid rs)$$

$$\mathrm{K}_{ij} = \sum_{p,q,r,s} c_{ip}c_{jq}c_{ir}c_{js}\,(pq \mid rs)$$

applying the Mulliken approximation[14], are given by the relations:

$$\mathrm{J}_{ij} = \sum_{p,q} (c_{ip}\sum_q c_{iq}S_{pq})\,(c_{jr}\sum_s c_{js}S_{rs})\,(pp \mid rr)$$

$$\mathrm{K}_{ij} = \sum_{p,q} [\tfrac{1}{2}(c_{ip}\sum_q c_{jq}S_{pq})+\tfrac{1}{2}(c_{jp}\sum_q c_{iq}S_{pq})]\cdot[\tfrac{1}{2}(c_{ir}\sum_s c_{js}S_{rs})+ \\ + \tfrac{1}{2}(c_{jr}\sum_s c_{is}S_{rs})]\,(pp \mid rr)$$

where

$$(pq \mid rs) = \int \chi_p^*(1)\chi_r^*(2)\,\frac{1}{r_{12}}\,\chi_q(1)\chi_s(2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2$$

On the other hand, if $\Phi_i = \Sigma a_{ir}\chi_r$ represents a molecular orbital when the "zero differential overlap" is introduced, the coulomb and exchange integrals are given by the relations:

$$\bar{\mathrm{J}}_{ij} = \sum_{p,r} a_{ip}{}^2 a_{jr}{}^2 (pp \mid rr)$$

$$\bar{\mathrm{K}}_{ij} = \sum_{p,r} a_{ip}a_{jp}a_{ir}a_{jr}(pp \mid rr)$$

Now, in order to have the same population analysis[15], the following relation must hold:

$$a_{ir}{}^2 = c_{ir}\sum_s c_{is}S_{rs} \tag{1}$$

Therefore the coulomb integrals in both cases are exactly given by the same expression

$$\mathrm{J}_{ij} = \sum_{p,r} (c_{ip}\sum_q c_{iq}S_{pq})\,(c_{jr}\sum_s c_{js}S_{rs})\,(pp \mid rr) = \sum_{p,r} a_{ip}{}^2 a_{jr}{}^2 (pp \mid rr) = \bar{\mathrm{J}}_{ij}$$

The exchange integrals are equal, provided that the quantities

$$[\tfrac{1}{2}(c_{ip}\sum_q c_{jq}S_{pq})+\tfrac{1}{2}(c_{jp}\sum_q c_{iq}S_{pq})]$$

are substituted by

$$a_{ip}a_{jp} = [(c_{ip}\sum_q c_{iq}S_{pq})\,(c_{jp}\sum_q c_{jq}S_{pq})]^{\frac{1}{2}}.$$

This corresponds to introducing the geometrical mean instead of the arithmetical mean.

The difference between the two quantities is given by the expression

$$[\tfrac{1}{2}(c_{ip}\sum_q c_{jq}S_{pq})+\tfrac{1}{2}(c_{jp}\sum_q c_{iq}S_{pq})]-a_{ip}a_{jp} = \tag{2}$$

$$= \tfrac{1}{2}c_{ip}c_{jp}\left(\frac{a_{ip}}{c_{ip}}-\frac{a_{jp}}{c_{jp}}\right)^2 = \tfrac{1}{8}c_{ip}c_{jp}\left[\sum_{q\neq p} S_{pq}\left(\frac{c_{iq}}{c_{ip}}-\frac{c_{jq}}{c_{jp}}\right)\right]^2+\ldots..$$

which is equal to zero when

$$\frac{a_{ip}}{c_{ip}} = \frac{a_{jp}}{c_{jp}} = \ldots\ldots\ldots = f_p \tag{3}$$

with f_p independent of the molecular orbital.

When such a condition is not verified, the difference depends upon terms of second and higher powers of the overlap integrals. It is usually rather small when such integrals are not larger than 0.3–0.35. This is clearly illustrated in Fig. 1 for the case of a basis of two atomic orbitals

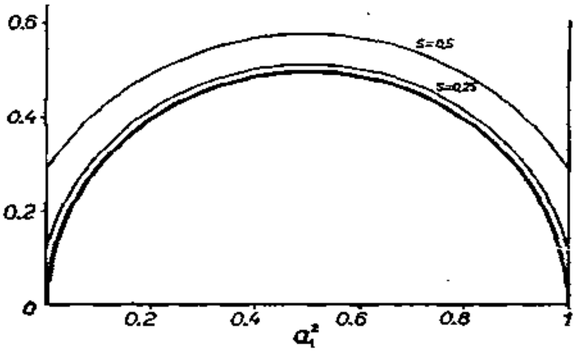

Fig. 1. Plot of a_1a_1 (——) and of $\frac{1}{2}[c_1(c_1^*+Sc_2^*)+c_1^*(c_1+Sc_2)]$ (——) for several values of S against a_1^2.

$$\phi = c_1\chi_2+c_2\chi_2 \qquad \bar{\phi} = a_1\chi_1+a_2\chi_2$$

$$\phi^* = c_1^*\chi_1+c_2^*\chi_2 \qquad \bar{\phi}^* = a_1^*\chi_1+a_2^*\chi_2$$

The quantities a_1a_1 and $\frac{1}{2}[c_1(c_1^*+Sc_2^*)+c_1^*(c_1+Sc_2)]$ for several values of S are plotted against a_1^2, which substantially represents the possible situations of bond polarity. The difference in this particular case is fairly constant and almost independent of the polarity.

With regard to the core integrals

$$\mathrm{H}_{ii} = \int \phi_i^* H_{\mathrm{core}} \phi_i \mathrm{d}\tau,$$

they are given respectively in the two cases by the following expressions:

$$\mathrm{H}_{ii} = \sum_{p,q} c_{ip} c_{iq} H_{pq} \qquad \overline{\mathrm{H}}_i = \sum_{p} a_{ip}{}^2 H_{pp} + 2 \sum_{p,q<p} a_{ip} a_{iq} \beta_{pq}$$

On the basis of the equality (1), these integrals are equal if β_{pq} is defined in this way

$$\beta_{pq} = \frac{c_{ip}}{a_{ip}} \cdot \frac{c_{iq}}{a_{iq}} [H_{pq} - \tfrac{1}{2} S_{pq}(H_{pp} + H_{qq})] \tag{4}$$

When the difference (2) is small, condition (3) is almost true and β_{pq} becomes a quantity nearly independent of the molecular orbital.

However, since in the semi-empirical molecular orbital calculations the β_{pq} quantities are usually evaluated a posteriori[11,16] in such a way as to fit some experimental data, this corresponds to satisfying equation (4).

With regard to the Mulliken approximation, it usually works rather well in the evaluation of the interelectronic repulsion integrals. Nevertheless, it cannot be used in the case of integrals of the type $(pq \mid pq)$, when χ_p and χ_q are atomic orbitals on the same atom. In fact they would be zero, due to the orthogonality of the atomic orbitals. Such integrals are usually small and can be evaluated semi-empirically from the Slater-Condon parameters.

b. One-centre integrals

According to Pariser and Parr, the one-centre integrals in an unsaturated hydrocarbon can be evaluated with the following relations:

$$\int \chi_p^*(T + U_p)\chi_p \, \mathrm{d}\tau = -I_p$$

$$\int \chi_p^*(1)\chi_p^*(2) \frac{1}{r_{12}} \chi_p(1)\chi_p(2) \, \mathrm{d}\tau_1 \, \mathrm{d}\tau_2 = I_p - A_p$$

where I_p and A_p are respectively the valence state ionization potential and electron affinity for the atomic orbital χ_p and U_p is the potential from the nucleus and from all the electrons around it.

In the case of a coordination compound the situation is complicated by the fact that each atom participates in the bonding with several atomic orbitals, and a separation similar to that of a π and σ system cannot be made.

In a more general sense the one-centre integrals must be quantities which reproduce as closely as possible the valence state energies of an atom as functions of the occupation numbers of the atomic orbitals, at least for values of occupation numbers rather close to those of the atom in the molecule.

This requirement is fulfilled by the relation[17]:

$$E = C + \sum_p U_p n_p + \tfrac{1}{2} \sum_{p,\,q(\neq p)} g_{pq} n_p n_q + \tfrac{1}{2} \sum_p g_{pp} n_p (n_p - 1)$$

where E is the valence state energy

n_p, n_q are occupation numbers

C, U_p, g_{pq}, g_{pp} are empirical constant quantities to be determined in such a way as to have the best fit with some known valence-state energies.

The quantities U_p, g_{pq} and g_{pp} can be considered as semi-empirical one-centre integrals defined in this way:

$$U_p = \int \chi_p^*(T + U_p)\chi_p \, \mathrm{d}\tau$$

$$g_{pq} = (pp \mid qq) - \tfrac{1}{2}(pq \mid pq)$$

$$g_{pp} = (pp \mid pp)$$

where U_p is the potential from the nucleus and all the non-valence electrons.

It may be shown that these quantities can be considered as a generalization of the Pariser and Parr criteria.

c. Two-centre integrals

Coulomb integrals

Pariser and Parr in their original papers[10,11] evaluated the two-centre coulomb integrals making an interpolation by means of a second degree polynomial. Indeed in the case of carbon atoms the semi-empirical value when $R = 0$ is known (R is the interatomic distance) and, when R is so large that the overlapping between the charge clouds of the involved atomic orbitals is quite small, the uniformly charged sphere approximation can be used.

In subsequent papers Pariser[18] and later Hoyland and Goodman[16] reported values which give the best agreement with the spectral data of benzene and ethylene.

In the case of coordination compounds the involved atomic orbitals belonging to different atoms are different, and the semi-empirical value of the integrals when $R = 0$ is not known. Therefore, one cannot make any interpolation.

In Fig. 2 the integral $(pp \mid qq)$, when χ_p and χ_q are $2p_\pi$ atomic orbitals of carbon, is plotted against R. The curves correspond to different criteria of evaluation. In particular curve c corresponds to the theoretical computation using Slater orbitals with exponent $\zeta = 1.040$. This value reproduces the semi-empirical one-centre integral $(pp \mid pp)$.

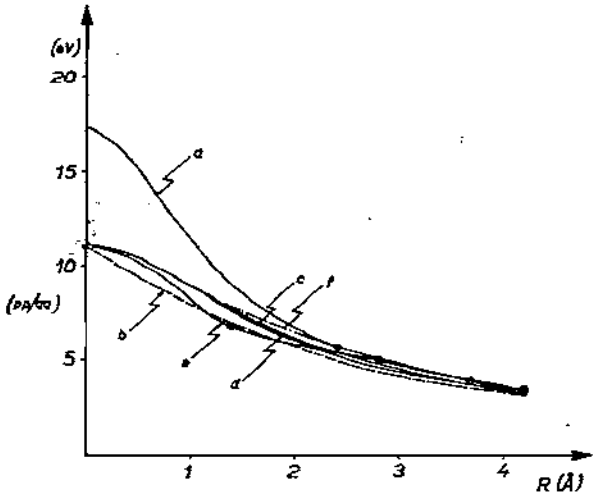

Fig. 2. Plot of the coulomb integral $(pp \mid qq)$ for carbon atomic orbitals against R. The different curves correspond as follows: a) Theoretical computation with Slater exponent; b) Pariser-Parr parabola; c) Theoretical computation with $\zeta = 1.040$; d) Uniformly charged sphere approximation with $R = 1.1046$ Å; e) Hoyland-Goodman curve; f) Inga Fischer-Hjalmars relation; ⊙ Pariser values

Curve d corresponds to the evaluation obtained by associating to each lobe of the orbitals a uniformly charged sphere with proper radius in such a way as to reproduce the semi-empirical one-centre integral $(pp \mid pp)$.

Both methods give very close values, slightly greater than those of Pariser and of Hoyland-Goodman, and slightly smaller than those which can be obtained from the polynomial expression proposed by Inga Fischer-Hjalmars[19]. Such an expression is based on a more general criterion than that of the best fit in a special molecule.

On the basis of this comparison we think that the method corresponding to curve c and especially that to curve d, which is particularly simple, can also be used in the case of coordination compounds.

A support in this sense is given by the rather close agreement of the data in Table I where the semi-empirical values of the one-centre coulomb integrals in-

TABLE I

ONE-CENTRE COULOMB INTEGRALS FOR Mn°

Coulomb integrals	*Semi-empirical value*	*From Slater a.o. with $\zeta = 1.953$*	*Sphere approxim. with $r = 0.625$ Å*
$(d_{z^2}d_{z^2} \mid d_{z^2}d_{z^2})$	14.694	14.694	14.694
$(d_{zx}d_{zx} \mid d_{zy}d_{zy})$	13.285	13.379	12.697
$(d_{zx}d_{zx} \mid d_{x^2-y^2}d_{x^2-y^2})$	13.285	13.379	12.806
$(d_{xy}d_{xy} \mid d_{x^2-y^2}d_{x^2-y^2})$	13.864	13.945	14.103
$(d_{z^2}d_{z^2} \mid d_{zx}d_{zx})$	13.672	13.756	13.671
$(d_{z^2}d_{z^2} \mid d_{xy}d_{xy})$	13.091	13.190	12.571

volving different 3*d* atomic orbitals of manganese are compared with the corresponding values obtained from the method used for curves c and d*.

Owing to the particular simplicity, in the calculations on tetroxo-ions we used the method corresponding to curve d.

β integrals

As already pointed out the β integrals in the case of unsaturated hydrocarbons are usually evaluated a posteriori in such a way as to fit some experimental data, *e.g.* the observed transitions of ethylene and benzene.

In the case of coordination compounds such criterion cannot be used because we have to deal with many atomic orbitals of different kinds and, consequently, with many different β integrals.

In order to discuss the possibility of establishing a different criterion of evaluation, in Fig. 3 the integral β_{pq} in the case of unsaturated hydrocarbons is plotted against R. The various curves correspond to different criteria of evaluation. In particular curves a (except the dotted part) and b give the integral β that we obtained in a previous paper[20] for the ethylene molecule by means of the Morse equation**.

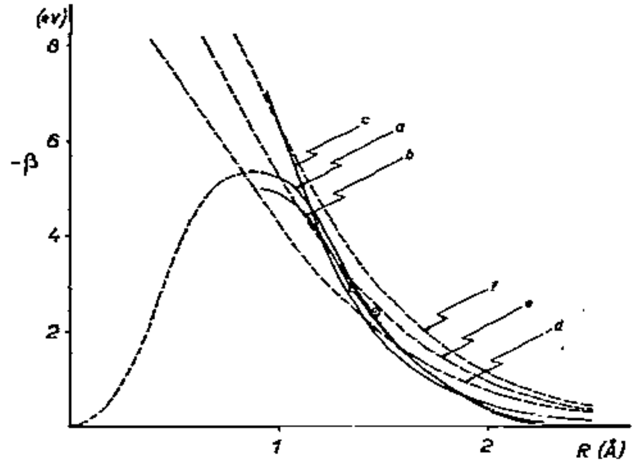

Fig. 3. Plot of β integral for carbon atomic orbitals against R. The different curves correspond as follows: a) and b) From ethylene molecule by means of the Morse equation; c) Hoyland-Goodman relation; d), e) and f) Mulliken's relation $\frac{1}{2}F(I_p+I_q)S_{pq}$ with $F = 0.8$, 1.0 and 1.2; ○ Pariser-Parr values for ethylene and benzene.

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* The orbital exponent ($\zeta = 1.953$) and the radius ($r = 0.625$) of the uniformly charged spheres are those which reproduce the semi-empirical value of the one-centre coulomb integrals involving the same atomic orbital.

** The two curves have been obtained by using two different values of ionization potential for the carbon atom, 11.54 eV and 9.84 eV.

Curve c represents the integral obtained from the empirical expression of Hoyland and Goodman[16]: $\log(-\beta) = 2.00054\text{–}1.17030R$.

Finally curves d, e and f have been obtained by means of Mulliken's expression[21]: $\beta_{pq} = -\frac{1}{2}(I_p+I_q)F\cdot S_{pq}$ assigning to F the values 0.8, 1.0 and 1.2.

From Fig. 3 it is clear that the value of F which gives the best agreement with the curves obtained from the experimental data, within the range of bonding 1.2–1.45 Å, is very close to 1.

The largest discrepancy appears when R is smaller than 1 Å. In fact, as it is clear from equation (4) the β integral must be equal to zero when $R = 0$, and, consequently, it must vary in a similar way to the dotted part of curve a.

On the basis of these considerations in the calculations on tetroxo-ions we used Mulliken's expression with $F = 1$. We think that it is only a fair approximation and a more accurate criterion needs to be found. For instance from some of our investigations it appears that Mulliken's expression cannot be applied when the involved atomic orbitals have very different energies.

Penetration integrals

The penetration integrals $(h\!:\!pp)$, which represent the potential energy of one electron in a χ_p atomic orbital in the field of the neutral atom h, are usually neglected in the case of unsaturated hydrocarbons. This approximation is justified by the fact that penetration integrals are usually small and that in many cases, in the calculation of electron transitions, only differences of penetration integrals are needed.

In the case of coordination compounds the central atom has a high coordination number, at least with respect to the coordination number of the ligands. As a consequence, the role of penetration integrals is extremely important and cannot be neglected. This appears clear when one takes into account that the sum of the penetration integrals for an atomic orbital on the central atom is much larger than the corresponding sum for an atomic orbital on a ligand.

In the calculations on tetroxo-ions we evaluated the penetration integrals by means of an empirical relation, which has no theoretical grounds

$$(h\!:\!pp) = f\sum_{q_h} n_{q_h}{}^{0}(pp \mid q_h q_h)$$

where $n_{q_h}{}^{0}$ is the number of electrons in the χ_{q_h} atomic orbital on the neutral atom h; f is an empirical factor which was evaluated in such a way as to reproduce, by an S.C.F. calculation, the experimental dissociation energies of the monoxides. Therefore, due to the procedure used in the evaluation, we think that this method is substantially valid since it gives quantities which both take into account the penetration integrals and introduce a correction for the approximations made in the evaluation of the other integrals.

4. DISCUSSION OF THE ROLE OF THE VARIOUS FEATURES IN THE CALCULATION SCHEME

a. The wave function of the ground state

When the molecule is a closed shell system, a good wave function can be obtained by using the S.C.F. scheme of Roothaan[22].

The diagonal elements of the secular equation, with the "zero differential overlap" approximation between atomic orbitals on different centres, are given by the expression[17]:

$$F_{p_hp_h} = U_{p_h} + \sum_{q_h(\neq p_h)} P_{q_hq_h}[(p_hp_h \mid q_hq_h) - \tfrac{1}{2}(p_hq_h \mid p_hq_h)] +$$

$$\tfrac{1}{2}P_{p_hp_h}(p_hp_h \mid p_hp_h) + \sum_{k(\neq h)} [-(k:p_hp_h) + \sum_{q_k} (P_{q_kq_k} - n_{q_k}{}^0)(p_hp_h \mid q_kq_k)]$$

where

$$U_{p_h} = \int \chi_{p_h}{}^* H_h{}^{\text{core}} \chi_{p_h}\, \mathrm{d}\tau \qquad P_{q_kq_k} = 2 \sum_{\substack{\text{filled}\\ \text{m.o.}}} c_{iq_k}{}^2$$

c_{iq_k} is the coefficient of the atomic orbital χ_{q_k} on atom k in the molecular orbital

$$\phi_i = \sum_k \sum_{q_k} c_{iq_k} \chi_{q_k}$$

$P_{q_kq_k}$ is the occupation number of χ_{q_k} in the molecule and $n_{q_k}{}^0$ in the neutral atom.

When the semi-empirical one-centre integrals are introduced, the expression can be written as follows:

$$F_{p_hp_h} = -I_{p_h} + \tfrac{1}{2}P_{p_hp_h}(I_{p_h} - A_{p_h}) + \sum_{k(\neq h)} [-(k:p_hp_h) +$$

$$\sum_{q_k} (P_{q_kq_k} - n_{q_k}{}^0)(p_hp_h \mid q_kq_k)]$$

where

$$-I_{p_h} = U_{p_h} + \sum_{q_h(\neq p_h)} P_{q_hq_h}[(p_hp_h \mid q_hq_h) - \tfrac{1}{2}(p_hq_h \mid p_hq_h)]$$

$$-A_{p_h} = U_{p_h} + \sum_{q_h(\neq p_h)} P_{q_hq_h}[(p_hp_h \mid q_hq_h) - \tfrac{1}{2}(p_hq_h \mid p_hq_h)] + \tfrac{1}{2}P_{p_hp_h}(p_hp_h \mid p_hp_h)$$

I_{p_h} represents the valence-state ionization potential relative to the atomic orbital χ_{p_h}, when it is considered mono-occupied, and is expressed as a linear function of the occupation numbers of the other atomic orbitals on the same atom h. A_{p_h} represents correspondingly the electron affinity or the ionization potential when χ_{p_h} is considered doubly occupied.

It is evident that the one-centre part of $F_{p_hp_h}$

$$-I_{p_h} + \tfrac{1}{2}P_{p_hp_h}(I_{p_h} - A_{p_h})$$

corresponds substantially to the diagonal elements of the secular equation in the

Wolfsberg-Helmholz scheme with the improvements of Ballhausen-Gray[1]. In particular when $P_{p_h p_h} = 1$ it becomes equal to the Mulliken electronegativity.

The two-centre part of $F_{p_h p_h}$

$$\sum_{k(\neq h)} [-(k:p_h p_h) + \sum_{q_k} (P_{q_k q_k} - n_{q_k}{}^0)(p_h p_h \mid q_k q_k)]$$

represents the field of all the other atoms on the atomic orbital χ_{p_h}. This quantity in the Wolfsberg-Helmholz procedure is completely neglected. When the electron distribution is not completely covalent, such a quantity becomes extremely important. This is illustrated by the data of Table II for the case of MnO_4^-, where it is clear that the two-centre part of $F_{p_h p_h}$ cannot be neglected. In fact it has a quite different value according to whether the involved atomic orbital is on the central atom or on a ligand.

Moreover the data of Table II explains the fact that the Wolfsberg-Helmholz method gives a wrong order for the first two antibonding levels[23,24] in the case of MnO_4^-. In fact according to the Wolfsberg-Helmholz scheme, the diagonal elements of the secular equation for the atomic orbitals d_{z^2}, $d_{x^2-y^2}$ (symmetry E) and d_{zx}, d_{zy}, d_{xy} (symmetry T_2) have the same value. As a consequence, in solving the secular equation, the energy of the antibonding molecular orbitals of symmetry E becomes higher than that of the corresponding T_2 molecular orbitals, in complete disagreement with the experiment results*.

TABLE II

THE DIAGONAL ELEMENTS OF THE SECULAR EQUATION OF MnO_4^-

Atomic orbitals	$F_{p_h p_h}$ *(eV)*		
	one-centre part	*two-centre part*	*total*
$4s$	−21.22	20.48	−0.74
$4p$	−15.73	16.52	+0.79
$3d_{z^2}$, $3d_{x^2-y^2}$	−27.86	19.73	−8.13
$3d_{zx}$, $3d_{zy}$, $3d_{xy}$	−27.73	20.82	−6.91
$2p_\sigma$	−2.75	−8.06	−10.81
$2p_\pi$	−3.89	−7.20	−11.09

On the contrary, taking into account the field of the oxygens, the diagonal elements of the atomic orbitals d_{z^2}, $d_{x^2-y^2}$ are lower than those of d_{zx}, d_{zy}, d_{xy} and the energy order of the antibonding orbitals is $E < T_2$, in agreement with the experimental findings.

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* Recently Viste and Gray[4] using the Wolfsberg-Helmholz scheme obtained the right order of levels by including in the calculations the $2s$ atomic orbitals of the oxygens. Nevertheless, such orbitals cannot be considered as the determining factor for obtaining the right order of levels. This is supported by the fact that by including the $2s$ atomic orbitals in the case of octahedral complexes even poorer results have been obtained[7].

b. The role of the configuration interaction

In the case of MnO_4^- only the transitions $T_2 \leftarrow A_1$ are allowed and the mono-excited configurations belonging to the irreducible representation T_2 can be divided in two non-interacting groups: one (group *a*) where the singlet wave function is expressed by two Slater determinants and another (group *b*) where the singlet wave function is expressed by a linear combination of four Slater determinants (Table III).

TABLE III

RESULTS OF THE CONFIGURATION-INTERACTION CALCULATION IN MnO_4^-

Configurations	*A*	*C.I. eigenvectors**				
Group a						
$(t_{1z})^{-1}(2e_{x^2-y^2})$	3.113	0.901	0.277	0.157	0.010	0.042
$(2t_{2xy})^{-1}(2e_{z^2})$	4.286	−0.409	0.729	0.427	−0.038	0.021
$(1t_{2xy})^{-1}(2e_{z^2})$	5.217	−0.047	−0.605	0.716	−0.056	0.078
$(1e_{z^2})^{-1}(3t_{2xy})$	6.142	−0.050	−0.028	−0.053	0.051	0.235
$(2t_{2xy})^{-1}(2a_1)$	6.773	0.057	−0.031	−0.261	−0.287	0.863
$(1a_1)^{-1}(3t_{2xy})$	7.674	0.099	0.138	0.440	0.070	0.405
$(1t_{2xy})^{-1}(2a_1)$	8.217	0.034	0.035	0.102	−0.006	−0.161
$(1e_{z^2})^{-1}(4t_{2xy})$	11.133	0.044	0.020	0.016	−0.055	0.013
$(1a_1)^{-1}(4t_{2xy})$	12.349	−0.020	−0.056	−0.073	−0.011	−0.050
B C.I. eigenvalues		2.351	3.315	5.777	6.033	6.739

Group b					
$\frac{1}{\sqrt{2}}[t_{1x})^{-1}(3t_{2zx})-(t_{1y})^{-1}(3t_{2zy})]$	2.208	0.973	−0.201	−0.096	0.014
$\frac{1}{\sqrt{2}}[(2t_{2zy})^{-1}(3t_{2zx})+(2t_{2zx})^{-1}(3t_{2zy})]$	5.198	0.219	0.770	0.496	−0.318
$\frac{1}{\sqrt{2}}[(1t_{2zy})^{-1}(3t_{2zx})+(1t_{2zx})^{-1}(3t_{2zy})]$	5.575	−0.026	−0.513	0.854	0.054
$\frac{1}{\sqrt{2}}[(t_{1x})^{-1}(4t_{2zx})-(t_{1y})^{-1}(4t_{2zy})]$	7.292	−0.049	−0.318	−0.120	−0.900
$\frac{1}{\sqrt{2}}[(2t_{2zy})^{-1}(4t_{2zx})+(2t_{2zx})^{-1}(4t_{2zy})]$	9.527	−0.045	0.039	−0.017	−0.292
$\frac{1}{\sqrt{2}}[(1t_{2zy})^{-1}(4t_{2zx})+(1t_{2zx})^{-1}(4t_{2zy})]$**	10.280				
B C.I. eigenvalues		2.039	4.697	5.874	7.441

* Only the eigenvectors corresponding with the lowest eigenvalues are reported here.
** This configuration has been neglected.

In each group there are many configurations with some of them having very close energies. As a consequence, there is a strong interaction, and the energies of the excited states (rows B of Table III) differ remarkably from those corresponding to the single excited configurations (column A of Table III)*.

This shows that, as previously pointed out, in coordination compounds, in order to give a correct assignment of the observed bands, it is extremely important to take into account the interaction of the excited state configurations.

5. CONCLUSION

On the basis of what has been discussed it is evident that in a semi-empirical molecular orbital calculation on a coordination compound the following facts are important:

i) The field of the charge distribution on the different atoms must be taken into account in the diagonal elements of the secular equation.

ii) In order to correctly assign the observed bands, the excitation energies must be evaluated taking into account configuration interaction.

We believe that the calculation scheme we applied to the tetroxo-ions, in spite of approximations, has the advantage of taking into account the above facts.

Therefore we think that such a scheme is a good approach toward the investigation of coordination compounds.

Appendix

i) The electronic repulsion energy between two uniformly charged spheres with a unit charge is given by the following expressions (R_1 and R_2 are the radii of the spheres; r is the distance of the centres):

$$1)\ \mathrm{V} = \frac{1}{r} \qquad r > R_1 + R_2$$

$$\begin{aligned}2)\ \mathrm{V} = \frac{1}{160 R_1{}^3 R_2{}^3 r} \cdot [&5(R_1{}^6 + R_2{}^6) - r^6 + 30 r R_1{}^2 R_2{}^2 (4R_1 + 4R_2 - 3r) + \\ &+ 80 R_1{}^3 R_2{}^3 - 40 r^3 (R_1{}^3 + R_2{}^3) - 24 r (R_1{}^5 + R_2{}^5) + 45 r^2 (R_1{}^4 + R_2{}^4) - \\ &- 45 R_1{}^2 R_2{}^2 (R_1{}^2 + R_2{}^2) + 15 r^4 (R_1{}^2 + R_2{}^2)] \qquad | R_1 - R_2 | < r < R_1 + R_2\end{aligned}$$

$$3)\ \mathrm{V} = \frac{1}{15 R_1{}^3} [15 R_1{}^2 - 3 R_2{}^2 - 5 r^2] \qquad r < R_1 - R_2\ (R_1 > R_2)$$

---

* Only the data corresponding to a dipole transition along the z axis and with Mn^0 reference oxidation state are reported in the table[8]. $(\Phi_l)^{-1}(\Phi_j)$ denotes a singlet wave function, linear combination of two Slater determinants, corresponding to the excitation $\Phi_l \rightarrow \Phi_j$. With $t_{1x} t_{1y} t_{1z}$, $t_{2zx} t_{2zy} t_{2xy}$ and $e_{z^2} e_{x^2-y^2}$ are denoted the molecular orbitals belonging to the irreducible representations T_1, T_2 and E which transform like $L_x L_y L_z$, $d_{zx}\ d_{zy} d_{xy}$ and $d_{z^2}\ d_{x^2-y^2}$ respectively.

ii) The charge cloud of the d_{zx}, d_{zy}, d_{xy}, $d_{x^2-y^2}$ atomic orbitals can be approximated to four tangent spheres. The charge cloud of the d_{z^2} atomic orbital is given by the expression

$$d_{z^2}{}^2 = \tfrac{1}{3}d_{z^2-x^2}{}^2 + \tfrac{1}{3}d_{z^2-y^2}{}^2 + \tfrac{2}{3}d_{z^2-x^2} \cdot d_{z^2-y^2}$$

where again $d_{z^2-x^2}{}^2$ and $d_{z^2-y^2}{}^2$ can be approximated to four tangent spheres and $d_{z^2-x^2} \cdot d_{z^2-y^2}$ to the two overlapping spheres of $d_{z^2-x^2}{}^2$ and $d_{z^2-y^2}{}^2$.

On the basis of the uniformly charged sphere approximation, the one-centre coulomb integrals involving d orbitals are given by the following expressions (r in Å is the radius of the spheres):

$$(d_{z^2}d_{z^2} \mid d_{z^2}d_{z^2}) = \frac{9.192}{r}\,(\mathrm{eV})$$

$$(d_{zx}d_{zx} \mid d_{zx}d_{zx}) = \frac{9.192}{r}$$

$$(d_{zx}d_{zx} \mid d_{zy}d_{zy}) = (d_{zx}d_{zx} \mid d_{xy}d_{xy}) = (d_{zx}d_{zx} \mid d_{x^2-y^2}d_{x^2-y^2}) = \frac{7.982}{r}$$

$$(d_{xy}d_{xy} \mid d_{x^2-y^2}d_{x^2-y^2}) = \frac{8.822}{r}$$

$$(d_{z^2}d_{z^2} \mid d_{zx}d_{zx}) = \frac{8.552}{r}$$

$$(d_{z^2}d_{z^2} \mid d_{xy}d_{xy}) = (d_{z^2}d_{z^2} \mid d_{x^2-y^2}d_{x^2-y^2}) = \frac{7.740}{r}$$

$$(d_{zx}d_{zx} \mid d_{x^2-y^2}d_{x^2-y^2}) = \frac{8.011}{r}$$

Note added in proof

With regard to a remark of Professor Jørgensen about the low values assigned to the fractional charges on the central atom, we wish to point out that our values are larger than +2[8]. Jørgensen's observation, which is formally correct, probably arises from some ambiguous use[8] of the terms "oxidation state" and "fractional charge".

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