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CNDO-Molecular Orbital Calculations of MnO_4^- and MnF_6^{4-}

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CNDO-MO calculations have been made for the tetrahedral MnO_4^- ion and the octahedral MnF_6^{4-} ion using a transferable parameter scheme for manganese. The results show that the orbital levels for both complex ions are consistent with the ligand field approach.

In recent years molecular orbital calculations on transition metal complexes have been reasonably successful in obtaining orbital levels, ionisation energies and in particular in reproducing the crystal field parameter $10\,Dq$ [1]. While the majority of these treatments have been isolated calculations for an individual complex ion, only a relatively small number of calculations have been attempted for a series of molecules using the same set of approximations [2–4]. Recent CNDO calculations on some tetrahedral transition metal complex ions [5, 6] have suggested that the central metal orbitals are considerably involved in the bonding molecular orbitals and in addition the ordering of the virtual orbitals was found to depend on the central metal in the complex ion. Both of these findings are opposed to traditional ligand field theory, where the highest occupied and /or the lowest vacant orbitals are assumed to be mainly "*d*" in character, with the *d*-orbitals split in T_d symmetry the *e* level lying below the t_2 level, and the reverse applying under O_h symmetry.

We report here a preliminary investigation into a systematic application of molecular orbital calculations to transition metal complexes using the CNDO method. The open-shell Hamiltonian matrix elements for molecules involving a transitional element which still retain all the approximations of the original CNDO method as outlined by Pople *et al.* [7] are [8]

$$\begin{aligned}
F^{\alpha}_{\mu\mu}(2s2s) = & -\tfrac{1}{2}(I_{2s}+A_{2s}) - (Z_{\mathrm{A}}-\tfrac{1}{2})\,\gamma^{0}_{2s2s} - (Z_{\mathrm{B}}-2)\,\gamma'_{2s3s} \\
& -2\gamma'_{2s4s} + [P_{\mathrm{AA}}(S) - P^{\alpha}_{\mu\mu}]\,\gamma^{0}_{2s2s} - \sum_{\mathrm{B}\neq\mathrm{A}} Z_{\mathrm{B}}\gamma'_{2s2s} \\
& + \sum_{\mathrm{B}\neq\mathrm{A}} [P_{\mathrm{BB}}(S)\,\gamma'_{2sns}] + P_{\mathrm{BB}}(D)\,\gamma'_{2s3s}\,, \\
F^{\alpha}_{\mu\mu}(4s4s) = & -\tfrac{1}{2}(I_{4s}+A_{4s}) - \gamma^{0}_{4s4s} - (Z_{\mathrm{A}}-\tfrac{3}{2})\,\gamma^{0}_{3s4s} + P_{\mathrm{AA}}(D)\,\gamma^{0}_{3s4s} \\
& + [P_{\mathrm{AA}}(S) - P^{\alpha}_{\mu\mu}]\,\gamma^{0}_{4s4s} + \sum_{\mathrm{B}\neq\mathrm{A}} [P_{\mathrm{BB}}(S) - Z_{\mathrm{B}}]\,\gamma'_{2s4s}\,, \\
F^{\alpha}_{\mu\mu}(3d3d) = & -\tfrac{1}{2}(I_{3d}+A_{3d}) + [P_{\mathrm{AA}}(D) - P^{\alpha}_{\mu\mu} - (Z_{\mathrm{A}}-\tfrac{5}{2})]\,\gamma^{0}_{3s3s} \\
& + [P_{\mathrm{AA}}(S) - 2]\,\gamma^{0}_{3s4s} + \sum_{\mathrm{B}\neq\mathrm{A}} [P_{\mathrm{BB}}(S) - Z_{\mathrm{B}}]\,\gamma'_{2s3s}
\end{aligned}$$

where orbital μ is on centre A, and B is any other centre. γ^0 and γ' represent one- and two-centre electron interaction integrals respectively. The other quantities are defined in Ref. [7].

The off-diagonal matrix elements become:

$$F^{\alpha}_{\mu\nu}(SS) = \beta^0_{AB} S_{\mu\nu} - P^{\alpha}_{\mu\nu}\gamma'(SS),$$

$$F^{\alpha}_{\mu\nu}(SD) = \beta^0_{AB} S_{\mu\nu} - P^{\alpha}_{\mu\nu}\gamma'(SD),$$

$$F^{\alpha}_{\mu\nu}(DD) = \beta^0_{AB} S_{\mu\nu} - P^{\alpha}_{\mu\nu}\gamma'(DD).$$

SS refers to an off-diagonal element between any two *s*-type orbitals. *SD* refers to an element where one orbital is *s*-type and the other one is *d*-type; and *DD* represents an element between any two *d*-orbitals.

In the Pople CNDO scheme an empirical parameter β^0_A, which is used in the evaluation of the off-diagonal matrix elements, is chosen for a given atom by comparison of the CNDO eigen-functions and eigen-values with ab initio results. This parameter is retained for calculations on all molecules involving that particular atom, and we have used Pople's [7] β^0 values for hydrogen and the first row elements. Two parameters are used for the transitional element, β^0_{3d} and β^0_{4s}, which have been determined previously [8] by comparison with ab initio calculations on transition metal monoxides [9–11]. In the calculations reported here a single exponential basis set has been used for the transitional element, with exponents which have been fitted to reproduce overlap integrals [12] using Watson's [13] extended basis functions. The results for a tetrahedral and an octahedral complex ion of manganese MnO_4^- and MnF_6^{4-} are given below.

The CNDO eigen-functions and eigen-values are given in Tables 1 and 2 and two features are immediately apparent. Firstly the ordering of the levels for both the tetrahedral and the octahedral complex ions is exactly that predicted by traditional ligand field theory, with the central metal 3*d*, 4*s* and 4*p* molecular orbitals lying at highest energy with $2e < 4t_2 < 3a_1 < 5t_2$ for MnO_4^- and $t_{2g} < e_g < a_{1g} < t_{1u}$ for MnF_6^{4-}; secondly the results suggest that for the tetrahedral complex the central metal orbitals are not as heavily engaged in the bonding orbitals as previous workers have found [5] and for this reason the highest energy orbitals are primarily "metal" in character. Table 1 clearly shows that the $3a_1$ and $5t_2$ orbitals are predominantly 4*s* and 4*p* in character respectively, while $4t_2$ is essentially 3*d*, which agrees closely with the findings of Oleari *et al.* [4]. CNDO calculations on some tetrahedral transition metal complexes [5, 6] have indicated that the highest energy orbitals are not necessarily "metal" in character although the symmetries of these do correspond to e, t_2, a_1 and t_2.

The eigen-functions for the octahedral complex ion MnF_6^{4-} show considerably less involvement of the metal orbitals in the bonding molecular orbitals, however this result is perfectly reasonable since this complex is expected to be substantially less covalent than the tetrahedral MnO_4^- ion. The orbital levels parallel those reported by Basch *et al.* [2] for FeF_6^{3-}. The final atom charges obtained for manganese are +2.09 for $Mn^{VII}O_4^-$ and +0.17 for MnF_6^{4-}.

Table 1. *Molecular orbitals for permanganate ion* MnO_4^- *(with* Mn–O = 1.559 Å*)*

	Eigen value	Eigen functions					
	a.u.	Metal orbitals			Ligand orbitals		
		$3d$	$4s$	$4p$	$2s$	$2p_\sigma$	$2p_\pi$
$1a_1$	−1.33868		0.4631		0.8852	0.0405	
$1t_2$	−1.201222	0.1376		−0.4136	0.8900	−0.1017	−0.1037
$2t_2$	−0.413952	0.4278		0.2645	0.1963	0.7185	0.5321
$1e$	−0.372961	0.4755					0.8797
$3t_2$	−0.355550	0.4072		0.1368	−0.1445	0.2588	−0.5711
$2a_1$	−0.328756		0.2194		−0.1588	0.9627	
$1t_1$	−0.259925						1.0000
$2e$	0.487406	0.8797					−0.4755
$4t_2$	0.540254	0.7504		−0.3725	−0.0064	−0.5412	−0.0735
$3a_1$	0.648557		0.8587		−0.4368	−0.2698	
$5t_2$	0.765214	0.3407		0.7756	−0.3844	−0.0076	−0.3660

Table 2. *Molecular orbitals for hexafluoromanganate(II) ion* $[MnF_6]^{4-}$ *(with* Mn–F = 2.12 Å*)*

	Eigen value	Eigen functions (α-spin)					
	a.u.	Metal orbitals			Ligand orbitals		
		$3d$	$4s$	$4p$	$2s$	$2p_\sigma$	$2p_\pi$
$1a_{1g}$	−0.633370		0.3729		0.9264	0.0522	
$1t_{1u}$	−0.598209			0.3363	0.9392	0.0328	0.0608
$1e_g$	−0.430678	0.0860			0.9949	−0.0526	
$2t_{1u}$	0.240435			−0.2948	0.1718	0.6638	0.6652
$2a_{1g}$	0.257750		0.3163		0.1798	0.9315	
$2e_g$	0.295954	0.5020			0.0024	0.8649	
$1t_{2g}$	0.304456	0.1960					0.9806
$1t_{2u}$	0.312860						1.000
$1t_{1g}$	0.315275						1.000
$3t_{1u}$	0.331192			−0.0764	−0.0047	0.6876	−0.7218
$2t_{2g}$	0.488211	0.9806					−0.1960
$3e_g$	0.553254	0.8606			−0.1006	−0.4992	
$3a_{1g}$	1.178604		0.8723		−0.3309	−0.3601	
$4t_{1u}$	1.257663			0.8911	−0.2972	−0.2912	−0.1810

Calculations run on the hypothetical ion $Mn^{II}O_4^{6-}$ using a metal-oxygen bond length of 1.95 Å produced an orbital picture identical to that in MnO_4^- with five unpaired electrons located in the $2e$ and $4t_2$ molecular orbitals.

In view of the difference in ligands, geometries and oxidation states of the central metal ion, the present CNDO method appears to give a satisfactory prediction of electronic ground states and orbital levels, which are compatible with traditional ligand field theory.

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