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Molecular Orbital Calculations on Transition Element Compounds

II. CNDO Type Studies of Permanganate and Chromate

R. D. Brown, B. H. James*, T. J. V. McQuade, and M. F. O'Dwyer
Department of Chemistry, Monash University, Clayton, Victoria, Australia 3168

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A series of SCFMO calculations on the ground states of MnO_4^- and CrO_4^{--}, and a corresponding series of configuration interaction calculations based on these ground state wave functions and all singly excited configuration, are reported. The molecular orbital calculations included all 24 valence electrons (ligand $2s$ electrons being regarded as part of the core) and included CNDO-type approximations. The various calculations illustrate the effect of different parameterizations upon the numerical results obtained and again emphasise the dangers of placing any quantitative reliance upon a single calculation. Predicted energies of excited states are sensitive to the value of the averaged one-centre electron repulsion integral for the metal atom orbitals, but not so sensitive to the value of the average one-centre nuclear attraction integral. The evaluation of the core Hamiltonian in a full overlap basis and transformation of the matrix to an orthogonal basis proves better than the approximate direct evaluation on an orthogonal basis. The use of scaling factors for two-centre integrals to reproduce most nearly the values obtained from Hartree-Fock orbitals does not lead to the optimum calculations. It is emphasized that the usual CNDO approximation of using averaged values integrals for all valence orbitals on a given centre produces "over-occupation" of $3d$ orbitals and "under-occupation" of $4s$ and $4p$ orbitals on the metal atom. By assigning the first three transitions in the spectrum of MnO_4^- to $2e \leftarrow t_1$, $2e \leftarrow 2t_2$ and $3t_2 \leftarrow t_1$ respectively (corresponding to ${}^1T_2 \leftarrow {}^1A_1$ in each case, the indicated excitations making the main contributions to the configuration-interaction functions) it proves possible to account for the observed magnetic circular dichroism of these transitions and to account for the observed oscillator strengths of the bands. This qualitative order of energies of the lowest excited states is obtained for a rather wide range of parameter values in the CNDO scheme. For CrO_4^{--} a similar assignment of the spectrum emerges but it seems particularly from the magnetic circular dichroism data, that the second and third transitions are superimposed.

Eine Reihe von SCFMO-Rechnungen für die Grundzustände von MnO_4^- und CrO_4^{--} sowie die Resultate der entsprechenden Konfigurationswechselwirkung von Grundzustand und allen einfach angeregten Konfigurationen werden mitgeteilt. Einbezogen in die CNDO-artigen Näherungsrechnungen werden alle 24 Valenzelektronen (die $2s$-Elektronen der Liganden zum Rumpf gerechnet). Die Rechnungen illustrieren den Effekt der verschiedenen Parameterisierung auf die Resultate und weisen erneut darauf hin, wie problematisch es ist, sich auf *eine* bestimmte Rechnung allein zu verlassen. Die Energien der angeregten Zustände hängen stark vom Durchschnittswert der Einzentren-Elektronenwechselwirkungsintegrale für die Metall-AO's, dagegen nicht so stark vom Durchschnittswert der Einzentren-Kernwechselwirkungsintegrale ab. Die Berechnung des Rumpf-Hamiltonoperators mit voller Einbeziehung der Überlappung und Übergang zu orthogonalierten Funktionen erweist sich als besser als die näherungsweise direkte Berechnung bei angenommener Orthogonalität. Der Verwendung von scaling-Faktoren für Zweizentrenintegrale zur Annäherung an Werte für Hartree-Fock Orbitale führen nicht zu den optimalen Ergebnissen. Es wird betont, daß die üblichen CNDO-Näherungen (Durchschnittswerte für Integrale für alle Valenzorbitale) zu „Überbesetzung" von $3d$-Zuständen und „Unterbesetzung" von $4s$ und $4p$ Zuständen führt. Weist man den ersten drei Banden im Spektrum von MnO_4^- die Übergänge $2e \leftarrow t_1$, $2e \leftarrow 2t_2$ und $3t_2 \leftarrow t_1$ zu (dies entspricht

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* Commonwealth of Australia, Department of Supply, Scientific Officer.

in jedem Fall ${}^1T_2 \leftarrow {}^1A_1$, die angezeigten Anregungen geben lediglich den Hauptanteil wieder), läßt sich zeigen, daß der beobachtete magnetische zirkulare Dichroismus dieser Übergänge und die beobachteten Oszillatorstärken der Bänder erklärt werden können. Die Reihenfolge der Energien der niedrigsten angeregten Zustände bleibt für einen ziemlich großen Bereich der CNDO-Parameterwerte unverändert. Für CrO_4^{--} ergibt sich eine ähnliche Zuweisung des Spektrums; allerdings deuten besonders die Werte für den magnetischen zirkularen Dichroismus darauf hin, daß der zweite und dritte Übergang einander überlagern.

Série de calculs SCFMO sur les états fondamentaux de MnO_4^- et CrO_4^{--} et de calculs d'interaction de configurations incluant toutes les configurations monoexcitées. Les calculs ont été effectués sur tous les 24 électrons de valence (les électrons $2s$ du ligand étant considérés comme faisant partie du coeur) en employant des approximations de type CNDO. Les différents calculs illustrent l'effet de la paramétrisation sur les résultats numériques obtenus, soulignant à nouveau le danger de se fier quantitativement à un seul calcul. Les énergies prédites pour les états excités sont sensibles à la valeur moyenne de l'intégrale de répulsion électronique monocentrique pour les orbitales de l'atome métallique, tout en étant moins sensibles à la valeur moyenne de l'intégrale de l'attraction nucléaire monocentrique. L'évaluation de l'hamiltonien de coeur dans une base avec recouvrement et la représentation de cette matrice dans une base orthogonale s'avère meilleure que l'évaluation directe approchée dans une base orthogonale. L'emploi de facteurs de réduction pour les intégrales bicentriques afin de reproduire au mieux les valeurs obtenues à partir des orbitales de Hartree-Fock ne conduit pas aux meilleurs calculs. On souligne que l'approximation CNDO habituelle employant des valeurs moyennes des intégrales pour tous les électrons de valence d'un centre produit une «sur-occupation» des orbitales $3d$ et une «sous occupation» des orbitales $4s$ et $4p$ sur l'atome métallique. Si l'on assigne les trois premières transitions du spectre de MnO_4^- à $2e \leftarrow t_1$, $2e \leftarrow 2t_2$ et $3t_2 \leftarrow t_1$ respectivement (ce qui correspond dans chaque cas à ${}^1T_2 \leftarrow {}^1A_1$, les excitations indiquées étant celles qui ont le plus grand poids dans la fonction d'interaction de configuration), on peut rendre compte du dichroïsme circulaire magnétique observé pour ces transitions ainsi que des forces oscillatrices observées pour ces bandes. L'ordre qualitatif des énergies des états excités les plus bas est obtenu pour un grand éventail de valeurs des paramètres en méthode CNDO. Pour CrO_4^{--} une assignation similaire du spectre apparaît, mais il semble en particulier à partir des données du dichroïsme circulaire magnétique que la seconde et la troisième transition sont superposées.

1. Introduction

The present paper seeks an interpretation of the ultraviolet spectra of MnO_4^- and CrO_4^{--} based on a series of CNDO type calculations, general details of the method having been presented in Part I. There have been many previous studies of the spectra of these ions [e.g. 1–10] and the deficiencies of these have been detailed previously [7, 8]. It suffices to point out that, apart from our preliminary work [7], only Oleari *et al.* [6] attempted to use proper spectroscopic configuration functions. In the most recent work Dahl and Johansen have again not used such functions in spite of the clear illustration in our previous paper of how unsatisfactory is the use of simple orbital excitation energies. From Tables 3, 4, and 5 of [7] it can be seen that the predicted energy of the "$2e \leftarrow t_1$", ${}^1T_2 \leftarrow {}^1A_1$ transition is 11.31 eV or 5.76 eV or 3.50 eV according as orbital energies, spectroscopic configuration function energies or configuration interaction function energies are used! Dahl and Johansen decided not to include the various two-electron integrals that represent the splitting of various spectroscopic states stemming from a given configuration, considering that such integrals would be much smaller than the molecular orbital coulomb integral J_{ik} that they did include. However Fig. 2 of Ref. [7] illustrates that such splittings can be so substantial that they cannot be ignored.

Recent studies [9, 10] have shown how the choice of basis functions to represent atomic orbitals can affect the calculated energies of molecular orbitals. The present work illustrated this sensitivity by varying the scaling factors for basic integrals, which is rather analogous to varying the atomic orbital functions on which the integrals are found.

We have not examined the dependence of the calculations on the value adopted for the metal-oxygen distance. Presumably there is a slight dependence of the kind found in Dahl and Johansens' calculations [9].

2. Method of Calculation

The CNDO LCAO MO SCF method is described in Part I. The central atom 3*d*, 4*s*, and 4*p* atomic orbitals and the oxygen 2*p* atomic orbitals have been included in the basis set. We have considered the oxygen 2*s* atomic orbitals to be part of the effective oxygen cores[1]. The molecules have been assumed to be perfect tetrahedra with the Mn–O and Cr–O bond lengths 1.629 Å [13] and 1.615 Å [14] respectively. The axes system used is illustrated in Fig. 1 and the corresponding symmetry-adapted molecular orbital basis functions are given in Table 1.

In applying the CNDO method to transition metal complexes the use of integrals involving *s* orbitals only as an average [15] is now a poor approximation. It is necessary to use an actual average, weighted for the numbers of each integral that arises. Thus, the nuclear attraction integrals V_A^{AA}, V_A^{BB}, and V_B^{AA} and electron repulsion integrals γ_A and γ_{AB} have to be determined as weighted averages. The appropriate scaling factors can be determined by the method described in Part I.

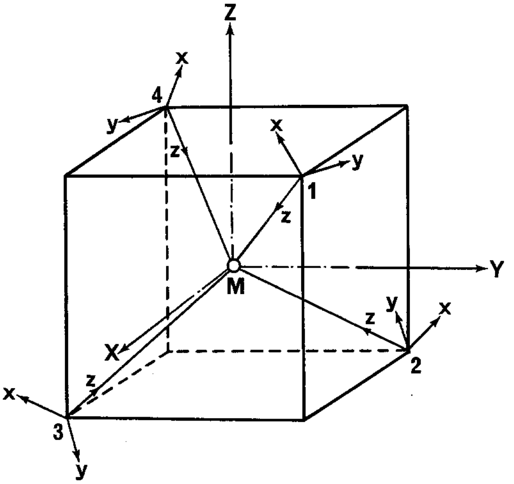

Fig. 1

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[1] Best, [12] from an analysis of the metal KX-ray spectra of the permanganate, chromate and vandate ions, has concluded that the central atom 3*p* atomic orbitals and the oxygen 2*s* atomic orbitals are not appreciably involved in bonding.

Table 1. *Molecular orbital basis functions for molecules belonging to the T_d point group*

Irreducible representation	Row	Central atom orbitals	
a_1		s	$\frac{1}{2}(p_{z1}+p_{z2}+p_{z3}+p_{z4})$
e	1	$d_{x^2-y^2}$	$\frac{1}{2}(-p_{y1}+p_{y2}+p_{y3}-p_{y4})$
	2	d_{z^2}	$\frac{1}{2}(p_{x1}-p_{x2}-p_{x3}+p_{x4})$
t_2	1	p_x, d_{yz}	$\frac{1}{2}(p_{z1}-p_{z2}+p_{z3}-p_{z4})$ $\frac{1}{4}(-p_{x1}-p_{x2}+p_{x3}+p_{x4}-\sqrt{3}(p_{y1}+p_{y2}-p_{y3}-p_{y4}))$
	2	p_y, d_{xz}	$\frac{1}{2}(p_{z1}+p_{z2}-p_{z3}-p_{z4})$ $\frac{1}{4}(-p_{x1}+p_{x2}-p_{x3}+p_{x4}+\sqrt{3}(p_{y1}-p_{y2}+p_{y3}-p_{y4}))$
	3	p_z, d_{xy}	$\frac{1}{2}(p_{z1}-p_{z2}-p_{z3}+p_{z4})$ $\frac{1}{2}(p_{x1}+p_{x2}+p_{x3}+p_{x4})$
t_1	1		$\frac{1}{4}(+p_{y1}+p_{y2}-p_{y3}-p_{y4}-\sqrt{3}(p_{x1}+p_{x2}-p_{x3}-p_{x4}))$
	2		$\frac{1}{4}(p_{y1}-p_{y2}+p_{y3}-p_{y4}+\sqrt{3}(p_{x1}-p_{x2}+p_{x3}-p_{x4}))$
	3		$\frac{1}{2}(-p_{y1}-p_{y2}-p_{y3}-p_{y4})$

To illustrate the effects that variations in the parameter scheme can have, the results of nine calculations on the permanganate ion, labelled CNDO 1 to CNDO 9 will be presented and discussed. CNDO 1 represents the most acceptable results that were obtained. The parameter schemes for CNDO 2 to CNDO 9 differ systematically from that for CNDO 1 to test the sensitivity of the results to parameter variations.

Analogous calculations were carried out on the chromate ion. The effects of variations in parameters mirrored those found for the corresponding permanganate ion calculation. Accordingly, only the chromate calculation that produced the most acceptable results is presented and discussed.

The CNDO 1 parameter scheme can be summarised as follows [11]. All integrals, with the exception of valence state ionisation potentials, were evaluated on a purely theoretical basis using single Slater-type wave-functions with Burns exponents. The manganese and oxygen weighted average one-centre repulsion integral scaling factors were 0.94 and 0.79 ("$I-A$" value) respectively. The Mn–O and O–O weighted average two-centre repulsion integral scaling factors were 0.97 and 1.00 respectively. All one-centre nuclear attraction integral scaling factors were 1.00. The full overlap core Hamiltonian matrix was evaluated and then transformed into a Löwdin basis.

The chromate calculation parameter scheme was analogous to the permanganate CNDO 1 scheme except that the value of the chromium weighted average one-centre repulsion integral scaling factor was 0.86. The fact that the most acceptable results for the permanganate and chromate ions was obtained with the same basic parameter scheme supports the hope that this scheme may be general for CNDO calculations on transition metal complexes.

Details of how the parameter schemes for CNDO 2 to CNDO 9 differ from that for CNDO 1 are given in Sect. 3.

The configuration interaction calculations involved 108 singly excited configurations which decompose under T_d into 15 T_2 states, 12 T_1, 9 E, 6 A_1, and 3 A_2 states.

3. Results and Discussion

The ground state results for the CNDO 1 calculation are presented in Fig. 2 and Tables 2 and 3. The atomic charges and orbital electron populations were determined from a Mulliken population analysis [16] in which each overlap population was equally divided between the two basis functions involved.

The predicted charge on the manganese atom of +0.167 appears to be rather low when compared with the experimental estimate of +1.28 [17]. The experimental value, obtained from the metal K X-ray spectrum, is probably subject to a large uncertainty. However, we feel that the predicted charge is too low and that this is a natural consequence of the CNDO method.

The following are typical values for manganese one-centre Coulomb repulsion integrals involved in determining the weighted average value, γ_A.

$$\begin{aligned}(4s\,4s\,|\,4s\,4s) &= 7.927\ \text{eV}\,,\\ (4p\,4p\,|\,4p\,4p) &= 5.063\ \text{eV}\,,\\ (3d\,3d\,|\,3d\,3d) &= 21.067\ \text{eV}\,,\\ \gamma_A &= 14.272\ \text{eV}\,.\end{aligned}$$

The lowering of a one-centre repulsion integral tends to cause electrons to occupy the orbitals concerned and vica versa. Hence it is to be expected that in a CNDO calculation the $3d$ orbitals will be "over-occupied" and the $4s$ and $4p$ orbitals "under-occupied". Best [12] has shown that the $4p$ orbitals are not involved to any appreciable extent in bonding so that the $3d$ orbitals must play the major role. Accordingly, there will be a greater flow of electrons into the $3d$ orbitals than there will be out of the $4s$ and $4p$ orbitals with the resultant effect of underestimating the charge on the manganese atom. As will be shown in Part III, MCZDO calculations, where the distinctions between one-centre integrals are maintained, predict charges consistently higher than those of CNDO calculations. The low occupation of 0.02 electrons in the manganese $4p$ orbitals agrees with the predictions of Best but because the $4p$ orbitals are probably "under-occupied" little significance can be placed in the result. Similarly with the low occupation of 0.10 electrons in the manganese $4s$ orbitals.

The form of the CNDO 1 t_2 molecular orbitals do not agree well with the predictions of Best. The highest energy filled t_2 molecular orbitals are composed mainly of oxygen atomic orbitals but these are $2p_\pi(2p_x, 2p_y)$ and not $2p_\sigma(2p_z)$. The lowest energy unfilled t_2 molecular orbitals are not composed principally of manganese $4p$ orbitals but are more like those predicted by Scharland [18] who, on the basis of an analysis of the e.s.r. spectrum of the manganate ion, predicted that they were spread over the whole molecule. The unfilled e molecular orbitals are in harmony with Scharland's prediction in that they are somewhat localised on the manganese atom.

The excited state results for the CNDO 1 calculation are given in Tables 4 to 6. On the basis of intensity calculations and a theoretical analysis of the magnetic circular dichroism data we have assigned all bands in the visible/near ultraviolet spectrum to symmetry-allowed ${}^1T_2 \leftarrow {}^1A_1$ transitions.

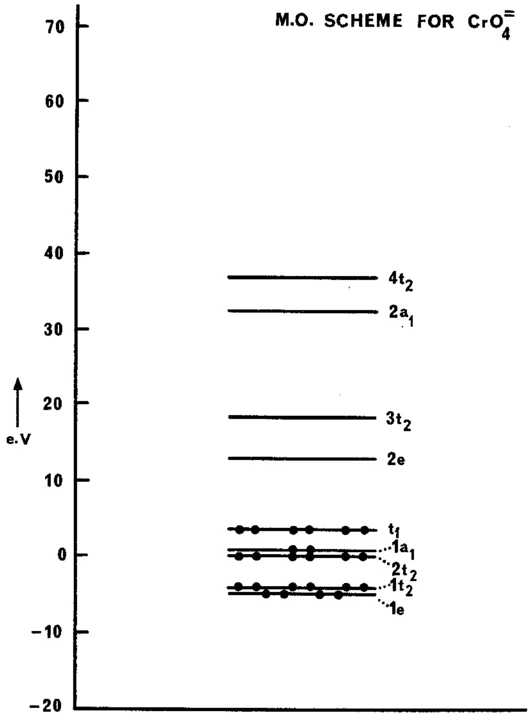

Fig. 2

Table 2. *The permanganate ion* VESCFCNDO 1

Atomic charges		Manganese orbital electron populations		
Manganese	Oxygen	3*d*	4*s*	4*p*
+0.167	−0.292	6.71	0.10	0.02

Table 3. *Molecular orbitals of the permanganate ion* VESCFCNDO 1

Symmetry	Eigenvalue eV	Eigenvectors[a] Mn 3*d*	Mn 4*s*	Mn 4*p*	O $2p_\sigma$	O $2p_\pi$
$4t_2$	62.5007	−0.0278		0.9863	0.0536	0.1536
$2a_1$	42.2644		−0.9647		0.2634	
$3t_2$	11.7451	−0.4895		−0.1028	0.8172	0.2860
$2e$	5.5770	−0.6830				0.7301
t_1	− 3.7255					−1.0000
$1a_1$	− 4.4208		−0.2635		−0.9646	
$2t_2$	− 5.3392	−0.1083		−0.1223	−0.3962	0.9032
$1e$	−10.6490	0.7304				0.6830
$1t_2$	−11.1946	−0.8648		0.0418	−0.4146	−0.2800

[a] These are symmetry adapted eigenvectors for the symmetry orbitals of Table 1.

Table 4. VESCFCICNDO 1 *calculation of lowest energy singlet states of the permanganate ion*

Energy			% Contributions from different configurations[a]							
State	Calculated eV	Experimental eV [21]	I	II	III	IV	V	VI	VII	others
$^1T_1$	1.48		99	0	0	0	0	0	0	1
^1E	2.02		0	0	0	0	0	100	0	0
$^1T_2$	2.16	2.27	69	29	0	0	0	0	0	2
$^1T_1$	2.99		0	99	1	0	0	0	0	0
$^1T_2$	4.13	3.47[b]	18	55	0	3	6	0	0	18
^1E	5.09		0	0	70	0	29	0	0	1
$^1T_2$	5.83	3.99	0	2	81	2	11	0	0	4
$^1T_1$	6.84		0	0	49	0	45	0	0	6
^1E	7.11		0	0	0	0	2	0	98	0
$^1A_2$	7.15		0	0	99	0	0	0	1	0
$^1T_1$	7.18		0	0	0	99	1	0	0	0
$^1T_2$	7.29	5.45[b]	0	1	2	94	1	0	0	2

[a] The appropriate spectroscopic state arising from the following one-electron orbital promotions: I $2e \leftarrow t_1$, II $2e \leftarrow 2t_2$, III $3t_2 \leftarrow t_1$, IV $2e \leftarrow 1t_2$, V $3t_2 \leftarrow 2t_2$, VI $2e \leftarrow 1a_1$, VII $2e \leftarrow 1e$.

[b] Shoulder.

Table 5. VESCFCICNDO 1 *calculation of the lowest* $^1T_2$ *excited states of the permanganate ion*

Spectroscopic state	Assignment	Calculated energy eV	Experimental energy eV	Calculated Faraday (A/D) parameter	Experimental Faraday (A/D parameter [22]
$^1T_2$	$2e \leftarrow t_1$	2.16	2.27	−0.139	−0.09
$^1T_2$	$2e \leftarrow 2t_2$	4.13	3.47	−0.001	≈0
$^1T_2$	$3t_2 \leftarrow t_1$	5.83	3.99	0.212	0.4 − 0.7
$^1T_2$	$2e \leftarrow 1t_2$	7.29	5.45	0.159	—

Table 6. VESCFCICNDO 1 *calculation of intensities of lowest energy symmetry-allowed transitions* ($^1T_2 \leftarrow {}^1A_1$) *of the permanganate ion*

Transition energy eV		Oscillator strength		
Experimental	Calculated	Calculated		Experimental [23]
		Dipole length operator	Dipole velocity operator	
2.27	2.16	0.009	0.231	0.032
3.47	4.13	0.063	0.038	0.021
3.99	5.83	0.018	0.020	0.035
5.45	7.29	0.016	0.102	0.04–0.07

The theoretical oscillator strengths of the four lowest energy ${}^1T_2 \leftarrow {}^1A_1$ transitions correlate quite well with the experimental values for the four bands in the observed spectrum. Where the values derived from the dipole length and dipole velocity operator differ significantly they bracket the experimental value, the dipole length result being the smaller. There are no intense ${}^1T_2 \leftarrow {}^1A_1$ transitions predicted even in the near vacumn ultra-violet region. Accordingly, if any bands in the visible/near ultra-violet spectrum are to be assigned to symmetry-forbidden or spin-forbidden transitions then these transitions must be very strongly coupled to the symmetry-allowed transitions.

The K values (see Eq. (33) of [11]) for the predicted lowest energy symmetry-forbidden transition coupling to the four lowest energy symmetry-allowed transitions are given in Table 7. We feel that it is more realistic to use experimental rather than theoretical energies to calculate the final oscillator strength ratios. The energy term $\varepsilon_B^0/\varepsilon_C^0(\Delta\varepsilon_{BC}^0)^2$ has a maximum value from the experimental permanganate spectrum of 6.5×10^{-8}. This occurs when ε_B^0 is 3.99 eV and ε_C^0 is 3.47 eV. With this factor and the K values from Table 7 only three of the oscillator strength ratios are over 6% and none are over 15%. With the other possible energy terms the percentages are of course lower. As discussed in Part I we feel that these values will be an overestimate of the degree of coupling.

The coupling factor for spin-forbidden transitions is $\xi/\Delta\varepsilon_{ST}$. As the spin-orbit coupling constant, ξ is of the order of 0.01 eV and the singlet-triplet energy difference, $\Delta\varepsilon_{ST}$ is unlikely to be less than 0.5 eV this factor is of the order of 0.02. It would appear unlikely then that any of the bands in the visible/near ultra-violet spectrum are due to symmetry-forbidden or spin-forbidden transitions.

The differences between the experimental oscillator strengths of the four bands is too small to verify from intensity calculations the assigned orbital promotions that contribute most to the ${}^1T_2 \leftarrow {}^1A_1$ transitions. There are however, differences in magnitude and sign between the experimental magnetic circular dichroism Faraday A/D parameters for the bands. Calculation of the Faraday A/D parameters (see Part I) therefore provides a sensitive test of the spectroscopic configuration functions involved in the transitions.

Table 7. *K values for the permanganate ion* CNDO 1

Orbital promotion	Transition	K (cm^2)			
		I[a]	II	III	IV
$2e \leftarrow t_1$	${}^1T_1 \leftarrow {}^1A_1$	2.81×10^5	4.03×10^5	2.21×10^2	1.27×10^5
$2e \leftarrow 2t_2$	${}^1T_1 \leftarrow {}^1A_1$	4.03×10^5	1.75×10^5	—	8.28×10^5
$3t_2 \leftarrow t_1$	${}^1T_1 \leftarrow {}^1A_1$	6.74×10^2	—	1.03×10^5	—
$3t_2 \leftarrow 2t_2$	${}^1T_1 \leftarrow {}^1A_1$	—	2.24×10^2	4.03×10^5	—
$2e \leftarrow 1t_2$	${}^1T_1 \leftarrow {}^1A_1$	1.27×10^5	8.28×10^5	—	4.29×10^5
$2e \leftarrow 1a_1$	${}^1E \leftarrow {}^1A_1$	—	7.84×10^5	—	2.24×10^6
$3t_2 \leftarrow \mathrm{t}_1$	${}^1E \leftarrow {}^1A_1$	—	—	3.11×10^5	—
$2e \leftarrow 1e$	${}^1E \leftarrow {}^1A_1$	9.22×10^5	1.04×10^6	—	2.21×10^5
$2e \leftarrow 1e$	${}^1A_1 \leftarrow {}^1A_1$	1.84×10^6	2.07×10^6	—	4.43×10^5

[a] I When coupled with the ${}^1T_2 \leftarrow {}^1A_1$ transition arising from the $2e \leftarrow t_1$ orbital promotion.
II ${}^1T_2 \leftarrow {}^1A_1$ transition arising from the $2e \leftarrow 2t_2$ orbital promotion.
III ${}^1T_2 \leftarrow {}^1A_1$ transition arising from $3t_2 \leftarrow t_1$ orbital promotion.
IV ${}^1T_2 \leftarrow {}^1A_1$ transition arising from $2e \leftarrow 1t_2$ orbital promotion.

The theoretical Faraday A/D parameters for the three lowest energy ${}^1T_2 \leftarrow {}^1A_1$ transitions correlate well with the experimentally observed values. The agreement is all the more encouraging since calculated Faraday A/D parameters obtained using the Viste and Gray [4] "extended" Hückel wave-functions and the Brown, James, O'Dwyer and Roby CNDO wave-functions [7] are in poor agreement with the experimental values.

Results obtained for the CNDO 2 to CNDO 9 calculations are given in Tables 8 to 10.

CNDO 1 and CNDO 3 illustrate the sensitivity of the predicted atomic charges and transitions energies to small changes in the manganese weighted averaged one-centre repulsion integral scaling factor. In CNDO 2 this factor was 1.00 and in CNDO 3 0.90 (0.94 for CNDO 1).

Table 8. VESCFCNDO *eigenvalues for the permanganate ion*

CNDO 1		CNDO 2		CNDO 3	
MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV
$4t_2$	62.5007	$4t_2$	67.1256	$4t_2$	60.4915
$2a_1$	42.2644	$2a_1$	48.4991	$2a_1$	39.3899
$3t_2$	11.7451	$3t_2$	14.7264	$3t_2$	10.9082
$2e$	5.5770	$2e$	9.7343	$2e$	4.2274
t_1	− 3.7255	t_1	− 1.6630	t_1	− 4.1489
$1a_1$	− 4.4208	$1a_1$	− 2.2555	$1a_1$	− 4.9600
$2t_2$	− 5.3392	$2t_2$	− 3.1245	$2t_2$	− 5.8643
$1e$	−10.6490	$1e$	− 7.3317	$1e$	−11.9705
$1t_2$	−11.1946	$1t_2$	− 8.0617	$1t_2$	−12.3527
CNDO 4		CNDO 5		CNDO 6	
MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV
$4t_2$	59.0913	$4t_2$	62.9181	$4t_2$	64.9841
$2a_1$	38.9998	$2a_1$	42.8977	$2a_1$	45.3338
$3t_2$	9.6424	$3t_2$	12.4635	$3t_2$	13.8645
$2e$	4.8428	$2e$	5.9215	$2e$	8.0458
t_1	− 3.9963	t_1	− 3.5120	t_1	− 1.9498
$2t_2$	− 6.8855	$1a_1$	− 5.0622	$1a_1$	− 2.6686
$1a_1$	− 7.1905	$2t_2$	− 5.4912	$2t_2$	− 3.5228
$1e$	−11.3616	$1e$	−11.0449	$1e$	− 8.5386
$1t_2$	−12.2355	$1t_2$	−11.5646	$1t_2$	− 9.0753
CNDO 7		CNDO 8		CNDO 9	
MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV
$4t_2$	65.6556	$4t_2$	63.6239	$4t_2$	69.5571
$2a_1$	41.6476	$2a_1$	38.9931	$2a_1$	44.1108
$3t_2$	16.0918	$3t_2$	15.2041	$3t_2$	22.3476
$2e$	10.7551	$2e$	9.4252	$2e$	15.5590
t_1	− 2.0789	t_1	− 2.3834	t_1	4.7889
$2t_2$	− 7.0112	$2t_2$	− 7.4325	$2t_2$	− 0.1758
$1a_1$	− 8.9316	$1a_1$	− 9.2830	$1a_1$	− 1.2212
$1t_2$	−12.9031	$1t_2$	−14.0782	$1t_2$	− 7.9337
$1e$	−13.6425	$1e$	−14.7988	$1e$	− 8.5422

Table 9. VESCFCNDO *results for the permanganate ion*

Calculation	Total electronic energy eV	Manganese atomic charge	Oxygen atomic charge	Manganese orbital electron populations		
				3*d*	4*s*	4*p*
CNDO 1	−2397	+0.167	−0.292	6.71	0.10	0.02
CNDO 2	−2351	+1.104	−0.528	5.79	0.09	0.02
CNDO 3	−2412	−0.345	−0.164	7.22	0.11	0.02
CNDO 4	−2420	+0.217	−0.304	6.67	0.10	0.01
CNDO 5	−2402	+0.185	−0.296	6.67	0.11	0.03
CNDO 6	−2369	+0.488	−0.372	6.40	0.09	0.02
CNDO 7	−2401	+0.595	−0.399	6.33	0.06	0.02
CNDO 8	−2413	+0.229	−0.307	6.69	0.06	0.02
CNDO 9	−2335	−0.252	−0.187	7.16	0.07	0.02

Table 10. VESCFCICNDO *results for the permanganate ion*

Calculation	Assignment ($^1T_2 \leftarrow {}^1A_1$)	Excitation energy eV	Calculation	Assignment ($^1T_2 \leftarrow {}^1A_1$)	Excitation energy eV
CNDO 1	$2e \leftarrow t_1$	2.16	CNDO 6	$2e \leftarrow t_1$	2.75
	$2e \leftarrow 2t_2$	4.13		$2e \leftarrow 2t_2$	4.53
	$3t_2 \leftarrow t_1$	5.83		$3t_2 \leftarrow t_1$	6.20
CNDO 2	$2e \leftarrow t_1$	4.11	CNDO 7	$2e \leftarrow t_1$	6.41
	$2e \leftarrow 2t_2$	5.40		$3t_2 \leftarrow t_1$	9.54
	$3t_2 \leftarrow t_1$	6.82		$2e \leftarrow 2t_2$	10.48
CNDO 3	$2e \leftarrow t_1$	1.22	CNDO 8	$2e \leftarrow t_1$	5.44
	$2e \leftarrow 2t_2$	3.60		$3t_2 \leftarrow t_1$	8.85
	$3t_2 \leftarrow t_1$	5.32		$2e \leftarrow 2t_2$	9.80
CNDO 4	$2e \leftarrow t_1$	1.95	CNDO 9	$2e \leftarrow t_1$	4.20
	$3t_2 \leftarrow t_1$	3.78		$3t_2 \leftarrow t_1$	7.74
	$2e \leftarrow 2t_2$	4.52		$2e \leftarrow 2t_2$	8.60
CNDO 5	$2e \leftarrow t_1$	2.41			
	$2e \leftarrow 2t_2$	4.74			
	$3t_2 \leftarrow t_1$	6.46			

Table 11. VESCFCICNDO 4 *Faraday parameters*

Spectroscopic state	Assignment	Calculated Faraday parameter (A/D)	Experimental Faraday parameter (A/D)
$^1T_2$	$2e \leftarrow t_1$	−0.170	−0.09
$^1T_2$	$3t_2 \leftarrow t_1$	0.178	≈0
$^1T_2$	$2e \leftarrow 2t_2$	0.039	0.4–0.7

In CNDO 4 the core Hamiltonian matrix elements were evaluated directly (but with the usual simplifying approximations) in a Löwdin basis. The ground state results are similar to those of CNDO 1 except that the order of the $1a_1$ and $2t_2$ molecular orbital energy levels has been reversed. The small differences are sufficient to reverse the CNDO 1 assignment for the second and third bands in the predicted visible/near ultra-violet spectrum. As can be seen from Table 11 this assignment cannot be supported.

The transformed full overlap core Hamiltonian matrix appears then to be more satisfactory in CNDO calculations than that calculated approximately in a Löwdin basis. This is in agreement with Brown and Roby [19] who have shown that this is also the case in NDDO calculations.

CNDO 5 illustrates the small effect that changes in the weighted average one-centre nuclear attraction integral scaling factors have upon the results obtained. In CNDO 5 the oxygen scaling factor was 1.12 (cf. 1.00 in CNDO 1).

In CNDO 6 the Mn–O weighted average two-centre repulsion integral scaling factor was 1.00 (cf. 0.97 in CNDO 1). The quantitative results show that the calculation is sensitive to small changes in this parameter. Qualitatively however, the results are in agreement with those of CNDO 1.

CNDO 7, CNDO 8 and CNDO 9 illustrate the effects of using approximate Hartree-Fock wave-functions to evaluate two-centre integrals. In CNDO 7 the parameter scheme was otherwise identical to that for CNDO 1 except that the weighted averaged one-centre attraction integral scaling factor were 1.12 (cf. 1.00 in CNDO 1). The results obtained are quite different from those of CNDO 1. The predicted spectral assignment is not supported by a comparison of calculated and experimental Faraday A/D parameters and furthermore the transition energies are too high.

CNDO 8 and CNDO 9 illustrate the unsuccessful attempts that were made to improve the correlation between the predicted and experimental excited state data. In CNDO 8 and CNDO 9 the parameter schemes were identical with that for CNDO 7 except that in CNDO 8 the manganese weighted average one-centre repulsion integral scaling factor was 0.90 (0.94 in CNDO 7) and in CNDO 9 the corresponding oxygen integral scaling factor was 0.90 (0.79 in CNDO 7). The qualitative results in both cases were the same as for CNDO 7.

It is obvious from the results of CNDO 7, CNDO 8 and CNDO 9 that in order to predict the lowest energy symmetry-allowed transition at above 2.2 eV while keeping the enhanced scaling factor for one-centre attraction integrals, drastic changes in the one-centre repulsion integral scaling factors are required. It is difficult to see any sound reason for doing this. Even if the scaling factors were so adjusted an unacceptably large negative charge (< -1) would be predicted on the manganese atom. Furthermore, it is unlikely that the assignment for the second and third bands would be reversed.

It is somewhat surprising that the use of approximate Hartree-Fock wave-functions to evaluate two-centre integrals produces results that are inferior to those obtained when these integrals are evaluated with Burns wave-functions. This suggests, and is supported by the results of CNDO 6, that the values of two-centre integrals are very important in CNDO calculations. This point is discussed in more detail in Part III.

No meaningful conclusions can be drawn from the calculated total electronic energies. Energy minimisation which is the basis of the derivation of the Roothaan equations via a variational procedure is only valid for an invariant Hamiltonian operator. The variation in parametrized basic integrals, as opposed to variation in molecular orbital coefficients or geometry, usually means variation in the Hamiltonian operator. For example, the downscaling of one-centre repulsion integrals should lower the total electronic energy but this does not validate the need for, or the extent of, the scaling.

The present study thus points clearly to the assignment of the UV spectrum of MnO_4^- listed in the last column in Table 12. Previous assignments are also summarised in the table. The main source of disagreement is the nature of the second and third transitions. Hitherto the assignments have rested on estimates

Table 12. *Assignments*[a] *of* UV *spectrum of* MnO_4^-

Experimental transit. energy eV	WH	BL	VG	DJ	BJMO[b]
2.27	$2t_2 \leftarrow t_1$	$2e \leftarrow t_1$	$2e \leftarrow t_1$	$2e \leftarrow t_1$	$2e \leftarrow t_1$
3.47			$2e \leftarrow 2t_2$[c]	$3t_2 \leftarrow t_1$	$2e \leftarrow 2t_2$
3.99	$2t_2 \leftarrow 1t_2$	$2t_2 \leftarrow t_1$	$2e \leftarrow 2t_2$	$2e \leftarrow 2t_2$	$3t_2 \leftarrow t_1$
5.45			$3t_2 \leftarrow t_1$	$3t_2 \leftarrow 2t_2$ $3t_2 \leftarrow 1e$	$2e \leftarrow 1t_2$

[a] Wolfsberg and Helmholz (1952): WH, Ballhausen and Liehr (1958): BL, Viste and Gray (1964): VG, Dahl and Johansen (1968): DJ, Present work: BJMO.

[b] Main configuration contributing to ${}^1T_2$ state.

[c] Assigned as forbidden transition to ${}^1T_1$ state.

Table 13. *The chromate ion*

Atomic charges		Chromium orbital electron populations		
Chromium	Oxygen	3*d*	4*s*	4*p*
−0.812	−0.297	6.56	0.10	0.16

Table 14. *Molecular orbitals of the chromate ion*

Symmetry	Eigenvalue eV	Eigenvectors				
		Cr 3*d*	Cr 4*s*	Cr 4*p*	O $2p_\sigma$	O $2p_\pi$
$4t_2$	37.1204	−0.1166		0.9383	0.1996	0.2572
$2a_1$	32.7508		−0.9705		0.2412	
$3t_2$	18.3723	−0.5073		−0.2921	0.7764	0.2332
$2e$	13.0520	−0.6801				0.7332
t_1	3.0777					−1.0000
$1a_1$	0.6681		0.2412		0.9908	
$2t_2$	0.4792	−0.1942		−0.1643	−0.4462	0.8580
$1t_2$	− 4.4533	0.8315		−0.0852	0.3974	0.3788
$1e$	− 4.7269	0.7331				0.6800

Table 15. VESCFCICNDO *calculation of the lowest* $^1T_2$ *excited states of the chromate ion*

Spectroscopic state	Assignment	Calculated energy eV	Experimental energy eV [24]	Calculated Faraday (A/D) Parameter	Experimental Faraday (A/D) parameter [22]
$^1T_2$	$2e \leftarrow t_1$	3.21	3.25	−0.157	−0.2 to −0.5
$^1T_2$	$2e \leftarrow 2t_2$	5.64	—	0.066	—
$^1T_2$	$3t_2 \leftarrow t_1$	6.16	4.59	0.235	0.3 to 0.7
$^1T_2$	$2e \leftarrow 1t_2$	9.17	—	0.080	—

Table 16. VESCFCICNDO *calculations of intensities of lowest energy symmetry-allowed transitions* ($^1T_2 \leftarrow {}^1A_1$) *of the chromate ion*

Transition energy eV		Oscillator strength		
Experimental	Calculated	Calculated		Experimental [23]
		Dipole length operator	Dipole velocity operator	
3.25	3.21	0.033	0.352	0.082
4.59	5.64 6.16	0.031 0.038	0.032 0.043	0.107

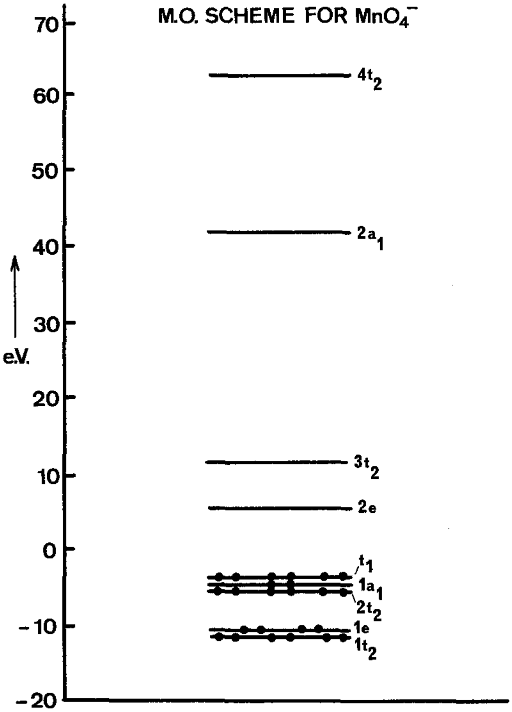

Fig. 3

of relative energies of excited states, supported at most by other rather indefinite considerations. We have previously emphasised [7] and more recent workers have re-emphasised [9] that predicted relative energies of states are rather sensitive to the details of the method of calculation and so we rely primarily on the magnetic circular dichroism data as confirming our assignment.

The results obtained for the chromate calculation are given in Tables 13 to 16 and Fig. 3. The results are qualitatively the same as those for the permanganate ion CNDO 1 calculation and are therefore not discussed in any detail.

The predicted charge on the chromium atom is -0.812 which is considerably lower than that predicted on the manganese atom in the permanganate ion. Significantly perhaps, the orbital occupations of the chromium and manganese atoms are very similar.

The second band in the experimental chromate visible/near ultra-violet spectrum is assigned to two nearly degenerate ${}^1T_2 \leftarrow {}^1A_1$ transitions arising from the $2e \leftarrow 2t_2$ and $3t_2 \leftarrow t_1$ orbital promotions. These are the same transitions that we have assigned to the second and third bands of the experimental permanganate spectrum. These results are in agreement with the predictions of Carrington and Jorgensen [20].

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Professor R. D. Brown
Department of Chemistry
Monash University
Clayton, Victoria, Australia 3168