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Molecular Orbital Calculations on Transition Element Compounds

III. MCZDO Studies of Permanganate and Chromate

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In an attempt to improve the theoretical treatment of the lower excited states of the permanganate and chromate anions beyond the simple treatment described in Part II, the MCZDO method of Brown and Roby has been investigated. Although this method includes one-centre exchange integrals and is able to discriminate between integrals involving atomic orbitals of different auxiliary quantum number, neither of which features is present in the CNDO calculations of Part II, we have been unsuccessful in devising a better interpretation of the spectra of MnO_4^- and CrO_4^{--} than that presented in Part II. The predicted energies of excited states have been found to depend strongly on the values used for two-centre nuclear attraction integrals $\langle\mu_A|V_B|\nu_A\rangle$ and on other two-centre integral values. It may be necessary to use more elaborate functions than Slater-type orbitals to evaluate these integrals satisfactorily. It would seem that a theoretical technique even more elaborate than the MCZDO method is required to give a consistently good account of the ultraviolet spectra of transition-element compounds. The success of the CNDO calculations reported in Part II for MnO_4^- and CrO_4^{--} is probably fortuitous.

Im Rahmen eines Versuches, die theoretische Behandlung der unteren angeregten Zustände des Permanganat- und Chromat-Anions über die einfache Behandlung von Teil II zu verbessern, wurde die MCZDO-Methode von Brown und Roby untersucht. Obwohl diese Methode die Einzentrenwechselwirkungsintegrale mit einschließt und zwischen Integralen für AO mit verschiedenen Nebenquantenzahlen unterscheidet, war der Versuch erfolglos, eine verbesserte Interpretation der Spektren von MnO_4^- und CrO_4^{--} zu entwickeln. Die Energien der angeregten Zustände waren stark abhängig von den Werten der Zweizentrenintegrale. Möglicherweise müssen andere Funktionen als solche vom Slater-Typ verwendet werden, um diese Integrale befriedigend auszurechnen. Es scheint überhaupt, daß nur subtilere Verfahren als die MCZDO-Methode gute Resultate für die Ultraviolettspektren mehrerer Übergangselement-Verbindungen gleichzeitig ergeben können und der Erfolg der CNDO-Rechnungen von II für MnO_4^- und CrO_4^{--} ist wahrscheinlich zufällig.

La méthode MCZDO de Brown et Roby a été étudiée lors d'une tentative pour améliorer le traitement théorique des états excités des anions permanganate et chromate au delà du traitement simple décrit dans la partie II. Quoique cette méthode introduise des intégrales d'échange monocentriques et distingue les intégrales entre des orbitales atomiques de nombres quantiques secondaires différents, ce qui n'est pas fait dans les calculs CNDO de la partie II, aucune interprétation plus satisfaisante des spectres de MnO_4^- et CrO_4^{--} n'a pu être obtenue. Les énergies prédites pour les états excités dépendent fortement des valeurs utilisées pour les intégrales d'attraction nucléaire bicentriques $\langle\mu_A|V_B|\nu_A\rangle$ et les autres intégrales bicentriques. Il peut s'avérer nécessaire d'utiliser des fonctions plus élaborées que les orbitales de Slater pour évaluer ces intégrales d'une manière satisfaisante. Il semblerait q'une technique théorique éventuellement plus élaborée que la méthode MCZDO soit nécessaire pour rendre compte des spectres électroniques des composés d'éléments de transition. Le succès des calculs CNDO de la partie II pour MnO_4^- et CrO_4^{--} est probablement fortuit.

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1. Introduction

In Part I [1] we described molecular orbital techniques, applicable to all valence electrons in transition element compounds, that could be suitable for the interpretation of various properties of such compounds, especially their electronic spectra. Two main kinds of approximate methods were described – CNDO and MCZDO. The application of the former, simpler method to MnO_4^- and CrO_4^{--} was described in Part II, where it was shown that it leads to a satisfactory interpretation of the spectra of these ions. We now proceed to investigate whether still better descriptions of the electronic structures of these ions may be derived by the MCZDO approximation.

2. Method of Calculation

The MCZDO LCAO MO SCF method has been described in Part I [1]. The molecular geometries, molecular axes system and atomic orbital basis set were the same as described in Part II [2].

For MCZDO calculations separate scaling factors are required for all one-centre integrals involving different sets of atomic orbitals. These scaling factors can readily be obtained by the method described in Part I but it is important to investigate what effects variation in these and other parameters have upon the results obtained. To illustrate this twelve calculations on the permanganate ion, labelled M 1 to M 12, will be presented and discussed. M 1 represents the most acceptable results that were obtained.

An analogous series of calculations were carried out on the chromate ion but as the effects of variations in parameters were found to be substantially the same as those for the corresponding permanganate calculations, only the chromate calculation that produced the most acceptable results will be presented and discussed.

The M 1 parameter scheme can be summarised as follows. 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. Two-centre integrals were evaluated assuming a charge of zero on the manganese atom and with each of the four oxygen atoms carrying a quarter of the charge on the molecule. 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 1.10. The oxygen one-centre repulsion integral scaling factor was 0.79 ("I-A" value) while those for the manganese integrals are summarised in Table 1. The full overlap core Hamiltonian matrix was evaluated and then transformed into a Löwdin basis.

The chromate calculation parameter scheme was analogous to the M 1 parameter scheme except for the values of the chromium one-centre repulsion integral scaling factors. These are summarised in Table 2. The M 2 to M 12 parameter schemes differ only marginally from that for M 1 and these differences are described in the next Section.

Table 1. *Manganese one-centre repulsion integral* M 1 *scaling factors*[a]

μ \ ν	3*d*	4*s*	4*p*
3*d*	0.90	1.20	0.95
4*s*	1.20	1.20	1.20
4*p*	0.95	1.20	0.95

[a] Integrals of form $\langle\mu\nu|\mu\lambda\rangle$ and $\langle\mu\mu|\nu\lambda\rangle$ were not scaled.

Table 2. *Chromium one-centre repulsion integral scaling factors*[a]

μ \ ν	3*d*	4*s*	4*p*
3*d*	0.85	1.10	0.90
4*s*	1.10	1.10	1.10
4*p*	0.90	1.10	0.90

[a] Integrals of form $\langle\mu\nu|\mu\lambda\rangle$ and $\langle\mu\mu|\nu\lambda\rangle$ were not scaled.

3. Results and Discussion

The results obtained from the M 1 calculation are presented in Tables 3 to 5. The molecular orbital energy level sequence is the same as that found for the CNDO 1 calculation [2] with the exception that the filled $1a_1$ orbital has been relatively lowered in energy and now lies below the filled $1e$ orbital. The molecular orbital energy level separations are, however, quite different from those of CNDO 1 and this is reflected in the high transition energies and in the different assignment of the visible/near ultra-violet spectrum. This assignment is not supported by a comparison of the calculated and experimental magnetic circular dichroism Faraday A/D parameters. Calculations on the relative intensities of symmetry-allowed, symmetry-forbidden and spin-forbidden transitions [1, 2] again support the assignment of all bands in the observed spectrum to symmetry allowed ${}^1T_2 \leftarrow {}^1A_1$ transitions.

Using the MCZDO method, we were unable to obtain excited state results that were a significant improvement on those of the M 1 calculation. Some possible reasons for this are advanced in the discussions of the results of the M 2 to M 12 calculations.

The predicted charge on the manganese atom of +1.217 is close to the Ovsynnikova and Brusentsev experimental value of +1.28 [3]. The manganese 4*p* orbitals are effectively unoccupied, thus supporting Best's prediction [4] and the CNDO 1 result that these orbitals are not significantly involved in the bonding of transition metal oxyanions. The manganese 4*s* orbital occupation of 0.08 electrons is slightly lower than that obtained from the CNDO 1 calculation (0.10 electrons) and results suggest that this orbital is also not important for bonding purposes. The five manganese 3*d* orbitals are almost equally occupied. There are 2.42 electrons in the $d\pi$ orbitals ($d_{x^2-y^2}$, d_{z^2}) and 3.28 electrons in the

Table 3. *The permanganate ion* M 1 *calculation*

Atomic charges		Manganese orbital electron populations		
Manganese	Oxygen	$3d$	$4s$	$4p$
$+1.217$	-0.554	5.70	0.08	0.00

Table 4. *Molecular orbitals of the permanganate ion* M 1 *calculation*

Symmetry	Eigenvalue eV	Eigenvectors[a]				
		Mn $3d$	Mn $4s$	Mn $4p$	O $2p\sigma$	O $2p\pi$
$4t_2$	38.4700	0.1070		-0.9740	-0.0886	-0.1788
$2a_1$	20.0284		0.9697		-0.2444	
$3t_2$	8.6244	0.6613		0.2083	-0.5494	-0.4664
$2e$	6.8596	-0.6286				0.7776
t_1	-4.9651					-1.0000
$2t_2$	-9.8296	-0.2861		-0.0881	-0.4174	0.8580
$1e$	-16.7735	0.7777				0.6286
$1a_1$	-19.1151		0.2444		0.9696	
$1t_2$	-21.7883	-0.6852		0.0122	-0.7184	-0.1196

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

Table 5. *Excited* $^1T_2$ *states of the permanganate ion* M 1 *calculation*

Spectroscopic state	Assignment	Calculated energy eV	Experimental energy eV	Calculated Faraday A/D parameter	Experimental Faraday A/D parameter
$^1T_2$	$2e \leftarrow t_1$	5.66	2.27	-0.101	-0.09
$^1T_2$	$3t_2 \leftarrow t_1$	6.98	3.47	0.099	$\simeq 0.0$
$^1T_2$	$2e \leftarrow 2t_2$	10.08	3.99	0.044	$0.4-0.7$
$^1T_2$	$3t_2 \leftarrow 2t_2$	13.35	5.45	—	—

$d\sigma$ orbitals (d_{xz}, d_{yz}, d_{xy}). Transition metal oxyanions, as expected, are therefore strongly π-bonded. The form of the molecular orbitals are similar to those obtained from the CNDO 1 calculation.

The M 2 parameter scheme was chosen early in this work on MCZDO calculations as being a reasonable one upon which to base investigations into the effects of variations in parameters. To allow the effects to be more clearly seen the parameter schemes for M 3 to M 12 varied from that for M 2 in only one or two respects.

The M 2 parameter scheme differed from that of M 1 in the following ways. Firstly, the Mn–O weighted average two-centre repulsion integral scaling factor was 1.00 (0.97). Secondly, the oxygen one-centre repulsion integral scaling factor was 0.90 (0.79); and thirdly, the manganese one-centre repulsion integral scaling factors were all 1.10 with the exception of that for integrals involving d orbitals only which was 0.95.

Table 6. VESCFMCZDO *eigenvalues for the permanganate ion*

M 2		M 3		M 4		M 5		M 6		M 7	
MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV
$4t_2$	48.1387	$4t_2$	48.3373	$4t_2$	42.6685	$4t_2$	47.1663	$4t_2$	48.8787	$4t_2$	43.5946
$2a_1$	19.0982	$2a_1$	24.4249	$2a_1$	19.0121	$2a_1$	19.6151	$2a_1$	17.5802	$2a_1$	15.6028
$3t_2$	17.6761	$3t_2$	17.6827	$3t_2$	17.3513	$3t_2$	16.7534	$3t_2$	12.1754	$3t_2$	15.5174
$2e$	15.7929	$2e$	15.8223	$2e$	15.7337	$2e$	14.9914	$2e$	10.0822	$2e$	13.8417
t_1	3.7312	t_1	3.7909	t_1	3.7134	t_1	3.6488	t_1	− 2.9367	t_1	2.2386
$2t_2$	− 1.0955	$2t_2$	− 1.0504	$2t_2$	− 1.1630	$2t_2$	− 1.3865	$2t_2$	− 7.4986	$2t_2$	− 2.6757
$1e$	− 8.0282	$1e$	− 8.0138	$1e$	− 8.1068	$1e$	− 9.0057	$1e$	−13.6726	$1e$	− 9.8285
$1a_1$	−11.3482	$1a_1$	−10.6986	$1a_1$	−11.3505	$1a_1$	−11.4533	$1a_1$	−17.3449	$1a_1$	−13.1306
$1t_2$	−12.9788	$1t_2$	−12.9984	$1t_2$	−13.0060	$1t_2$	−13.7721	$1t_2$	−18.9934	$1t_2$	−14.6403

M 8		M 9		M 10		M 11		M 12	
MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV	MO Symmetry	Eigenvalue eV
$4t_2$	48.4437	$4t_2$	21.2799	$4t_2$	58.1841	$4t_2$	59.5753	$4t_2$	43.0277
$2a_1$	18.6162	$2e$	15.4994	$2a_1$	32.5117	$2e$	24.5420	$2a_1$	21.1332
$3t_2$	15.8609	$2a_1$	6.7009	$3t_2$	31.1406	$3t_2$	21.9003	$3t_2$	18.4428
$2e$	13.8855	$3t_2$	5.9016	$2e$	28.7652	$2a_1$	19.7839	$2e$	17.0291
t_1	1.6024	t_1	0.9387	t_1	16.0258	t_1	5.1474	t_1	5.0494
$2t_2$	− 3.1471	$2t_2$	− 7.2592	$2t_2$	11.4300	$2t_2$	− 3.6796	$2t_2$	− 0.1980
$1e$	− 9.8934	$1e$	− 9.9579	$1e$	4.3134	$1e$	−11.5349	$1e$	− 6.5261
$1a_1$	−13.2391	$1t_2$	−15.0669	$1a_1$	1.6049	$1a_1$	−13.8930	$1a_1$	−11.2647
$1t_2$	−14.9491	$1a_1$	−16.7595	$1t_2$	− 0.2344	$1t_2$	−15.3731	$1t_2$	−11.4868

Table 7. VESCFMCZDO *results for the permanganate ion*

Calculation	Total electronic energy eV	Mn Atomic charge	O Atomic charge	Mn Orbital electron populations		
				$3d$	$4s$	$4p$
M 2	−2415	+1.152	−0.538	5.64	0.21	0.00
M 3	−2413	+1.227	−0.557	5.65	0.12	0.00
M 4	−2416	+1.133	−0.533	5.65	0.22	0.00
M 5	−2430	+0.824	−0.456	5.99	0.19	0.00
M 6	−2475	+1.648	−0.662	5.21	0.14	0.00
M 7	−2440	+0.942	−0.485	5.81	0.25	0.00
M 8	−2434	+1.322	−0.580	5.50	0.18	0.00
M 9	−2398	−0.834	−0.041	4.25	0.58	3.00
M 10	−2109	+1.189	−0.547	5.53	0.27	0.01
M 11	−2445	+1.215	−0.554	5.70	0.08	0.00
M 12	−2398	+1.224	−0.556	5.47	0.29	0.02

Table 8. VESCFCIMCZDO *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
M 2	$2e \leftarrow t_1$	5.64	M 8	$2e \leftarrow t_1$	5.94
	$3t_2 \leftarrow t_1$	6.95		$3t_2 \leftarrow t_1$	7.29
	$2e \leftarrow 2t_2$	10.04		$2e \leftarrow 2t_2$	10.27
M 3	$2e \leftarrow t_1$	5.62	M 9	$3t_2 \leftarrow t_1$	−0.97
	$3t_2 \leftarrow t_1$	6.94		$2e \leftarrow t_1$	6.74
	$2e \leftarrow 2t_2$	10.01		$3t_2 \leftarrow 2t_2$	7.26
M 4	$2e \leftarrow t_1$	5.52	M 10	$2e \leftarrow t_1$	6.38
	$3t_2 \leftarrow t_1$	6.49		$3t_2 \leftarrow t_1$	7.74
	$2e \leftarrow 2t_2$	9.97		$2e \leftarrow 2t_2$	10.74
M 5	$2e \leftarrow t_1$	4.93	M 11	$3t_2 \leftarrow t_1$	9.97
	$3t_2 \leftarrow t_1$	6.28		$2e \leftarrow t_1$	13.63
	$2e \leftarrow 2t_2$	9.52		$2a_1 \leftarrow 2t_2$	15.87
M 6	$2e \leftarrow t_1$	6.71	M 12	$2e \leftarrow t_1$	5.30
	$3t_2 \leftarrow t_1$	8.19		$3t_2 \leftarrow t_1$	6.46
	$2e \leftarrow 2t_2$	10.86		$2e \leftarrow 2t_2$	10.05
M 7	$2e \leftarrow t_1$	5.25			
	$3t_2 \leftarrow t_1$	6.53			
	$2e \leftarrow 2t_2$	9.74			

The results obtained for the M 2 calculation were not significantly different from those of the M 1 calculation. They are given together with those for M 3 to M 12 in Tables 6 to 8. All comments made in the discussion of these results are by comparison with those for the M 2 calculation.

Calculations M 3 to M 8 illustrate the effects of changes in the repulsion integral scaling factors. In M 3 the scaling factors for the manganese one-centre repulsion integrals involving the 4*s* orbitals was 1.20 (1.10). In M 4 the corresponding $4p$ scaling factor was 0.95 (1.10) in M 5 the corresponding $3d$ scaling factor was 0.90 (0.95) and in M 6 the oxygen one-centre scaling factor was 0.79 (0.90). In M 7 the scaling factor for the Mn–O two-centre weighted average repulsion integral was 0.97 (1.00) while in M 8 the corresponding O–O scaling factor was 0.97 (1.00). The results obtained indicate that reasonable changes in the values of these parameters, though relatively important, are unlikely to produce a significant improvement in the excited state results.

In M 9 weighted average two-centre Coulomb repulsion integrals, γ_{AB}, were replaced by average Coulomb repulsion integrals per set of orbitals on each centre, $\gamma_{\bar{\mu}\bar{\lambda}}$. The $\gamma_{\bar{\mu}\bar{\lambda}}$ are average two-centre Coulomb repulsion integrals over all orbitals χ_ν and χ_σ having the same l quantum numbers as χ_μ and χ_λ and being on the same respective centre. With this scheme rotational invariance is fully maintained. It has previously been proposed [5] as a simple means of introducing into the calculation differences between repulsion integrals involving different orbitals on the two-centres. Unfortunately, this calculation produced very poor results. The order of the unoccupied molecular orbital energy levels was completely rearranged and negative transition energies were predicted. The use of this approximation in MCZDO calculations appears then to be a poor one.

M 10 illustrates the effects of changes in the values of two-centre nuclear attraction integrals. In this calculation all two-centre nuclear attraction integrals were scaled by 0.90. The effect was principally to raise all molecular orbital energies by about 12 eV. The molecular orbital energy separations, and hence the predicted ultra-violet spectrum therefore depend significantly upon the values of these integrals.

Further effects of changes in the values of two-centre integrals are illustrated by calculation M 11 where approximate Hartree-Fock values were used. The order of unoccupied molecular orbitals is different from that of M 2 and is not supported by the experimental evidence of Carrington, Ingram, Lott, Schonland, and Symons [6]. The predicted ultra-violet spectrum is also unacceptable as is shown in Table 9 by a comparison of the calculated and experimental Faraday *A/D* parameters.

The predicted charge on the manganese atom is closer to +1 than to zero. Consequently, in M 12 all two-centre integrals were evaluated with Burns wavefunctions assuming a charge of +1 on the manganese atom and −1/2 on each of the four oxygen atoms. The results differed only slightly from those of M 2.

The best chromate MCZDO results are presented in Tables 10 to 12. They are qualitatively the same as those found for the permanganate M 1 calculation.

Table 9. *Lowest* $^1T_2$ *excited states of the permanganate ion* M 11 *calculation*

Spectroscopic state	Assignment	Calculated energy eV	Experimental energy eV	Calculated Faraday *A/D* parameter	Experimental Faraday *A/D* parameter
$^1T_2$	$3t_2 \leftarrow t_1$	9.72	2.27	0.255	−0.09
$^1T_2$	$2e \leftarrow t_1$	13.63	3.47	−0.175	≃0.0
$^1T_2$	$2a_1 \leftarrow 2t_2$	15.87	3.99	0.039	0.4→0.7

Table 10. *The chromate ion*

Atomic charges		Chromium	Orbital electron populations	
Chromium	Oxygen	$3d$	$4s$	$4p$
+0.119	−0.530	5.84	0.04	0.00

Table 11. *Molecular orbitals of the chromate ion* VESCFMCZDO

Symmetry	Eigenvalue eV	Eigenvectors Cr $3d$	Cr $4s$	Cr $4p$	O $2p\sigma$	O $2p\pi$
$4t_2$	36.5216	−0.1685		0.9548	0.1470	0.1960
$2a_1$	17.7828		0.9846		−0.1748	
$3t_2$	15.3190	−0.6215		−0.2922	0.5444	0.4812
$2e$	14.9332	0.6427				−0.7664
t_1	1.7865					−1.0000
$2t_2$	−4.0051	−0.2685		−0.0540	−0.4668	0.8432
$1e$	−10.3883	−0.7661				−0.6426
$1a_1$	−13.1453		0.1748		0.9848	
$1t_2$	−14.6556	0.7164		−0.0087	0.6812	0.1488

Table 12. VESCFCIMCZDO *calculation of lowest* $^1T_2$ *excited states of the chromate ion*

Spectroscopic state	Assignment	Calculated energy eV	Experimental energy [10] eV	Calculated Faraday A/D parameter	Experimental Faraday A/D parameter
$^1T_2$	$3t_2 \leftarrow t_1$	6.45	3.25	0.079	$-0.2 \rightarrow -0.5$
$^1T_2$	$2e \leftarrow t_1$	7.86	—	−0.063	—
$^1T_2$	$2e \leftarrow 2t_2$	11.93	4.59	0.056	$0.3 \rightarrow 0.7$

As was found in the CNDO calculations the atomic orbital occupations of the chromium and manganese atoms in the chromate and permanganate ions are very similar. Accordingly, the charge on the chromium atom is again approximately one protonic unit less than that of the manganese atom. The predicted ultra-violet spectrum correlates poorly with the available experimental data.

4. Conclusions

As with the CNDO results the MCZDO results illustrate the need for accurate values of two-centre integrals. Integral values obtained with approximate Hartree-Fock wave-functions differ significantly from those obtained with Burns wave-functions. The poor overall results obtained when both sets of values are used suggests that neither set of wave-functions is accurate enough for adequately representing metal: ligand interaction.

It is especially important that accurate values for two-centre nuclear attraction integrals of the type $\langle \mu_A | \hat{V}_B | \nu_A \rangle$ be obtained. Any error in these integral values will be greatly magnified in actual calculations as these integrals are multiplied by the core charge [1] (7 for manganese). This is borne out by a comparison of the results of M 10 and M 2.

It is unfortunate that there are no semi-empirical methods for the evaluation of two-centre integrals. In view of this it would seem necessary to investigate the use of the very elaborate Watson wave-functions [7]. There is also a need to investigate the making of correlation corrections to two-centre nuclear attraction integrals.

We had hoped that the MCZDO procedure would be an improvement on the CNDO method but it is clear that in its present form this is not so. It is likely that calculations including doubly excited configurations in the configuration interaction would improve matters by predicting smaller excitation energies for lowest excited states. We have selected our best procedure by first seeking those that give excitation energies of the correct general magnitude and then, as a more definitive test, finding the one that best accounts for the observed Faraday parameters. We may have discarded MCZDO procedures that satisfactorily account for the MCD observations but were ruled out on energy grounds. It is possible that the neglect of one centre exchange and hybrid integrals in the CNDO calculations roughly compensates for the neglect of doubly excited configurations in the energy calculations.

We conclude that, although it seems that a satisfactory account can now be given of the MnO_4^- and CrO_4^{--} spectra (see Part II), further studies are necessary to determine the limits of reliability of the present techniques.

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