Ab Initio Molecular Orbital Calculations of the Electronic Structure of the Permanganate and Chromate Ions

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Summary The electronic structures of the permanganate and chromate ions are described by *ab initio* SCFMO calculations.

SINCE the semi-empirical molecular orbital calculations on MnO_4^- and CrO_4^{2-} by Wolfsberg and Helmholz,[1] a number of calculations,[2–4] particularly on MnO^- have been performed, using different semi-empirical schemes. These have resulted in a number of different orderings of the filled and vacant orbitals and have shown the need for *ab initio* m.o. calculations on these ions. For this reason, and because of the almost total lack of non-empirical calculations on inorganic complexes we here report the results of such calculations. The ions were taken to be tetrahedral with Mn–O and Cr–O bond lengths of 1·59 and 1·65 Å, respectively.[5] A Gaussian basis set was used in which three such functions are used to describe each member of a basis set of Slater-type orbitals. The orbital exponents of the latter, except for the metal 4*p*, were taken as the best atom values given by Clementi and Raimondi.[6] The 4*p* exponents were taken to be 1·06 and 1·04 for manganese and chromium, respectively, from the work of Richardson *et al.*[7] The results of the calculations are summarized in the Table. The order of the predominantly metal 3*d* vacant orbitals ($2e$, $7t_2$ for MnO_4^-, and $2e$, $8t_2$ for CrO_4^{2-}) is in line with the e.s.r. measurements on MnO_4^{2-},[8] and agrees with the predictions of crystal-field theory. However, there are large separations (0·2—0·3 a.u.) between the $3d(e)$ and $3d(t_2)$ diagonal elements of the Fock matrix, the $3d(e)$ being of higher energy, such anisotropy due in large measure to one-centre Coulomb terms, being reproduced in the CNDO method of Pople *et al.*[9] A feature of the orbital populations obtained by a Mulliken analysis are the large $4p$ populations and small $3d$ populations compared with the results of semi-empirical calculations. The major difference in the populations of the manganese and chromium atoms lies in the smaller $3d$ and larger $4p$ populations of the latter. The ordering of the filled and vacant orbitals differs in the two ions. In particular the highest filled and lowest unfilled levels are calculated to be the $6a_1$ and $2e$ in MnO_4^- and the $1t_1$ and $7a_1$ in CrO_4^{2-}. However, it can be seen that the separations amongst the virtual and higher filled orbitals are very small so that the relative ordering of the levels is likely to be sensitive to the basis set used, and also in semi-empirical schemes to the approximations employed. Furthermore, these small separations confirm that any calculation of transition energies must include interaction amongst the excited configurations.[3]

TABLE

	MnO_4^-	CrO_4^{2-}
Atomic populations		
Metal		
$3d(e)$	0·88	0·79
$3d(t_2)$	3·29	2·46
$4s$	0·28	0·36
$4p$	1·29	1·75
Oxygen		
$2s$	1·93	1·91
$2p$	4·64	4·76
Orbital energies (a.u.)		
$8t_2$	0·502	0·776
$7a_1$	0·482	0·686
$7t_2$	0·455	0·696
$2e$	0·404	0·702
$6a_1$	−0·073	0·169
$1t_1$	−0·107	0·185
$6t_2$	−0·157	0·124
$1e$	−0·230	0·080
$5t_2$	−0·320	−0·001
$4t_2$	−0·970	−0·673
$5a_1$	−0·989	−0·694

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[1] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, 1952, **20**, 837.

[2] R. F. Fenske and C. Sweeney, *Inorg. Chem.*, 1964, **3**, 1105; A. Viste and H. B. Gray, *ibid.*, 1113; J. P. Dahl and H. Johansen, *Theor. Chim. Acta*, 1968, **11**, 8; L. Oleari, G. De Michelis, and L. Di Sipio, *Mol. Phys.*, 1966, **10**, 111.

[3] R. D. Brown, B. H. James, M. F. O'Dwyer, and K. R. Roby, *Chem. Phys. Letters*, 1967, **1**, 459.

[4] R. M. Canadine and I. H. Hillier, *J. Chem. Phys.*, 1969, **50**, 2984.

[5] *Chem. Soc. Special Publ. No.* 11, 1958.

[6] E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 1963, **38**, 2686.

[7] J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *J. Chem. Phys.*, 1963, **38**, 796.

[8] A. Carrington and M. C. R. Symons, *J. Chem. Soc.*, 1960, 889; D. S. Schonland, *Proc. Roy. Soc.*, 1960, *A*, **254**, 111; A. Carrington and D. S. Schonland, *Mol. Phys.*, 1960, **3**, 331; A. Carrington and C. K. Jørgensen, *ibid.*, 1960, **4**, 395.

[9] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, S136.