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The CNDO-type Molecular Orbital Calculations of MnO_4^-, CrO_4^{2-}, PdX_4^{2-}, and PdX_6^{2-}

Shigeyoshi SAKAKI and Hiroshi KATO*
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606
**Department of General Education, Nagoya University, Chikusa-ku, Nagoya 464*

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Since the molecular orbital (MO) calculations of MnO_4^- and CrO_4^{2-} were presented by Wolfsberg and Hermholz,[1] various MO methods have been used in the MO calculations of transition-metal complexes; the Extended Hückel,[2] SCCC,[3] CNDO-type,[4] INDO-type,[5] *ab-initio*,[6] and the others[7] methods. However, none of these methods was perfectly satisfactory, because an effective method for some compounds can not always give reasonable results in other cases. In order to re-examine the usefulness of the CNDO-type MO calculation of transition-metal complexes except for the estimation of the intra-atomic triplet transition, we calculated the electronic structures of MnO_4^-, CrO_4^{2-}, PdX_4^{2-}, and PdX_6^{2-} (X=halogen), for the CNDO-type approximation avoids the difficulties of the rotation invariance and of the estimation of the one-center exchange integral. The calculated results of the electronic population, the strength of the Pd–X bonds, and the electronic spectra of these complexes will be presented in this paper.

Method

We start from Roothaan's familiar closed-shell SCF equation[8] and separate the Hartree-Fock matrix element, F_{rs}, into the one-electron part, H_{rs}, and the two-electron part;

$$\begin{aligned} &|F_{rs}-\varepsilon S_{rs}| = 0 \\ &F_{rs} = H_{rs} + \sum_{t,u}^{occ} P_{tu}[(rs|tu)-0.5(rt|su)] \end{aligned} \qquad (1)$$

where r, s, t, and u denote the atomic orbitals and whose P_{tu} is the t, u density matrix element. Then, the following approximations are introduced into Eq. (1): (I) The zero-differential overlap approximation[9] is introduced:

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

[2] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

[3] R. F. Fenske and C. C. Sweeney, *ibid.*, **3**, 1105 (1964).

[4] a) R. D. Brown, B. H. James, M. F. O'Dwyer, and K. R. Roby, *Chem. Phys. Lett.*, **1**, 459 (1967). b) R. D. Brown, B. H. James, and M. F. O'Dwyer, *Theor. Chim. Acta*, **17**, 262, 279 (1970).

[5] a) L. Oleari, G. De Michelis, and L. De Sipio, *Mol. Phys.*, **10**, 111 (1966). b) W. Th. A. M. Van Der Lugt, *Chem. Phys. Lett.*, **10**, 117 (1971).

[6] I. H. Hillier and V. R. Saunders, *Proc. Roy. Soc. Ser A*, **320**, 161 (1970).

[7] H. Katô, This Bulletin, **45**, 1281 (1972).

[8] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[9] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, s 129 (1965).

$$S_{rs} = \delta_{rs} \tag{2}$$

$$(rs|tu) = \delta_{rs}\delta_{tu}(rr|tt) \tag{3}$$

(II) The diagonal element, H_{rr}, of the one-electron part can be written as follows:[10]

$$H_{rr} = U_{rr} + \sum_{B \neq A} (B|rr) \tag{4}$$

$$U_{rr} = -I_r - (N_r - 1)(rr|rr) - \sum_{s \neq r}^{A} N_s(rr|ss) \tag{5}$$

$$(B|rr) = -\sum_{s}^{B} N_s(rr|ss) \tag{6}$$

where N_r and I_r represent the number of electrons on the atomic orbital (AO), r, in the neutral atom, A, and the ionization potential of AO r respectively. $\sum^A$ indicates the summation on the A atom.

(III) The off-diagonal element, H_{rs} ($r \neq s$), is approximated according to Wolfsberg and Hermholz:[1]

$$H_{rs} = -0.5kS_{rs}(I_r + I_s) \tag{7}$$

where k is a parameter equal to 1.1.

(IV) The one-center Coulomb repulsion integral (rr|rr) and the two-center Coulomb repulsion integral (rr|ss) are estimated by Pariser's approximation[11] and Ohno's approximation[12] respectively.

In order to calculate S_{rs}, Clementi's AO[13] and Burns' AO[14] were used for ligands and metals respectively. The same orbital exponents were used for s- and p-orbitals. The values obtained by Hinze and Jaffé.[15] were used for the I_r and (rr|rr) values of ligands. The values used for the metals are listed in Table 1.

Table 1. The ionization potential (I_r) and one-center Coulomb repulsion integral (J_{rr})

		I_r(eV)	J_{rr}[18] (eV)
Cr	3d	−20.28[16]	14.03
	4s	−14.73	6.80
	4p	−10.31	5.80
Mn	3d	−21.64[16]	14.70
	4s	−15.35	7.09
	4p	−10.62	5.95
Pd	4d	− 8.54[17]	13.87
	5s	− 7.60	7.46
	5p	− 3.84	6.22

Results and Discussion

MnO_4^- and CrO_4^{2-}. For the purpose of comparing our results with previous ones,[4–6] we calculated the MO's of MnO_4^- and CrO_4^{2-}. The net charge on the Mn atom in MnO_4^- was found to be 1.28 from the metal K–X ray spectra.[4b] However, in our results, negative net charge on the Mn atom was obtained. This may be due to the too large electron population of the 4s and 4p orbitals of the Mn atom compared with the results of Oleari *et al.*[5a] and Hillier and Saunders[6] (MnO_4^-; 4s, 0.81 and 4P, 0.78: CrO_4^{2-}; 4s, 0.81 and 4p, 0.78 in our results).

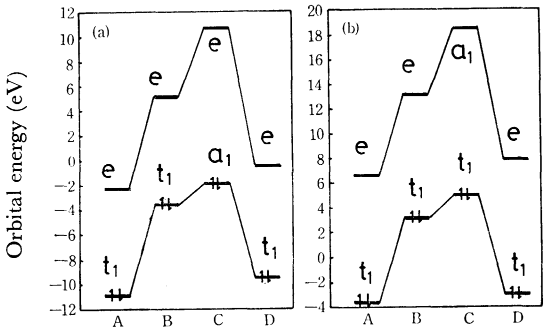

Fig. 1. HOMO and LUMO of MnO_4^-(a) and CrO_4^{2-}(b) by various Methods.
⇅: HOMO, —; LUMO
A: Oleari *et al.*[5b] by INDO, B: Brown *et al.*[4a] by VE-SCF-CNDO. C: Hillier *et al.*[6] by *ab-initio*, D: ours by CNDO.

The highset occupied (HO) MO and the lowest unoccupied (LU) MO are considered to be represented by t_1[4,5] and e[19] respectively. Our results with respect to HOMO and LUMO are compared with previous ones in Fig. 1. The results of Oleari *et al.*[5a] seem to be quite reasonable. However, the calculation by Brown *et al.*[4b] gave a positive orbital energy for the HOMO of CrO_4^{2-}. Also, in the case of Hillier's calculation,[6] the representations of HOMO and LUMO are not t^1 and e respectively, and the HOMO of CrO_4^{2-} has a positive orbital energy. In contrast to these results, our result are reasonable regarding the orbital energy and the orbital symmetry.

The calculated transition energies are given in Table 2. Our results agree fairly with the experimental results.

PdX_4^{2-} and PdX_6^{2-}. We then calculated the MO's of PdX_4^{2-} and PdX_6^{2-} in order to examine the validity of our method for different types of complexes. The net charge of Pd decreases with a decrease in the electronegativity of halogens, as is shown in Table 3. This tendency agrees with the results obtained by means of photoelectron spectroscopy.[21] However, we obtained a negative net charge on the Pd atom due to the large electron population of 5s- and 5p-orbitals. As is shown in Table 3, the absolute value of the two atomic part of the total energy, $|E_{Pd-Cl}|$,[9] is larger than $|E_{Pd-Br}|$ in PdX_4^{2-} and PdX_6^{2-}, and $|E_{Pd-X}|$ in

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[10] T. Yonezawa, K. Yamaguchi, and H. Kato, This Bulletin, **40**, 536 (1967); H. Kato, H. Konishi, H. Yamabe, and T. Yonezawa, *ibid.*, **40**, 2761 (1961).

[11] R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953).

[12] K. Ohno, *Theor. Chim. Acta*, **2**, 219 (1964).

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

[14] G. Burns, *ibid.*, **41**, 1521 (1964).

[15] J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1961); *J. Phys. Chem.*, **67**, 1504 (1963).

[16] C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, Inc., New York (1965), p. 120.

The electron configuration of neutral Mn atom is d^5s^2. However, we can not obtain the I_r for d^5s^2 except with I_{4s}, because of the lack of the observed atomic spectra. Therefore we investigated the effect of I_r and choose the suitable values. We show this value in Table 1.

[17] I. H. Hillier and R. M. Canadine, *Discuss. Faraday Soc.*, **47**, 27 (1969).

[18] L. De Sipio, E. Tondello, G. De Michelis, and L. Oleari, *Chem. Phys. Lett.*, **11**, 287 (1971).

[19] A. Carrington, D. J. E. Ingram, K. A. K. Lott, D. S. Schonland, and M. C. R. Symons, *Proc. Roy. Soc., Ser. A*, **254**, 101 (1960).

PdX_6^{2-} is larger than $|E_{Pd-X}|$ in PdX_4^{2-}. These results agree with the experimental results.[22)]

Though the order of bond strength agrees with the experimental results, we failed to obtain reasonable transition energies for PdX_4^{2-}. The calculated first transition energies seem too small for $PdCl_4^{2-}$ (0.019 eV) and $PdBr_4^{2-}$ (0.028 eV). Furthermore, neither is the d-d transition which is to be expected as the first transition.[23)] For $PdCl_6^{2-}$, the calculation gives almost reasonable results, as is shown in Table 2.

As has been described above, by treatment with the same approximation as was used in MnO_4^- and CrO_4^{2-} we can obtain reasonable trends of electron population and bond strength for Pd-halogen complexes, but not successful results for any transition energies except PdX_6^{2-}. Attempts to improve this approximation are under way, for example the inclusion of one-center exchange integrals and further refinements in the parametrization of H_{rs} will be described in the near future.

TABLE 2. TRANSITION ENERGIES OF MnO_4^-, CrO_4^{2-}, AND $PdCl_6^{2-}$

	Experimental (eV)	Calculated (eV)
MnO_4^- [20b)]	1.79 $^3T_1$or $^1T_1$[20a)]	1.44 $^1T_1$
	2.38 $^1T_2$	2.45 $^1T_2+^1E$
		3.65 $^1T_2$
	3.44 $^1T_1$	4.27 $^1T_1$
	4.13 $^1T_2$	4.47 $^1T_2$
CrO_4^{2-} [20c)]	3.00 $^1T_1$	3.36 $^1T_1$
		3.78 $^1T_1$
	3.56 $^1T_2$	5.15 $^1T_2$
	4.65 $^1T_2$	6.47 $^1T_2$
	6.20	6.70 $^1T_1$
$PdCl_6^{2-}$ [24)]	2.27	3.98 T_{1g}
	3.64	4.13 T_{2g}
		5.94 T_{1u}
	5.17	6.45 T_{2u}

TABLE 3. ELECTRON POPULATION AND E_{Pd-X} OF PdX_4^{2-} AND PdX_6^{2-}

	Electron Population			Net Charge on Pd			Obsd[22)]	
	Pd		X					
	d	sp		Calcd	Expt.[21)]	E_{Pd-X}[c)]	f_{Pd-X}[a)]	ν_{Pd-X}[b)]
$PdCl_4^{2-}$	8.075	2.259	7.417	−0.333	0.42	-15.882_{ev}	1.355	310
$PdBr_4^{2-}$	8.049	2.343	7.402	−0.392	0.23	−14.688		187
PdF_6^{2-}	7.137	2.219	7.441	0.644		−19.124		
$PdCl_6^{2-}$	7.177	3.043	7.297	−0.220	0.72	−16.300	1.90	317
$PdBr_6^{2-}$	7.157	3.203	7.273	−0.360		−14.920	1.58	198

a) The force constant of Pd-X stretching vibration. (mdyn/Å)

b) The symmetric stretching frequency of Pd-X. (cm^{-1})

c) $E_{A-B}=2\sum_r^A\sum_s^B P_{rs}H_{rs}-\frac{1}{2}\sum_r^A\sum_s^B P_{rs}^2(rr/ss)+\sum_r^A\sum_s^B(P_{rr}-N_r)(P_{ss}-N_s)(rr/ss)$

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20) a) P. Day, L. De Sipio, and L. Oleari, *Chem. Phys. Lett.*, **5**, 533 (1970); b) L. W. Johnson and S. P. McGlynn, *J. Chem. Phys.*, **55**, 2985 (1971); c) L. W. Johnson and S. P. McGlynn, *Chem. Phys. Lett.*, **7**, 618 (1970).

21) G. Kumer, J. R. Blackburn, R. G. Albridge, W. E. Moddeman, and M. M. Jones, *Inorg. Chem.*, **11**, 296 (1972).

22) P. J. Hendra and P. J. D. Park, *Spectrochim. Acta*, **23A**, 1635 (1967).

23) A. J. MacCaffery, P. N. Schatz, and P. J. Stephens, *J. Amer. Chem. Soc.*, **90**, 5730 (1968).

24) C. K. Jorgensen, *Adv. Chem. Phys.*, **5**, 119 (1963); *Mol. Phys.*, **2**, 309 (1959).