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A COMMENT ON THE MULLIKEN POPULATION ANALYSIS OF CHARGE DISTRIBUTION: THE CASE OF $[Co(CN)_6]^{3-}$

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Ab initio mo calculations on different basis sets gave $[Co(CN)_6]^{3-}$ states with nearly identical energies but with different charge distributions; they were proved to represent the same state. This shows that charge distributions estimated on the Mulliken analysis must not be taken too literally.

Previously we reported preliminary results of ab initio LCAO MO SCF calculations for the ground state of the $[Co(CN)_6]^{3-}$ ion.$^{1)}$ The calculations were made with three different basis sets: full-double-zeta,$^{2)}$ semi-double-zeta,$^{3)}$ and single-zeta.$^{4)}$ The semi-double-zeta set differs from the full-double-zeta set only in that the Co 4s and 4p functions are described by single-zeta functions. The charge distributions obtained according to the Mulliken population analysis$^{5)}$ remarkably depended on the basis sets. In this paper we shall discuss why the different charge distributions were derived from the calculations on the different basis sets.

Table 1 shows the results of the Mulliken analysis of valence-orbital populations and the total energies of the $[Co(CN)_6]^{3-}$ ion, obtained on the bases of the full-double-zeta, semi-double-zeta, and single-zeta sets of molecular orbitals. The full-double and semi-double sets gave total energies very similar to each other, while the single-zeta set resulted in an energy ca. 4 a.u. higher than them. The cobalt atomic charge calculated with the full-double-zeta set is +3.138, which significantly differs from the values, +1.301 and +1.369, obtained on the other basis sets. The difference in the calculated cobalt population mostly results from the differences in the Co 4s and 4p orbital populations. The three basis sets, on the other hand, give a good agreement in the Co 3d orbital population. The calculated carbon atomic charges also depend on the basis sets, whereas the nitrogen populations are less dependent.

Table 2 shows two sets of values for bond overlap populations calculated on the double-zeta and semi-double-zeta bases. The two sets of values well compare with each other in the overlap populations between Co 3d and C orbitals, whereas they take diverse values in those between Co 4s and 4p orbitals and C 2s and 2p orbitals; in the latter cases, the full-double and semi-double sets show the

Table 1. Orbital population of $[Co(CN)_6]^{3-}$ ion

		full-double-zeta	semi-double zeta	single-zeta
Co	3dσ	1.042	1.040	1.071
	3dπ	5.885	5.885	5.906
	4s	0.094	0.242	0.222
	4p	-1.029*	0.667	0.177
	Atomic charge	+3.138	+1.301	+1.369
C	2s	1.661	1.562	1.358
	2pσ	1.249	1.164	1.163
	2pπ	1.772	1.619	1.749
	Atomic charge	-0.676	-0.338	-0.260
N	2s	1.675	1.622	1.664
	2pσ	1.289	1.335	1.513
	2pπ	2.390	2.427	2.298
	Atomic charge	-0.347	-0.379	-0.468
Total energy(a.u.)		-1934.4016	-1934.3811	-1930.4042

* This negative value is an artifact resulting from the process of the Mulliken population analysis. Our Co4p$_2$ orbitals incidentally have high values in the region of the C 2s and 2p orbitals, and are used to a great extent for the optimization of the 6t$_{1u}$ orbitals of mainly C character. (See Fig. 2 and Table 3.) This situation has led to the formal result that the 6t$_{1u}$ charge belonging mainly to C has come in part from Co 4p orbitals which in the zeroth approximation contained no electrons.

Table 2. Bond-overlap population of $[Co(CN)_6]^{3-}$ ion

		full-double-zeta	semi-double-zeta	single-zeta
Co - C	s - s	-0.143	0.019	0.021
	s - pσ	-0.127	-0.024	-0.030
	pσ - s	-1.126	0.101	0.121
	pσ - pσ	-0.076	0.029	(-0.008)
	pπ - pπ	-0.563	0.005	
	dσ - s	0.059	0.059	0.049
	dσ - pσ	0.063	0.062	(0.066)
	dπ - pπ	0.018	0.018	
C - N	s - s	-0.631	-0.068	0.013
	s - pσ	0.098	0.111	0.158
	pσ - s	0.465	0.344	0.121
	pσ - pσ	0.363	0.384	(1.341)
	pπ - pπ	1.082	1.046	

Table 3. Molecular orbital coefficients of a 6t$_{1u}$ orbital

full-double-zeta

0.030 Co2p$_{x1}$ +0.022 Co2p$_{x2}$ -0.082 Co3p$_{x1}$ -0.092 Co3p$_{x2}$ +0.176 Co4p$_{x1}$ -0.717 Co4p$_{x2}$
-0.093 C1s$_1$ -0.125 C1s$_2$ +0.300 C2s$_1$ +1.030 C2s$_2$ -0.190 C2p$_{x1}$ -0.190 C2p$_{x2}$
+0.069 N1s$_1$ +0.091 N1s$_2$ -0.232 N2s$_1$ -0.519 N2s$_2$ -0.260 N2p$_{x1}$ +0.017 N2p$_{x2}$
+0.132 C'2p$_{x1}$ +0.260 C'2p$_{x2}$ +0.090 N'2p$_{x1}$ -0.026 N'2p$_{x2}$

semi-double-zeta

0.030 Co2p$_{x1}$ +0.023 Co2p$_{x2}$ -0.085 Co3p$_{x1}$ -0.079 Co3p$_{x2}$ +0.072 Co4p$_{x1}$
-0.093 C1s$_1$ -0.127 C1s$_2$ +0.352 C2s$_1$ +0.443 C2s$_2$ -0.194 C2p$_{x1}$ -0.078 C2p$_{x2}$
+0.069 N1s$_1$ +0.093 N1s$_2$ -0.249 N2s$_1$ -0.414 N2s$_2$ -0.260 N2p$_{x1}$ -0.069 N2p$_{x2}$
+0.125 C'2p$_{x1}$ -0.002 C'2p$_{x2}$ +0.085 N'2p$_{x1}$ +0.045 N'2p$_{x2}$

contradictory bonding characters: antibonding and bonding.

Table 3 gives $6t_{1u}$ wave functions of the full-double-zeta and semi-double-zeta basis sets. The notations of atomic orbitals involved can be seen from Fig. 1. Considerable differences are found not only in the Co 4p coefficients but also in the coefficients of C 2s and C' 2p orbitals. In the full-double-zeta calculation, the large negative overlap populations between Co 4p and C 2s and 2p orbitals result partly from the large negative value of the $Co4p_{x2}$ coefficient. The semi-double-zeta set, on the other hand, does not contain $Co4p_{x2}$. This situation yields the large differences in the Co charge obtained by population analysis. In view of these significant differences between the results derived from the two kinds of basis sets, it is interesting to see whether or not the wavefunctions of full-double and semi-double sets represent the same electronic orbital. For this purpose, two kinds of examinations have been made: comparison of their electron density distributions along the bond and evaluation of overlap integrals between corresponding molecular orbitals belonging to one and the other basis set. If the two wavefunctions are equivalent, the two electron density distributions will be alike and the absolute values of the overlap integrals will be very close to unity.

Figure 2(a) represents the electron density ψ^2 of the $6t_{1u}(x)$ mo's along the Co-C-N axis (x axis), two ψ^2 curves obtained on the two basis sets being practically identical. The electron density curve has maxima on C and N atoms and the residual electron distribution spreads outward of the C-N group. This suggests that $6t_{1u}$ is a C-N antibonding mo, and is related to 5σ and 4σ orbitals of the CN^- ion, which are characterized as predominantly C lone pair and N lone pair, respectively. The absolute values of overlap integrals between corresponding mo's of the two sets are approximately 1.0, with the lowest value of 0.9991 for the $6t_{1u}$ mo's. These results demonstrate that two corresponding mo wavefunctions described by the full-double-zeta and semi-double-zeta basis sets represent an identical orbital.

In Fig. 2(b), the $Co4p_{x1}$, $Co4p_{x2}$, $C2p_{x1}$, and $C2p_{x2}$ orbital functions are depicted as functions of the distance from the atomic sites of Co and C. The $Co4p_{x2}$ function has its maximum value at a distance of about 2.2 a.u. from the cobalt atom and extends beyond the ligating carbon atom. Thus this function can as well contribute to the description of carbon orbitals as do the carbon 2s and 2p orbitals. This may explain why $Co4p_{x2}$ contributes a large quota to the $6t_{1u}$ mo of dominantly C lone-pair character.6)

The choice of the basis set did not appreciably affect the energies, but considerably influenced some of the orbital coefficients and also the resultant charge distribution on the Mulliken population analysis. However, the geometrical charge distribution was unaffected by the basis set. As was pointed out in a previous paper,1) allocation of the charge to each atom in a molecule is an artifact. The present results show that charge distributions estimated on the Mulliken population analysis must not be taken too literally; especial care must be taken when the analysis is applied to a molecular orbital consisting of atomic orbitals appreciably different in size, although the Mulliken analysis is

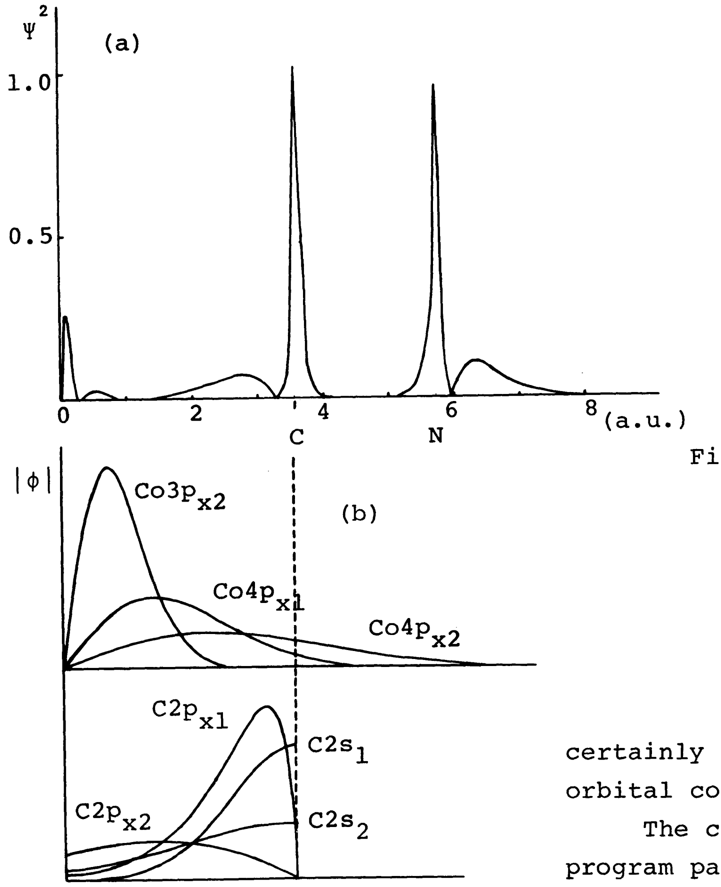

Fig. 2 (a) Electron density of the $6t_{1u}(x)$ mo along the Co-C-N axis (x axis). (b) $Co4p_{x1}$, $Co4p_{x2}$, $C2s_1$, $C2s_2$, $C2p_{x1}$, and $C2p_{x2}$ orbital functions plotted along the x axis.

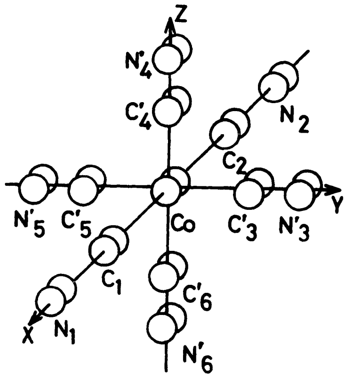

Fig. 1 Notations of atomic orbitals constituting t_{1u} mo
$C = \alpha(C_1 + C_2)$, $N = \beta(N_1 + N_2)$
$C' = \gamma(C'_3 + C'_4 + C'_5 + C'_6)$
$N' = \delta(N'_3 + N'_4 + N'_5 + N'_6)$
α, β, γ, δ: Normalization constants

certainly a good approximation for a molecular orbital consisting of similar atomic orbitals.

The calculations were carried out with a program package JAMOL2.$^{7)}$ The authors are grateful to Professor Kimio Ohno of Hokkaido University and Professor Hiroshi Kashiwagi of Institute for Molecular Science for invaluable suggestions. The computations reported in this paper have been carried out on FACOM 230-75 computers of Nagoya University Computation Center and Hokkaido University Computing Center.

References and Notes.

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3) (11,7,4/9,5/9,5) are contracted to [7,5,2/4,2/4,2].
4) (12,8,4/7,3/7,3) are contracted to [5,4,1/2,1/2,1] with double 4s and 4p functions. Co: *ibid.* C and N: B. Roos and P. Siegbahn, Theoret. Chim. Acta, 17, 209(1970).
5) R. S. Mulliken, J. Chem. Phys., 23, 1833(1955).
6) The negative value of the Co $4p_{x2}$ coefficient (as compared with the positive value for Co $4p_{x1}$) may indicate that $6t_{1u}$ on the full-double-zeta basis involves a Co 5p orbital and that the choice of the Co 4p exponents was not quite adequate. However, the almost perfect overlap of two sets of molecular orbitals shows that possible unsatisfactoriness in the choice of a few component functions were in both cases recovered by optimizing the coefficients.
7) Program JAMOL2 written for the Program Library at the Hokkaido University Computing Center by H. Kashiwagi, T. Takada, E. Miyoshi, and S. Obara.

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