

## CNDO bonding parameters in transition metal atoms

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**Abstract.** The method of calculating CNDO bonding parameters developed recently is extended to transition metal atoms. It is shown that one of the approximations introduced earlier can also be deduced by a more complete treatment of the imbalance problem in CNDO-MO theory. The conventionally calibrated bonding parameters indirectly incorporate important contributions from two-particle interactions. The parameters developed are used to compute the coefficients of metal-to-ligand transfer of spin in many hexafluoro metallate ions of transition metals. The results are compared with those obtained by conventional CNDO-MO calculation. Comparison of the computed bonding parameters with other available values is also made.

**Keywords.** CNDO bonding; transition metal; bond parameter; spin transfer coefficient.

### 1. Introduction

Recently we suggested a method (Bhattacharyya and Chowdhury 1976; hereinafter referred to as I and II) to calculate CNDO bonding parameters and developed a semitheoretical method of parametrisation which could fairly successfully predict molecular ionisation potentials, nuclear quadrupole coupling constants, etc., of simple molecules without transition metal atoms. The present paper aims at extending this method to molecules containing transition metal atoms. The general strategy adopted is similar to the one followed in I and II. This method is then tested by performing the reparametrised CNDO-MO calculations on a number of fluoride complexes of transition metals and comparing the computed isotropic and anisotropic spin-transfer coefficients with their experimental counterparts and also with the results obtained by other CNDO-MO calculations on the same species. The emphasis throughout has been on the conceptual side, viz. to clarify the true nature of the bonding parameters and suggest some degree of justification for the treatment of off-diagonal core matrix elements in the original CNDO theory.

## 2. Calculation of diatomic bond parameters

Clack *et al* (1972) calibrated  $\beta_A$  parameters of the transition metal atoms (from Sc to Cu) by adopting the usual fitting technique suggested by Pople *et al* (1965) and assuming that  $\beta_{AB} = \frac{1}{2}(\beta_A + \beta_B)$ . The calibrated bonding parameters of the 3*d*-transition metals, however, show a high degree of dependence on the actual magnitudes of the exponents of the Slater type orbitals (STO) used as basis functions and reveals a lack of uniqueness of the calibrated bonding parameters. A theoretical method to calculate  $\beta_A$  parameters is thus desirable so that the parameters are consistent with the use of a specific "basis-set". The method reported in I and II is fairly sensitive to the choice of the basis set. It thus seems worthwhile to attempt an extension of the method to include transition metals. Let us consider a transition metal atom (*M*) bonded to a ligand atom (*L*). Let *M* be described by a basis set consisting of 3*d*, 4*s* and 4*p* functions and the ligand by *ns*, *np* functions only. Since 3*d*, 4*s* and 4*p* orbitals belong to two different valence shells, one has to use (i) a set of two  $\beta_{ML}$  parameters, viz.  $\beta_{ML}^{3d}$  and  $\beta_{ML}^{4s}$  (Clack *et al* 1972), (ii) different exponents for 3*d* and 4*s*-4*p* orbitals, (iii) different values of the two-electron integrals involving 3*d* and 4*s*, 4*p* orbitals. For the computation of the  $\beta_{ML}$  parameters it is, therefore, necessary to consider only two distinct types of off-diagonal *F*(CNDO) matrix elements the conventional expressions of which are as follows:

Case (a) :

$$F_{\mu\nu}^{ML}(\text{CNDO}) = \langle \chi_\mu^M | F | \chi_\nu^L \rangle = \langle \chi_\mu^M | h^{\text{core}} | \chi_\nu^L \rangle - \frac{1}{2} P_{\mu\nu} G_{\mu\mu,\nu\nu}^{ML} \quad (1)$$

where  $\chi_\mu^M$  is a 3*d* orbital on the metal atom. Adopting the modified definition of off-diagonal *F*(CNDO) matrix elements given in I, we can write

$$F_{\mu\nu}^{ML} = F_{\mu\nu}^{ML}(\text{CNDO}) + \sum_r^M n_{rr} \langle \chi_\mu^M \chi_\nu^L | \chi_r^M \chi_r^M \rangle + \sum_s^L n_{ss} \langle \chi_\mu^M \chi_\nu^L | \chi_s^L \chi_s^L \rangle, \quad (2)$$

$n_{rr}$  and  $n_{ss}$  denote the occupation numbers of various metal and ligand orbitals and are either 0 or 1 by the definition. Obviously equation (2) contains an overcounting of the electron repulsion terms as our modified definition of  $F_{\mu\nu}^{ML}$  in (2) incorporates only the additional coulomb repulsion terms (contributed by *J*-matrix elements) needed for the elimination of the imbalance inherent in the conventional treatment of one and two-electron interactions in the off-diagonal of Fock matrix elements in the CNDO-MO theory. This overcounting can be eliminated by including comparable 2-electron integrals ( $\langle \chi_\mu^M \chi_\nu^L | \chi_r \chi_r \rangle$  type) contributed by the corresponding *K*-matrix elements. This eliminates the self-interaction of the electron under consideration. In our previous work the same result was obtained by introducing the condition that  $P_{\mu\mu} = P_{\nu\nu} = 0$  in an *ad hoc* manner. That assumption amounts to the inclusion of certain specific integrals contributed by the *K*-matrix elements. Thus a consistent and balanced definition of  $F_{\mu\nu}^{ML}$  would be as follows:

$$F_{\mu\nu}^{ML}(\text{CNDO}) + \sum_r^M n_{rr} \langle \chi_\mu^M \chi_\nu^L | \chi_r^M \chi_r^M \rangle + \sum_s^L n_{ss} \langle \chi_\mu^M \chi_\nu^L | \chi_s^L \chi_s^L \rangle \\ - n_{\mu\mu} \langle \chi_\mu^M \chi_\nu^L | \chi_\mu^M \chi_\mu^M \rangle - n_{\nu\nu} \langle \chi_\mu^M \chi_\nu^L | \chi_\nu^L \chi_\nu^L \rangle. \quad (3)$$

Let us assume that the electronic configuration of  $M$  is  $(3d^m 4s^1 4p^0)$  and remains fixed (see also § 3.1).

If we now split the summation over  $r$  in (3) into separate sums over  $3d$ ,  $4s$  and  $4p$  orbitals respectively, we have

$$\begin{aligned}
 F_{\mu\nu}^{ML} = & F_{\mu\nu}^{ML}(\text{CNDO}) + \sum_r^{3d} n_{rr} \langle \chi_\mu^M \chi_\nu^L | \chi_r^M \chi_r^M \rangle \\
 & + \sum_{r'}^{4s, 4p} \langle \chi_\mu^M \chi_\nu^L | \chi_{r'}^M \chi_{r'}^M \rangle n_{r'r} + \sum_i^L \langle \chi_\mu^M \chi_\nu^L | \chi_i^L \chi_i^L \rangle n_{ii} \\
 & - n_{\mu\mu} \langle \chi_\mu^M \chi_\nu^L | \chi_\mu^M \chi_\mu^M \rangle - n_{\nu\nu} \langle \chi_\mu^M \chi_\nu^L | \chi_\nu^L \chi_\nu^L \rangle.
 \end{aligned} \tag{4}$$

The following definitions are now introduced for compact representation :

$$\sum_r^{3d} n_{rr} = m ; \quad \sum_{r'}^{4s, 4p} n_{r'r} = m_1 ; \quad \sum_i^L n_{ii} = n_1.$$

If we now apply Mulliken approximation for simplifying the evaluation of all the two-electron integrals in (4) and for calculating the one-electron integrals in (4), adopt the same methodology as followed in paper I, equation (4) expands to,

$$\begin{aligned}
 F_{\mu\nu}^{ML} = & \frac{1}{2} S_{\mu\nu}^{ML} [(U_\mu^M + \sum_r^{3d} \langle \chi_\mu^M \chi_\mu^M | \chi_r^M \chi_r^M \rangle) \\
 & + \sum_{r'}^{4s, 4p} n_{r'r} \langle \chi_\mu^M \chi_\mu^M | \chi_{r'}^M \chi_{r'}^M \rangle - n_{\mu\mu} \langle \chi_\mu^M \chi_\mu^M | \chi_\mu^M \chi_\mu^M \rangle) \\
 & + (U_\nu^L + \sum_i^L n_{ii} \langle \chi_\nu^L \chi_\nu^L | \chi_i^L \chi_i^L \rangle - n_{\nu\nu} \langle \chi_\nu^L \chi_\nu^L | \chi_\nu^L \chi_\nu^L \rangle)] \\
 & + \frac{1}{2} \left\langle \chi_\mu^M \left| \frac{Z_M}{r} + \frac{Z_L}{r} \right| \chi_\nu^L \right\rangle + \frac{1}{2} S_{\mu\nu}^{ML} [\sum_i^L n_{ii} \langle \chi_\mu^M \chi_\mu^M | \chi_i^L \chi_i^L \rangle \\
 & + \sum_{r'}^{4s, 4p} n_{r'r} \langle \chi_\nu^L \chi_\nu^L | \chi_{r'}^M \chi_{r'}^M \rangle + \sum_r^{3d} \langle \chi_\nu^L \chi_\nu^L | \chi_r^M \chi_r^M \rangle n_{rr} \\
 & - (n_{\mu\mu} + n_{\nu\nu}) \langle \chi_\mu^M \chi_\mu^M | \chi_\nu^L \chi_\nu^L \rangle] - \frac{1}{2} P_{\mu\nu} G_{\mu\mu, \nu\nu}^{ML}.
 \end{aligned} \tag{5}$$

Recalling that  $n_{rr}$  or  $n_{ii}$ , etc is zero for the unoccupied and one for the occupied basis functions in the atoms in their normal electronic configurations, equation (5) at once simplifies to

$$\begin{aligned}
 F_{\mu\nu}^{ML} = & \frac{1}{2} S_{\mu\nu}^{ML} \{ [U_\mu^M + (m-1) G^{MM}(3s, 3s) + m_1 G^{MM}(3s, 4s)] \\
 & + \{U_\nu^L + (n_1-1) G^{LL}(ns', ns')\} + \frac{1}{2} \left\langle \chi_\mu^M \left| \frac{Z_M}{r} + \frac{Z_L}{r} \right| \chi_\nu^L \right\rangle \\
 & + \frac{1}{2} S_{\mu\nu}^{ML} [(m-2) G^{ML}(3s, ns') + n_1 G^{ML}(3s, ns') \\
 & + m_1 G^{ML}(4s, ns')] - \frac{1}{2} P_{\mu\nu} G^{ML}(3s, ns').
 \end{aligned} \tag{6}$$

where  $G^{MM}(3s, 3s)$  represents the one-centre electron repulsion integral between any two  $3d$  functions,  $G^{MM}(3s, 4s)$  that between a  $3d$  and a  $4s$  or  $4p$  functions on  $M$ ,  $G^{LL}(ns', ns')$  represent the one-centre electron repulsion integral for the  $ns'$  valence orbitals on the ligand (all of which are equal in CNDO approximation) while  $G^{ML}(3s', ns')$ ,  $G^{ML}(4s, ns')$  are the two unique two-centre (metal-ligand) electron repulsion integrals. By following the development of paper I, (6) can easily be reduced to the following form:

$$\begin{aligned} F_{\mu\nu}^{ML} = & -\frac{1}{2} S_{\mu\nu}^{ML} (I_{3d}^L + I_{nv}^L) - \frac{1}{2} k' (Z_M + Z_L) G'_{ML} \cdot S_{\mu\nu}^{ML} \\ & + \frac{1}{2} S_{\mu\nu}^{ML} [(m-2) G^{ML}(3s, ns') + n_l G^{ML}(3s, ns') \\ & + m_l G^{ML}(4s, ns')] - \frac{1}{2} P_{\mu\nu} G^{ML'}(3s, ns'). \end{aligned} \quad (7)$$

$G'_{ML}$  represents the magnitude of Mataga-Nishimoto type of two-centre electron repulsion integral (Mataga and Nishimoto 1957) between a  $3d$  orbital and any ligand function separated by a distance of half the metal-ligand bond length. Comparison of (7) with the conventional definition of  $F_{\mu\nu}^{ML}$  (CNDO) suggests that,

$$\begin{aligned} \beta_{ML}^{3d} = & -\frac{1}{2} (I_{3d}^M + I_{nv}^L) - \frac{1}{2} k' (Z_M + Z_L) G_{ML} \\ & + \frac{1}{2} [(m + n_l - 2) G^{ML}(3s, ns') + m_l G^{ML}(4s, ns')]. \end{aligned} \quad (8)$$

Case (b) : Proceeding exactly in the same way as done in case (a) it can be shown that from the definition of

$$F_{\mu\nu}^{ML}(\text{CNDO}) = \langle \chi_{\mu}^M | F | \chi_{\nu}^L \rangle$$

where  $\chi_{\mu}^M$  is a  $4s$  or  $4p$  function on the metal atom, we can deduce that

$$\begin{aligned} \beta_{ML}^{4s} = & -\frac{1}{2} [I_{nv}^M(4s, 4p) + I_{nv}^L] - \frac{1}{2} k'' (Z_M + Z_L) G''_{ML} \\ & + \frac{1}{2} [m_l G^{ML}(3s, ns') + (m_l + n_l - 2) G^{ML}(4s, ns')], \end{aligned} \quad (9)$$

where  $\beta_{ML}^{3d}$  is the bond-parameter for the covalent interactions of the  $4s$  or  $4p$  orbitals of the metal atom with any symmetry-matched orbital ( $ns, np$ ) of the ligand.  $G''_{ML}$  is defined exactly like  $G'_{ML}$  with  $3d$  orbitals replaced by  $4s$  or  $4p$  (equivalent) orbital.

If we have to adopt this scheme of calculating  $\beta^{ML}$  parameters appropriate for an approximately orthogonalised basis (to first order in  $S$ ), it is easy to show (see paper I) that

$$\begin{aligned} \beta_{ML}^{3d}(II) = & -\frac{1}{2} k' (Z_M + Z_L) G'_{ML} + \left\{ \frac{1}{2} (m + n_l - 2) G_{ML}(3s, ns') \right. \\ & \left. + m_l G^{ML}(4s, ns') \right\} \text{ and} \\ \beta_{ML}^{4s}(II) = & -\frac{1}{2} k'' (Z_M + Z_L) G''_{ML} + \frac{1}{2} \{ m G^{ML}(3s, ns') \\ & + (m_l + n_l - 2) G^{ML}(4s, ns') \}. \end{aligned} \quad (10)$$

The constants  $k'$  and  $k''$  can be adjusted to produce the fit desired.

### 3. Results and discussion

The different practical aspects of the parametrisation have been discussed at length in Bhattacharyya (1979).

#### 3.1. Comparison of $\beta^{AB}$ parameters with other values

It would be interesting to see how far our computed  $\beta^{AB}$  parameters ( $\beta_{ML}^{3d}$  in particular) agree with conventionally calibrated parameters given by Clack *et al* (1972). Table 1 presents the  $\beta_{MF}^{3d}$  parameters computed by this method and those using the  $\beta_M^{3d}$  parameters for transition metal atoms of Clack *et al* and the  $\beta_F^\circ$  values of Pople *et al* (1965). The two sets of values are fairly close to each other. The computed  $\beta_{MF}^{3d}$  parameters (for  $K' = 0.75$  and  $1.0$ ) are also reported in table 1 along with the calibrated (Clack *et al* 1972) parameters for comparison. The fairly good agreement provides further support to the model proposed for rationalising the two-centre off-diagonal matrix elements of  $F^{CNDO}$ . This rationalisation suggests that the two-centre core parameters ( $\beta_{AB}$ ) incorporate the effects of a sizable portion of two-electron interactions. This means that the overlap charge ( $\chi_\mu^A \chi_\nu^B$ ) sees screened core-charges of the atoms *A* and *B* and not the full ones as assumed in CNDO theory. In this sense, the core matrix element  $h_{\mu\nu}^{AB}$  should be redefined using appropriately screened core-charges  $Z_A^{off}$  and  $Z_B^{off}$  in the following way:

$$h_{\mu\nu}^{AB}(\text{core}) = \left\langle \chi_\mu^A \left| T(1) + \frac{Z_A^{off}}{r} + \frac{Z_B^{off}}{r} \right| \chi_\nu^B \right\rangle,$$

With  $Z_A^{off} = Z_A - \sigma_A$  and  $Z_B^{off} = Z_B - \sigma_B$ ,

**Table 1.** Parameters computed with the conventionally calibrated values of Clack *et al* (1972) and Pople *et al* (1965).

M-F	Calculated values of		Calibrated values of bond parameters			
	$-\beta_{MF}^{3d}$ (eV)	$-\beta_{MF}^{4s}$ (eV)	$-\beta_{MF}^{3d}$	$-\beta_{MF}^{3d**}$	$-\beta_{MF}^{4s}$	$-\beta_{MF}^{4s**}$
V-F	24.25 ( $K' = 0.75$ )	20.58 ( $K'' = 0.75$ )	27.75	30.00	21.25	25.5
	28.68 ( $K' = 0.85$ )	30.52 ( $K'' = 1.00$ )				
Cr-F	25.00 ( $K' = 0.75$ )	20.71 ( $K'' = 0.75$ )	28.15	31.00	22.25	28.0
	30.07 ( $K' = 0.75$ )	31.50 ( $K'' = 1.00$ )				
Fe-F	27.32 ( $K' = 0.75$ )	20.91 ( $K'' = 0.75$ )	28.75	33	25.5	32.5
	33.01 ( $K' = 0.85$ )	33.36 ( $K'' = 1.00$ )				
Ni-F	29.35 ( $K' = 0.75$ )	20.97 ( $K'' = 0.75$ )	29.25	39	31.8	36.0
	36.05 ( $K' = 0.85$ )	35.14 ( $K'' = 1.00$ )				
Co-F	28.53 ( $K' = 0.75$ )	19.74 ( $K'' = 0.75$ )	29.00	38.5	28.25	34.0
	35.02 ( $K' = 0.85$ )	33.28 ( $K'' = 1.00$ )				

† Parameters used in our computations correspond to  $K' = 0.85$ ,  $K'' = 1.00$ .

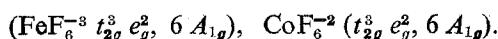
\*  $\beta$  parameters for Burn's orbitals.

•  $\beta$  parameters for Gouterman's orbitals.

where  $\sigma_A$  and  $\sigma_B$  are the appropriate screening constants. Jug (1971) has shown that a considerable extent of screening effect has to be incorporated to reproduce Pople's  $\beta_A^0$  parameters. One point should, however, be mentioned. The  $\beta^{ML}$ -parameters reported here have been computed with reference to specific electronic configurations of the metal ions. But experience has shown that even considerable variations in the valence electronic configuration of the metal ion do not lead to any appreciable change in the computed parameters. One may, however, evaluate  $\beta_{ML}$  for a number of configurations and take an average. It may also be allowed to vary at each iteration. The bonding parameters thus estimated cannot be interpreted as a diatomic property as these would be coupled to the entire molecular structure. This would allow each molecule to optimise its own bonding parameters depending on the specific chemical environment.

### 3.2. Calculation of spin-transfer coefficients

The usefulness of the scheme of parametrisation suggested in the preceding sections is tested by performing this reparametrised version of CNDO-MO calculations on a number of hexafluorometallate ions of the iron group of metals and calculating the transferred spin density on the ligands. This enables us to assess the extent of covalency operating in the M-L bonds and to compare the theoretical spin-transfer coefficients with the experimental counterparts. However, the neglect of all one-centre exchange integrals in CNDO-MO theory fails to induce proper degree of spin-polarisation (SP) in the orbitals of different symmetries. Thus the computed spin-transfer coefficients almost entirely reflect spin-delocalisation (SD) effects. The following complex ions have been studied:



The calculations were performed by using the UHF version of LCAO-MO-SCF-methodology (Pople and Nesbet 1954, Amos and Hall 1961) at the CNDO level without spin projection.\*

In our calculations, experimental bond lengths were used. The  $\xi_{3d}$  exponents were scaled ( $\xi_{3d} = \xi_{3d}(\text{Clementi}) \times k_{3d}$ ) as also the calibration constants  $K'$  and  $K''$  in equations (8) and (9) in the test calculation on the  ${}^3A_{1g}$  ground state of octahedral  $\text{NiF}_6^{-4}$  ion. The objective was to investigate (i) the effect of variations in 3d-radial functions on the computed spin transfer coefficients; (ii) the effect of changing bond ( $\beta_{AB}$ ) parameters and (iii) the possibility of generating a set of these calibration constants which apply over a range of molecules. Table 2 summarises some of the results of calibrating calculations on the  $\text{NiF}_6^{-4}$  ion for several sets of  $K_{3d}$  parameters and a number of values of  $K'$  and  $K''$ . This table shows that Clementi's single  $\xi$ -3d-radial functions (Clementi and Raimondi 1963) are too much contracted to produce any significant degree of overlap among the metal 3d and ligand orbitals and predict to very low values of the computed spin-transfer coefficients. Thus

\* It can be shown that as a consequence of CNDO approximation  $\psi_{\text{UHF}}$  in all the cases reported here becomes forced eigen-functions of spin ( $S^z$  operator). This point would be discussed elsewhere.

Table 2. Parameter dependence of the spin fraction on ligands (%) computed by our RPCNDO-MO method in  $\text{NiF}_6^{4-}$  ion (a test case)\*.

Magnitudes of the variable parameters	Spin fraction on fluorine orbitals in $\text{NiF}_6^{4-}$	
	$f_s$ %	$(f_{2p\sigma} - f_{2p\pi})$ %
$K_1^{**} = 0.8$ ; $K_2^{**} = 1.0$ ; $K_{3d} = 1.0$	0.01	0.29
$\xi_{3d} = \xi_{3d}^{\text{Clementi}} K_{3d}$		
$K_1 = 0.85$ ; $K_2 = 1.0$ ; $K_{3d} = 0.65$	0.24	3.39
$K_1 = 0.65$ ; $K_2 = 0.75$ ; $K_{3d} = 0.65$	0.13	2.27
$K_1 = 0.75$ ; $K_2 = 0.85$ ; $K_{3d} = 0.65$	0.19	3.20
$K_1 = 0.65$ ; $K_2 = 0.75$ ; $K_{3d} = 0.85$	0.02	0.50
$K_1 = 0.65$ ; $K_2 = 0.75$ ; $K_{3d} = 0.75$	0.04	1.11

\* Experimental values for  $f_s$ ,  $(f_{2p\sigma} - f_{2p\pi})$  are summarised in table 2.

\*\*  $K_1 \equiv K'$ ;  $K_2 \equiv K''$ .

keeping the bond parameters fixed ( $K' = 0.8$  and  $K'' = 1.0$ ), if  $\xi_{3d}$  (Clementi) is scaled down by 35% ( $K_{3d} = 0.65$ ), computed spin densities on ligand orbitals improve considerably, indicating that the scaled  $3d$  radial functions are diffuse enough to produce sufficient amount of covalent interactions. From a comparison of the different sets of results on the test case ( $\text{NiF}_6^{4-}$ ) with the corresponding experimental data (table 2) it appears that  $K' = 0.85$ ,  $K'' = 1.0$  and  $K_{3d} = 0.65$  would be the best choice. These values are used throughout for all other metal atoms.

Table 3 summarises the coefficients of transferred spin-densities on different ligand orbitals ( $f_s, f_{p\sigma}, f_{p\pi}$ ) together with the anisotropic spin-transfer coefficient ( $f_{p\sigma} - f_{p\pi}$ ) computed by the present method. For comparison we have also included in the table the relevant quantities calculated by Clack *et al* 1972 (CNDO-MO) available experimental data. It is seen that the agreement of computed coefficients of (metal-to-ligand) spin-transfer with experimental data is somewhat better than that found by Clack *et al* in his CNDO-MO calculations. From our results obtained with  $\text{NiF}_6^{4-}$ , it is seen that all the unpaired electron density transferred to the  $F^-$  ions are localised on the system of  $\sigma$ -orbitals ( $2s, 2p$ ) with zero spin density on the ligand  $\pi$ -system. Neither do the  $3d\pi$  or  $4s, 4p$  orbitals on the Ni atom contain any unpaired spin. This is a consequence of neglecting all one-centre exchange integrals in CNDO-MO theory which leads to zero values of all the  $\sigma-\pi$  exchange integrals (in MO basis) and consequently to no spin-polarisation of the  $\pi$  orbitals in the present case. The low magnitude of transferred spin-density on the fluorine  $2s$  orbital indicates the relatively unimportant role played by these orbitals in metal-ligand covalent interactions. The dominant  $\sigma$ -bonding effects arise from  $3d\sigma - 2p\sigma$  interactions.

The unpaired electrons in  $\text{Cr}^{\text{III}}$  or  $\text{V}^{\text{II}}$  hexafluoro complexes occupy  $t_{2g}^*$  (anti-bonding) orbitals of  $\pi$ -type symmetry in  $O_h$  point group. The CNDO-MO calculations as expected, predict all the transferred spin density to be localised on the ligand  $\pi$ -orbitals. The anisotropic spin-transfer coefficients are negative and conform with the experimental results. The increase in this quantity in going from

Table 3. Computed spin fractions on the fluoride ligand orbitals in a series of  $MF_6^-$  complex ions compared with the experimental counterparts.

Method	$NiF_6^{4-}$		$FeF_6^{3-}$		$CrF_6^{3-}$		$VF_6^{4-}$		$CoF_6^{2-}$	
	2s%	( $2P_\sigma - 2P_\pi$ )/% 2s%	( $2P_\sigma - 2P_\pi$ )/% 2s%	( $2P_\sigma - 2P_\pi$ )/% 2s%	( $2P_\sigma - 2P_\pi$ )/% 2s%	( $2P_\sigma - 2P_\pi$ )/% 2s%	( $2P_\sigma - 2P_\pi$ )/% 2s%	( $2P_\sigma - 2P_\pi$ )/% 2s%	( $2P_\sigma - 2P_\pi$ )/% 2s%	( $2P_\sigma - 2P_\pi$ )/%
Our CNDO method	0.24	3.39	0.50	7.45	0	..	0	-1.99	0.65%	6.05%
<i>Clack's method</i>										
CNDO-B	0.02	0.33	0.15	7.97	-0.003	-0.415		-0.200	..	..
CNDO-G	0.15	1.39	0.44	7.38	-0.01	-0.74	0	-0.300	..	..
Observed data	NMR—0.538, 3.78 <sup>a</sup>		..	..	..	..	..	..	..	..
	ESR—0.490, 4.51		0.763	3.3 <sup>b</sup>	-0.031	-4.78 <sup>b</sup>	-0.072	-2.8 <sup>c</sup>	..	..

<sup>a</sup>Shulman and Sugano (1963). <sup>b</sup>Hall *et al* (1963). <sup>c</sup>Nakatsuji *et al* (1969).

V<sup>II</sup> to Cr<sup>III</sup> (isoelectronic) complex is correctly predicted. One should note, however, that for these  $d^3$  ions  $f_\sigma$  computed by any CNDO type of theory would be  $\approx 0$ , though *ab initio* calculations (Brown *et al* 1970; Larson 1974) predict substantial magnitudes of  $f_\sigma$  in them. This is a general feature of CNDO parametrisation and not peculiar to our model. In  $\text{FeF}_6^{3-}$ , there are unpaired electrons in both  $t_{2g}^*$  and  $e_g^*$  shells (both half-filled). Our calculations predict  $f_{2s}$  in close agreement with experimental data (better than either set of CNDO calculations reported by Clack *et al* 1972). However, our calculations also predict too large an anisotropy in the transferred spin-density on the ligand 2p orbitals (compared to experimental data) and this agrees with the results of Clack *et al* 1972. This indicates that the SD effect switched through the participation of  $\sigma$ -orbitals of the metal and the appropriate  $\sigma$  orbital system of the ligand atoms is overestimated as compared to the SD effect arising from  $\pi$ -type of metal-ligand covalent interactions. However, it may be noted that Larson and Conolly (1975), in their MS-X $\alpha$  calculation on  $\text{FeF}_6^{3-}$  obtained a high anisotropy in the spin-population of  $F^-$  and ascribed it to the neglect of correlation effects.

For  $\text{CoF}_6^{4-}$  (isoelectronic with  $\text{FeF}_6^{3-}$ ) the degree of anisotropy in the transferred spin density on  $F^-$  (see table 2) is much less than that in  $\text{FeF}_6^{3-}$  although the extent of spin delocalisation (as measured by  $f_{2s}, f_{2p\sigma}, f_{2p\pi}$  individuals) is much larger in the latter. This is expected since a higher oxidation number and higher nuclear-charge on  $\text{Co}^{\text{IV}}$  favours higher covalency effects in  $\text{Co}^{\text{IV}}$  than in  $\text{Fe}^{\text{III}}$  compounds. The trend observed in V<sup>II</sup> and Cr<sup>III</sup> is also quite justified in that sense.

#### 4. Conclusions

Our experience can be summarised by observing that our method of generating  $\beta$  parameters for non-transitional atom-pairs proposed recently can be extended to systems where one of the bonded pair is a transitional atom. The calibration constants ( $K', K''$ ) have enough flexibility. However, some important points about the  $\beta$  parameter have been left unexplored. For example, the "strict diatomic character" of the "bond-parameter" assumed in this work needs further scrutiny. The energy dependence of  $\beta$ -parameters should also be investigated within the framework of the present model. These are being studied at present.

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