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Transferred Hyperfine Structure Interactions in Transition Metal Complexes*

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The transferred hyperfine interactions of octahedral transition metal complexes are discussed. The necessity of using a model which accounts for spin polarization is stressed. Results obtained by molecular orbital calculations using the multiple scattering method are presented for thirteen different octahedral clusters. The agreement with experiments is satisfactory except for the contact term where it is only moderately good. Even in the latter case, however, the calculations yield some valuable information, particularly concerning the core polarization contribution.

Key words: Transferred hyperfine interactions – Transition metal complexes – Multiple scattering method

1. Introduction

The interaction between hyperfine structure measurements and quantum mechanical calculations of the electronic structure is of great value. The experiments provide a direct test of the accuracy of the calculated wave functions and at the same time the calculations may suggest improved models for the interpretation of the experimental results. As an example the anisotropic transferred hyperfine structure of a transition metal complex gives information on the difference $f_\sigma - f_\pi$, where f_σ and f_π are the fractions of unpaired spin on the ligand in σ and π orbitals respectively [1]. In for instance CrF_6^{3-} the unpaired orbitals are π-orbitals and in the conventional model without core-polarization $f_\sigma = 0$. Calculations based on the unrestricted Hartree-Fock (UHF) method show, however, that there is a large negative contribution to f_σ due to exchange polarization of the bonding σ-orbitals. These results can be verified by combining ESR or NMR data with neutron scattering data. Unfortunately there is still disagreement as to the precise value of f_σ and f_π as we will see in section 4.

The interpretation of isotropic hyperfine interactions, i.e. the Fermi contact term presents a very difficult problem which hardly can be solved without detailed calculations. In the complex mentioned above the contact term on the ligand would be zero in a non-polarized model since the unpaired orbitals have a node at the ligand nucleus. The experimental value is different from zero which again suggests that we have to use a model which accounts for spin-polarization, either directly or by configuration interaction. In section 4 results will be presented

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from calculations using the multiple scattering method [2, 3]. This is a molecular orbital approach where the orbitals are obtained by direct integration without recourse to basis sets. Approximations have to be made in the effective hamiltonian for the orbitals. Although the results for this reason should be taken *cum grano salis* they will give important information on the magnitude of the different contributions, for instance the much disputed contribution from the inner shells. The latter is quite independent of the approximations in the method.

2. Method of Calculation

In applications of the multiple scattering (MS) method one first simplifies the one-particle equations by using a local exchange approximation [4]:

$$V_{\mathrm{ex}}(\boldsymbol{r}) = -6\alpha[(3/4\pi)\tfrac{1}{2}\varrho(\boldsymbol{r})]^{1/3}, \tag{1}$$

$$\varrho(\boldsymbol{r}) = \textstyle\sum_{i=1}^{N} \varphi_i(\boldsymbol{r})\varphi_i^*(\boldsymbol{r}). \tag{2}$$

In the unrestricted or spin-polarized approach one uses one potential, $V_{\mathrm{ex}}^{(\uparrow)}$, for spin-up orbitals and one, $V_{\mathrm{ex}}^{(\downarrow)}$, for spin-down orbitals. $\varrho_\uparrow$ to be used in Eq. (1) in place of $1/2\varrho$ to define $V_{\mathrm{ex}}^{(\uparrow)}$ is then obtained from Eq. (2) by summing only over orbitals associated with up-spin

$$\varrho_\uparrow(\boldsymbol{r}) = \textstyle\sum_i (\uparrow)\varphi_i(\boldsymbol{r})\varphi_i^*(\boldsymbol{r}). \tag{3}$$

$\varrho_\downarrow$ is similarly obtained by summing only over orbitals with spin-down. The value 2/3 has been suggested for α [5], but here we will use a slightly larger value $\alpha = 0.72$ since values in the range 0.71–0.73 have given the best agreement with Hartree-Fock orbitals [6]. We will not here discuss the accuracy of the local exchange approximation, but refer to a paper by Wilson *et al.* [7]. A more severe approximation is in any case the muffin-tin approximation to the potential and charge density. In spherical regions around each atomic site spherical averages of these functions are taken. This is also done in the outer region, whereas a constant average is used in the interstitial region. The radii of the spheres were for CrF_6^{3-} determined [8] by letting the central ion and ligand spheres tangent each other close to the charge density minimum along the bonding axis. Subsequently the same R_{F} was used for all complexes with fluorine ligands and the same R_{Cr} for all chromium complexes. The radii are given in Table 1. The method of integration, matching across sphere boundaries, etc. are described in other works [3, 17]. The outer sphere was also used as a "Watson sphere" with a uniformly distributed charge large enough to neutralize the whole cluster.

The orbitals will have muffin-tin structure. Denoting the atomic regions I, II, etc., the interstitial region Θ, and the outer region Ω an orbital φ may be written

$$\varphi(\boldsymbol{r}) = \varphi_{\mathrm{I}}(\boldsymbol{r}) + \varphi_{\mathrm{II}}(\boldsymbol{r}) + \ldots + \varphi_\Theta(\boldsymbol{r}) + \varphi_\Omega(\boldsymbol{r}) \tag{4}$$

where the functions φ_{I}, φ_{II}, etc., φ_Θ, and φ_Ω are zero outside their own region. In the atomic region I we have

$$\varphi_{\mathrm{I}}(\boldsymbol{r}) = \textstyle\sum_{l,m} C_{nlm} R_{nlm}(r) Y_{lm}(\theta, \varphi) \tag{5}$$

and similarly in other atomic regions and in Ω (expressed in local coordinates r, θ, φ). In Θ the expansion is in terms of known analytical functions. R_{nlm} are determined by numerical integration in each atomic sphere. The criterion for an eigensolution is that the functions and their derivatives should match at the sphere boundary and this determines the eigenvalue and the remaining constants. The expansion Eq. (5) should be taken far enough to ensure a converged result. In practice only short expansions are necessary for convergence in the expectation values of interest in this paper.

A quite surprising result of the calculations is that the atomic parts of the orbitals are so close to their counterparts for free atoms and ions. As an example we may take the t_{2g} orbital in octahedral FeF_6^{3-}, which has only a d component in the Fe region. This d component resembles the $3d$ function for free Fe^{3+} to such an extent that the radius, $r_{\max}$, of the maximum of the radial distribution function $(r \cdot R_2(r))$ is only about 1% larger than $r_{\max}$ for free Fe^{3+}. This maximum as well as the maxima of the ligand valence orbitals are well inside the respective atomic spheres. It therefore becomes meaningful to use the concept "occupancy of atomic orbitals" for metal $3d$ and ligand valence orbitals (but hardly for metal $4s$ and $4p$ orbitals). The occupancy may be defined as

$$q_{\mathrm{M}}(\varphi) = \int_I \varphi_{\mathrm{I}}(\boldsymbol{r}) \varphi_{\mathrm{I}}^*(\boldsymbol{r}) dv \tag{6}$$

M refers to the metal region. In the ligand region we may similarly define q_{L} from φ_{II}. From these quantities we may then easily obtain f_σ and f_π (in the octahedral case):

$$\begin{aligned} f_\sigma &= 2\left[\textstyle\sum_i q_{\mathrm{L}}(e_g^{(i)}\uparrow) - \sum_j q_{\mathrm{L}}(e_g^{(j)}\downarrow)\right] \\ f_\pi &= \tfrac{3}{2}\left[\textstyle\sum_i q_{\mathrm{L}}(t_{zg}^{(i)}\uparrow) - \sum_j q_{\mathrm{L}}(t_{2g}^{(j)}\downarrow)\right] . \end{aligned} \tag{7}$$

q_{L} refers to charges equally distributed on all six equivalent ligand sites. The factors 2 and 3 respectively then enter because of the degeneracy and the factor 1/2 for f_π since there are two π-orbitals at each site.

3. Charge Distributions

The mechanism for charge and spin transfer in complexes with one-atom ligands is as follows [1]. The bonding σ- and π-orbitals (which in crystal field theory are ligand orbitals) usually have a large ligand component q_{L} and a rather small metal $3d$ component, q_{M}, on the central ion. The antibonding orbitals (which in crystal field theory are $3d$ orbitals) will have the opposite charge distribution with q_{L} on the central ion and q_{M} on the ligands. If a bonding orbital is occupied but not its antibonding counterpart, a charge q_{M} is transferred from the ligand to the central ion. If a bonding and an antibonding orbital are both occupied there is no total charge transfer relative to the ionic case. This result which automatically follows in limited basis set calculations with only one relevant basis function on each center, shows up as a result also in the MSXα calculations, interestingly

Table 1. Integrated valence shell charges within central ion sphere compared to free ion charges within a sphere of the same size

	CrF_6^{3-}	$CrCl_6^{3-}$	CrO_6^{9-}	MnF_6^{2-}	MnF_6^{4-}	$MnCl_6^{4-}$	FeF_6^{3-}	FeO_6^{9-}	NiF_6^{2-}	NiF_6^{4-}	$NiCl_6^{4-}$
M–L distance (a. u.)	3.65[a]	4.50[b]	3.58[c]	3.29[d]	3.96[e]	4.97[f]	3.61[g]	3.58[c]	3.21[h]	3.79[i]	4.64
Sphere radius (a. u.)	1.80	1.80	1.80	1.44	2.11	2.11	1.76	1.80	1.36	1.94	1.94
a_{1g} (4s)	0.06	0.03	0.08	0.03	0.10	0.09	0.07	0.12	0.03	0.12	0.11
t_{1u} (4p)	0.10	0.06	0.16	0.09	0.12	0.07	0.09	0.16	0.06	0.12	0.09
e_g ($3d\sigma$)	0.76	1.07	0.85	1.15	2.07	2.11	2.36	2.59	1.62	2.32	2.57
t_{2g} ($3d\pi$)	2.76	2.73	2.79	2.75	2.85	2.87	3.00	3.20	5.31	5.63	5.61
Sum	3.68	3.89	3.88	4.02	5.14	5.14	5.52	6.07	7.01	8.19	8.37
Corresp. free ion value	2.72	2.72	2.72		4.66	4.66			6.38	7.42	7.42

[a] K_2NaCrF_6, Ref. [9].

[b] $CeCl_3$, Ref. [10]

[c] Al...O distance in $LaAlO_3$, see Ref. [11]. The calculations were originally done to to study the spin-density on Al^{3+} in the impurity systems $Cr:LaAlO_3$ and $Fe:LaAlO_3$.

[d] K_2MnF_6, Ref. [12].

[e] $KMnF_3$, Ref. [13].

[f] Cd...Cl distance in K_4CdCl_6, see Ref. [14].

[g] K_2NaFeF_6, Ref. [13].

[h] Rb_2NiF_6, Ref. [15].

[i] $KNiF_3$, Ref. [16].

enough. Thus ligand-to-metal charge redistribution can only take place in those bonding orbitals whose antibonding counterparts are unoccupied. Similar conclusions have been reached by others [1, 18]. For the moment we are disregarding smaller effects like 4*s* and 4*p* "occupancies", small charge build-ups in the bonding region of the bonding orbitals etc. Since there are more electrons in bonding than antibonding orbitals the net charge transfer is directed from ligand to metal. The calculated result is given in Table 1. The net charge transfer is larger for a larger formal ionic charge (= oxidation) state). It also depends on other factors. Mn^{2+} complexes have a small charge transfer, which is related to the smaller ligand field stabilization energy and comparatively large interatomic distance. Concerning the ligands we find a larger charge transfer for a less electronegative ligand as expected.

From the charge distributions given in Table 1 it is possible to derive approximate values for electric quadrupole coupling constants. For $CrCl_6^{3-}$ the charges of the bonding e_g orbitals is 1.07 units within the Cr sphere. Since a free ion 3*d* orbital is only 90% within the metal sphere we may obtain a more accurate "occupancy" by increasing all integrated charges (Eq. (6)) by 11%. The Fig. 1.07 above should thus be increased to 1.18 units. This means that the $3p\sigma$ charge is depleted by $1.18/6=0.197$ units. The corresponding depletion for the π-orbitals is only 0.005 units. The calculated excess hole density in the $3p\alpha$ orbital is thus 19% of an electron. The experimental value derived from the quadrupole coupling constant is 23% [19, 20]. The agreement is as good as can be expected, particularly since we have not included any Sternheimer factors.

4. Anisotropic Hyperfine Interactions

With regard to spin transfer we may, of course, also apply the rule that only bonding orbitals whose antibonding counterparts are unoccupied can redistribute electrons. In the d^5 case the spin is thus transferred through the bonding spin-down σ and π-orbitals. In the d^8 case only the bonding spin-down σ-orbitals are available and thus $f_\pi = 0$. In the d^3 case the bonding $\sigma\uparrow$, $\sigma\downarrow$, and $\pi\downarrow$ orbitals may transfer electron spins, and since the $\sigma\uparrow$ transfer is larger than the $\sigma\downarrow$ transfer we obtain a non-zero f_σ.

For transferred anisotropic interactions we define [1]

$$A_p = \tfrac{4}{5} g_N \beta \beta_N \langle r^{-3} \rangle \tag{8}$$

where $\langle r^{-3} \rangle$ is evaluated for the valence shell p-orbital on the ligand. The coupling constants A_σ and A_π may then be written

$$A_\sigma = \frac{f_\sigma A_p}{2s}, \tag{9}$$

$$A_\pi = \frac{f_\pi A_p}{2s}. \tag{10}$$

Here we have assumed that the molecular orbitals can be expressed to a good approximation in terms of a single free atom orbital ($2p$ for F, $3p$ for Cl, etc.) and that the inner shells do not contribute. The former assumption is to a large extent confirmed in our calculations. The latter is justified since in the atomic case the inner shells contribute less than 5% of the valence shell contribution.

The results of the calculations are given in Table 2. The agreement with experiments is fairly satisfactory. Our f_π are always numerically smaller than the f_σ values. For the clusters CrO_6^{9-} and FeO_6^{9-} Freund *et al.* have obtained experimental values for f_π by combining resonance data for Cr^{3+} and Fe^{3+} as impurities in MgO [26] with neutron diffraction results [27] on the antiferromagnetic salt. A similar method has been used for MnF_2 [1]. The value of f_π for CrO_6^{9-} estimated in this way is remarkably large particularly compared to f_π for FeO_6^{9-}. It seems more reasonable that f_π should be uniformly small for all complexes, as obtained in the present calculations.

In the MSXα results are compared to the theoretical results of Brown and Burton [22] and Clack *et al.* [23] we find in general good agreement. One exception is NiF_6^{4-} where the latter two methods yield a much smaller value. NiF_6^{4-} has been a testing ground for *ab initio* methods. Moskowitz *et al.* [32] obtained $f_\sigma = 6.3\%$, Soules *et al.* [33] $f_\sigma = 2.2\%$, and Wachters and Nieuwpoort [34] $f_\sigma = 2.9\%$. Table 1 in the latter paper contains further results obtained by *ab initio* methods. Another case where the MSXα result disagrees with other results is CrF_6^{3-} where Clack *et al.* [23] obtained $f_\sigma \approx 0$ whereas Brown and Burton [22] obtained larger f_σ and f_π than by MSXα. In d^3 complexes the f_σ value is due to spin-polarization in bonding σ-orbitals, whereas in the other complexes examined here the f_σ value arises because of bonding in $\sigma\downarrow$ orbitals. The failure of the CNDO method to predict an f_σ significantly different from zero may then be traced to the neglect of one-center exchange in the CNDO method.

Table 2. Spin density coefficients obtained from the calculated charge distribution of the bonding t_{2g} and e_g orbitals. Contribution from other orbitals are negligible

Clusters		CrF_6^{3-}	$CrCl_6^{3-}$	CrO_6^{9-}	MnF_6^{2-}	MnF_6^{4-}	$MnCl_6^{4-}$	FeF_6^{3-}	FeO_6^{9-}	NiF_6^{4-}	$NiCl_6^{4-}$
Configuration		d^3	d^3	d^3	d^3	d^5	d^5	d^5	d^5	d^8	d^8
f_ϱ (%)	MSXα[a]	−4.8	−10.2	−3.3	−7.2	2.4	3.5	7.9	9.0	6.3	10.4
	MCZDO[b]	−2.1			−2.0	2.2		6.2		0.4	
	CNDO[c]	−0.0			−0.0	2.4		7.4		1.4	
	experiment			−3.6±0.9[f]		1.2[h]			6.8±0.6[f]		
f_π (%)	MSXα[a]	1.0	0.4	0.3	1.5	0.7	0.5	2.2	3.2	0.0	0.1
	MCZDO[b]	2.5			4.5	0.3		1.2		0.0	
	CNDO[c]	0.7			2.3	0.2		0.7		0.0	
	experiment			3.5±0.6[f]		1.0[h]			1.1±0.4[f]		
$f_\sigma - f_\pi$ (%)	MSXα[a]	−5.8	−10.5	−3.6	−8.7	1.7	3.0	5.7	5.8	6.3	10.4
	MCZDO[b]	−4.6			−6.5	1.9		5.1		0.4	
	CNDO[c]	−0.7			−2.4	2.2		6.7		1.4	
	experiment	−4.9		−7.1±0.7[f]	−9.2[g]	0.2[d]	3.9±0.4[i]	3.4–3.8[j]	5.7±0.7[f]	3.8[k]	7.3[m]
		−4.9[d]				0.3–1.2[e]				3.4[k]	

[a] This paper, see also Ref. [21].
[b] Ref. [22].
[c] Ref. [23].
[d] NMR, Ref. [9]
[e] ESR, Refs. [24, 25].
[f] Estimated in Ref. [26] using ENDOR and neutron scattering results of Ref. [27].
[g] ESR, Ref. [28].
[h] Estimated using NMR of Ref. [9] and neutron scattering results of Ref. [29].
[i] ESR, Ref. [14].
[j] ESR, Refs. [25, 28].
[k] NMR, Ref. [30].
[l] ESR, Ref. [25].
[m] NMR, Ref. [31].

In order to study the influence of the next nearest neighbours calculations were also carried out on the larger clusters $CrO_6Al_6^{9+}$ and $FeO_6Al_6^{9+}$ with a Watson sphere charge equal to $-9e$. Experimental results have been obtained for the spin density coefficients on Al^{3+} in Cr:$LaAlO_3$ and Fe:$LaAlO_3$ [11]. For Cr^{3+} the f_σ of O was increased to -3.9% and f_π increased to 1.4% and for Fe^{3+} f_σ decreased to 5.8% and f_π increased to 3.8%. The calculated "supertransferred" hyperfine structure parameters on the Al^{3+} ion were much too large, a fact which may have to do with the negatively charged Watson sphere. This question will be examined further in the future. The calculations show, however, that f_σ and f_π are sensitive to the next neighbours, and that the latter should be included in the calculations. It is not possible to represent them by just an electrostatic field, as has been done in several works.

f_σ is considerably larger for a heavier halogen ion. This is in agreement with experiments, for instance a larger $f_\sigma - f_\pi$ for $MnCl_6^{4-}$ than for MnF_6^{4-} [14]. Larger charge transfer in the bonding orbitals is considered equivalent to a stronger covalent bond. The antibonding orbital is at the same time more antibonding with higher orbital energy. Larger covalency in σ-orbitals than π-orbitals is thus consistent with the fact that the antibonding σ^*-orbitals have larger orbital energies than the antibonding π^*-orbitals. The calculated orbital energy difference $\varepsilon(\sigma^*) - \varepsilon(\pi^*)$ for the higher halides, however, is smaller than for the fluorides [21] although the σ-bonding, but not the π-bonding, is stronger. This is quite remarkable and confirms the well-known fact that the spectrochemical series does not correlate well with bonding strength.

5. Isotropic Hyperfine Interactions

The isotropic part of the hyperfine interaction may be written [1]

$$A_s = \frac{1}{2S}\frac{16\pi}{3} g_N \beta \beta_N [\varrho_\uparrow(\boldsymbol{R}_a) - \varrho_\downarrow(\boldsymbol{R}_a)] \tag{11}$$

$\varrho_\uparrow$ and $\varrho_\downarrow$ are defined by Eq. (3), and evaluated at the appropriate nuclei $\boldsymbol{R}_a$. The contact term at the central ion nucleus $4\pi[\varrho_\uparrow(0) - \varrho_\downarrow(0)]$ is difficult to obtain theoretically since the positive contribution from the valence orbitals and the negative contribution from the central ion core due to spin-polarization almost cancel [35]. In this paper we will only be concerned with the ligand contact term $4\pi[\varrho_\uparrow(\boldsymbol{R}_L) - \varrho_\downarrow(\boldsymbol{R}_L)]$ which gives the isotropic contribution to the transferred hyperfine interactions. The calculated results are given in Table 3, where we have also translated the spin-density at the nucleus into fractions of the charge density at the nucleus for the highest s-orbital, i.e. $2s$ for F and O and $2s$ for Cl. These fractions can be directly compared to those evaluated in experiments.

In Table 3 the different contributions arise from the following sources:

(1) s-admixture into valence orbitals,

(2) polarization of highest s-orbitals of ligand,

(3) polarization of inner s-orbitals of ligand (ξ_0).

Regarding the polarization of the inner s-orbitals, it was only calculated in a few cases. In those cases it was found to be nearly proportional to the inner shell part

Table 3. Fermi contact term $4\pi[\varrho_{\uparrow}(\boldsymbol{R}_{\mathrm{L}})-\varrho_{\downarrow}(\boldsymbol{R}_{\mathrm{L}})]$ at ligand nucleus (a. u.)

Cluster		CrF_6^{3-}	$CrCl_6^{3-}$	CrO_6^{9-}	MnF_6^{2-}	MnF_6^{4-}	$MnCl_6^{4-}$	FeF_6^{3-}	FeO_6^{9-}	NiF_6^{4-}	$NiCl_6^{4-}$
d^n configuration		d^3	d^3	d^3	d^3	d^5	d^5	d^5	d^5	d^8	d^8
valence and	a_{1g}	−0.09	−0.11	−0.11	−0.11	0.01	0.01	0.12	0.10	0.08	0.06
outer core	t_{1u}	−0.23	−0.26	−0.25	−0.27	0.01	−0.01	0.31	0.20	0.22	0.13
orbitals	e_g	−0.12	−0.18	−0.27	−0.07	0.70	0.50	1.05	1.72	0.78	0.79
sum		−0.44	−0.55	−0.63	−0.46	0.72	0.50	1.45	2.01	1.08	0.98
inner core orbitals		0.19	0.14^{d}	0.11^{d}	0.26	-0.19^{d}	-0.06^{d}	−0.66	-0.62^{d}	0.31^{d}	-0.15^{d}
total		−0.25	−0.41	−0.52	−0.20	0.53	0.44	0.82	1.39	0.77	0.83
% of highest	MSXα[a]	−0.17	−0.30	−0.55	−0.13	0.37	0.33	0.57	1.47	0.53	0.62
ns orbital	CNDO[b]	−0.01			−0.03	0.34		0.62		0.15	
	exp.	-0.02^{c}		-0.14^{e}	0.10^{f}	0.52^{g}	0.40^{h}	0.81^{i}	1.05^{e}	0.45^{j}	0.58^{k}

[a] This paper.

[b] Ref. [23].

[c] NMR, Ref. [9]; ESR Refs. [25, 28].

[d] Estimated value, see text.

[e] ENDOR, Ref. [26].

[f] ESR, Ref. [28].

[g] NMR, Ref. [9]; see also Refs. [24, 25] (ESR).

[h] ESR, Ref. [14].

[i] ESR, Ref. [28]; see also Ref. [25] (ESR).

[j] NMR, Refs. [9, 30]; see also Ref. [25] (ESR).

[k] NMR, Ref. [31].

of the contact term for the free atom $\xi_0^{(a)}$

$$\xi_0 = \frac{f_\sigma + 2f_\pi}{n} \xi_0^{(a)} \tag{12}$$

where n is the number of unpaired spins for the free atom. In other cases $\xi_0^{(a)}$ was obtained in atomic calculations with the same $X\alpha$ exchange as in the cluster calculations and subsequently ξ_0 from Eq. (12). The contributions to the spin density at the nucleus from each shell is within 20% of the spin-polarized Hartree-Fock (SPHF) results [35, 36] (non-local exchange).

The inner shell contributions are sometimes in the literature obtained by orthogonalization of the inner shells to the valence shell. I examined this procedure in an atomic SPHF calculation for the fluorine atom. The 1*s* orbitals were frozen but spin-polarization of the 2*s* orbitals allowed. Subsequently the $1s\alpha$ and $1s\beta$ orbitals were orthogonalized to $2s\alpha$ and $2s\beta$ respectively. The resulting contact term using this procedure was 5.7 a. u. compared to the normal UHF value 1.7 a. u. (the calculations were carried far enough to be basis independent), which shows that orthogonalizing the 1*s* orbitals to the valence shell orbitals is not a permissible method.

A part of the contributions (1) and (2) above is an "atomic" contribution like (3). Another part is due to bonding effects. We may get an understanding of the nature of the latter part by studying a simple configuration interaction (CI) wave function for the high spin d^5 clusters of a type that was originally suggested by Hubbard *et al.* [37]

$$\Psi = C_0 |3d_{z^2}\alpha 2p_z\alpha 2p_z\beta 2s\alpha 2s\beta| + C_1 |3d_{z^2}\alpha 2p_z\alpha 3d_{z^2}\beta 2s\alpha 2s\beta| \tag{13}$$

The orbitals are here ordinary non-orthogonal, atomic orbitals. The wave function Ψ accounts for the transfer of β-spin from ligand to central ion in the bonding orbitals just like our one-determinantal MO wave function. This transfer is rather small as we have found which means that C_0^2 is close to one and C_1^2 quite small. A similar wave function was used by Taylor *et al.* to calculate the contact term on Al^{3+} in $Cr{:}LaAlO_3$ and $Fe{:}LaAlO_3$ [11]. Here we will only be interested in how the contact term on the ligand arises. To that end we calculate the best overlap (BO) orbitals of Ψ, i.e. those satisfying

$$\int \Psi \Phi_{BO} d_1 \dots d_N = \max\,, \tag{14}$$

where Φ_{BO} is the Slater determinant of the BO orbitals. By calculating these orbitals, which can be done by an iteration procedure [38]. we obtain directly a relationship between the CI function and the independent-particle model. The unnormalized best overlap orbitals are in the first iteration

$$\begin{aligned}
3d\alpha(BO) &= 3d\alpha + 2s\alpha\langle 3d|2s\rangle - 2p\alpha\langle 3d|2p\rangle \\
2p\alpha(BO) &= 2p\alpha + [2s\alpha\langle 3d|2s\rangle\langle 3d|2p\rangle - 3d\alpha\langle 3d|2p\rangle]a_1 \\
2p\beta(BO) &= 2p\beta + \frac{C_1}{C_0} 3d\beta + \frac{C_1}{C_0} 2s\beta\langle 3d|2s\rangle \\
2s\alpha(BO) &= 2s\alpha - [3d\alpha\langle 3d|2s\rangle + 2p\alpha\langle 3d|2s\rangle\langle 3d|2p\rangle]a_2 \\
2s\beta(BO) &= 2s\beta
\end{aligned} \tag{15}$$

where

$$a_1 = 1 - \langle 2s|3d \rangle^2 \approx 1$$

$$a_2 = C_0 + C_1 \langle 2p|3d \rangle (1 - \langle 2p|3d \rangle^2) \approx 1 \,. \tag{16}$$

The $2p\alpha$ and $3d\alpha$ admixtures into the $2p\alpha$(BO) and $3d\alpha$(BO) arise for orthogonality reasons. As we see there will be s-admixtures in all the orbitals $3d\alpha$(BO), $2p\alpha$(BO), $2p\beta$(BO). The largest admixture will be in $3d\alpha$(BO) where the admixture coefficient is $\langle 3d|2s \rangle$. In addition we find that some of the charge of $2s\alpha$(BO) is in $3d\alpha$ and $2p\alpha$. To sum up we will thus find a positive contribution to the spin density from the valence orbitals which are composed of metal $3d\alpha$ and $3d\beta$ and ligand $2p\alpha$ and $2p\beta$ orbitals and a negative contribution from the $2s$ orbitals. As we may see in Eqs. (15) these contributions tend to cancel each other. We will not here discuss the accuracy of this CI-LCAO approach, nor will we use it for evaluation of any numbers. It was found, however, that the calculated contributions by the multiple scattering independent particle model followed quite well the scheme implied by Eqs. (15).

We may assume that the "atomic" and "bonding" contributions to (2) are additive. The "atomic" contribution may be obtained in the same way as the one from (3) by using Eq. (12). With $X\alpha$ exchange ($\alpha = 0.72$) the contribution (2) is about the same as (3) for O and F but with the reversed sign. In SPHF (2) is about -115% of (3). The total contact term in the SPHF method for free O and F is thus -15% of the contribution from the $1s$ shell. The experimental value is about 1/2 of the SPHF value for the whole series from B to F [39–41]. The correlation corrections thus also seem to be proportional to the total accumulated spin density in the $2p$ orbitals. If we want to correct an experimental value for core-polarization, i.e. (2) plus (3) above we may thus use a rule like Eq. (12) where $\xi_0^{(a)}$ now is the experimental value of the contact term for the free atom. This was done by Davies *et al.* [42].

The agreement with experiments is fairly good except for the d^3 systems. Some trends are reproduced, however, for instance a larger value for MnF_6^{2-} than for CrF_6^{3-} and a smaller value for CrO_6^{9-} than for CrF_6^{3-}. When the larger cluster was tried for $Cr{:}LaAlO_3$ and $Fe{:}LaAlO_3$ a reduction to about one half of the value for CrO_6^{9-} was obtained. Since contact terms seem to be little dependent on next nearest neighbours [1] this may be an error reduction rather than a physical effect.

Unlike the case for the anisotropic hyperfine interactions it seems hard to directly interpret experimental contact terms in terms of a simple physical model. Our results do not, unfortunately, give any clue to the solution of this problem. In order to make efficient use of experimental contact terms for, for instance, structure determinations it is therefore necessary to carry out detailed calculations, preferably with a more reliable method than the one used here.

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