

Transition-Element Hexafluoride Systems in Ionic Lattices. A SUHF Molecular Orbital Study

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An unrestricted Hartree-Fock SCFMO method, based on the MCZDO method of Brown and Roby, suitable for computing spin densities in transition-element compounds, is described. The method is used to study spin densities on fluorine in Cs_2MnF_6 , K_2NaCrF_6 , K_2MnF_6 , K_2NaFeF_6 , KMnF_3 , RbMnF_3 and KNiF_3 using a "cluster" approximation in which a MF_6^{n-} unit is explicitly considered. Excellent agreement is obtained between calculated and experimental spin parameters. The effect of the lattice is incorporated by using the electrostatic approximation of Brown, O'Dwyer and Roby. The lattice potential for these highly symmetric systems is found to have little effect on spin densities and charge distributions, but it effects substantial stabilization of the anion molecular orbitals. A general feature of the results is that central-atom $4p$ orbitals are scarcely involved in bonding, this being confined to the $3d$ and to some extent the $4s$ orbitals. Comments are offered on the lack of spin symmetry in the unrestricted Hartree-Fock wavefunctions of these systems, and the need to evaluate the core hamiltonian as accurately as possible.

Es wird eine UHF-Methode, die sich auf das Verfahren von Brown und Roby stützt, zur Berechnung von Spindichten in Verbindungen der Übergangselemente beschrieben und auf folgende Systeme angewendet: Cs_2MnF_6 , K_2NaCrF_6 , K_2MnF_6 , K_2NaFeF_6 , KMnF_3 , RbMnF_3 und KNiF_3 mit MF_6^{n-} als Baustein. Die Übereinstimmung mit den experimentellen Spinparametern ist ausgezeichnet. Die elektrostatischen Gittereinflüsse werden mittels einer Näherung von Brown, O'Dwyer und Roby berücksichtigt. Sie haben allerdings nur geringe Änderungen der Spindichte und Ladungsverteilung zur Folge, bewirken aber eine wesentliche Stabilisierung der MOs der Anionen. In allen Fällen gehen die $4p$ -Orbitale kaum in die Bindung ein. Der Mangel an Symmetrie der UHF-Funktionen dieser Systeme wird diskutiert und auf die Notwendigkeit eines guten Rumpfpotentials hingewiesen.

Description d'une méthode SCF MO sans restrictions de spin, basée sur la méthode MCZDO de Brown et Roby, et appropriée au calcul des densités de spin dans les composés des éléments de transition. La méthode est utilisée pour étudier les densités de spin sur le fluor dans Cs_2MnF_6 , K_2NaCrF_6 , K_2MnF_6 , K_2NaFeF_6 , KMnF_3 , RbMnF_3 , et KNiF_3 ; on utilise une approximation «d'essai» dans laquelle une unité MF_6^{n-} est explicitement considérée. Un très bon accord est obtenu entre les paramètres de spin calculés et expérimentaux. L'effet du réseau est introduit en employant l'approximation électrostatique de Brown, O'Dwyer et Roby. Le potentiel du réseau de ces systèmes hautement symétriques a peu d'influence sur les densités de spin et les distributions de charge, mais il provoque une nette stabilisation des orbitales moléculaires de l'anion. Un trait général des résultats est la faible importance dans le liaison des orbitales $4p$ de l'atome central, les orbitales $3d$ et $4s$ jouant le rôle essentiel. L'absence de symétrie de spin dans les fonctions d'onde HF sans restrictions pour ces systèmes, et la nécessité d'évaluer l'hamiltonien de coeur aussi précisément que possible sont l'objet de commentaires.

Introduction

One of the difficulties to be faced in trying to develop an adequate molecular orbital treatment of inorganic complexes is the scarcity of experimental data that will serve as an unambiguous test of the reliability of approximate

wavefunctions for the ground states of these complexes. However, in the case of open-shell complexes it is sometimes possible to obtain fairly direct information, by ESR or NMR techniques, on the distribution of unpaired spin density within such complexes in crystalline environments. One of the most popular groups of crystals for this type of experimental study is that where first transition series metal ions are surrounded by coordination octahedra of fluoride ions. For the octahedral clusters within these crystals, direct information on bonding is available in the form of transferred hyperfine interaction parameters from ESR data, or shifts in the ^{19}F NMR resonance frequency, which reflect the transfer of spin density between the metal ion and the fluorine ligands in the crystals. These experimental data can be reduced to yield estimates of the spin density of p character associated with each fluorine.

Our aim has been to develop a MO method suitable for studying the electronic structures of these systems, using consistent and well-founded approximations.

Initially we have restricted the testing of our open-shell cluster wavefunctions to the prediction of charge densities and spin properties. We have studied the series of crystals Cs_2MnF_6 , K_2NaCrF_6 , K_2MnF_6 , K_2NaFeF_6 , KMnF_3 , RbMnF_3 and KNiF_3 , using a standard cluster approximation (i.e. an MF_6^- unit only is treated explicitly in the MO method). These were chosen to cover representatives of the high spin d^3 , d^5 and d^8 complexes, where the ground states can be described to moderate accuracy with single-determinant wavefunctions [1–3], and to yield information on the effect of the lattice on the cluster wavefunctions, for the various types of lattice encountered.

Where the octahedral cluster approximation is crystallographically accurate – isolated octahedra occur in the first four crystals mentioned – our MO method yields very satisfactory results, with predicted charge distributions being readily rationalized, and with spin properties accurately mimicking experimental magnitudes and trends. For the latter three crystals, of the cubic fluoroperovskite structure, our results show that the cluster approximation is not entirely adequate, for while reasonable charge distributions are predicted, some loss of agreement with experiment occurs in prediction of spin properties.

Method

To calculate spin distributions within these open shell complexes, a simplified form of the spin-unrestricted Hartree Fock (SUHF) method has been used, yielding “different orbitals for different spin”. We have selected a limited Slater type atomic orbital set as the basis for construction of valence shell molecular orbitals, by means of the variational LCAO-SCF procedure of Roothaan [4].

For systems containing heavy atoms such as those of the first transition series, many schemes of evaluation of the matrix elements occurring in this method [5], such as the semi-empirical scheme of Pople, Beveridge and Dobosh [6], break down because of the lack of required experimental and *ab-initio* data, especially for the basis sets we have chosen. However Brown and

Roby [7], after extensive investigations into the form and evaluation of the matrix elements of various approximate MO methods, have presented a completely general non-empirical scheme applicable to such systems. Their rotationally invariant [8] MCZDO method (integrals involving many-centre differential overlap, or charge distributions arising from the product of orbitals on different centres, only being neglected; the scheme lying in complexity between the CNDO and NDDO methods [8]) involves direct inclusion of all one- and two-centre one-electron integrals (three-centre nuclear attraction integrals being approximated by the Ruedenberg formula), and all one-centre two-electron integrals but only atom-atom averaged two-centre two-electron integrals. All other integrals are neglected. Integrals included are evaluated analytically using the *C*-function [9] method, in terms of the Slater type basis functions.

Generalization of the Brown-Roby MCZDO method to the open shell case yields the UHFMCZDO method used here, the matrix elements of which take the following form for the non-orthogonal basis set $\{\chi\}$ chosen:

$$\begin{aligned} {}^x F^\alpha {}^x C^\alpha &= S {}^x C^\alpha g^\alpha, \\ {}^x F^\beta {}^x C^\beta &= S {}^x C^\beta g^\beta. \end{aligned} \quad (1)$$

For the α (majority spin) electrons (similar equations apply to the β electrons),

$${}^x F_{\mu\nu}^\alpha = {}^x H_{\mu\nu} + G_{\mu\nu}^\alpha. \quad (2)$$

This separation into parts represents the separated interaction of valence electrons with atomic cores (nuclei and frozen, point-charge inner shells), $H_{\mu\nu}$, and with the other valence electrons, $G_{\mu\nu}^\alpha$. To attain pseudo-eigenvalue form for Eqs. (1), the Löwdin transformation [10] is applied. For the now orthogonal basis $\{\lambda\}$,

$${}^\lambda F^\alpha {}^\lambda C^\alpha = {}^\lambda C^\alpha g^\alpha \quad (3)$$

where

$$\begin{aligned} {}^\lambda F^\alpha &= {}^\lambda H + {}^\lambda G^\alpha, \\ {}^\lambda C &= S^{-\frac{1}{2}} {}^x C, \\ {}^\lambda H &= S^{-\frac{1}{2}} {}^x H S^{-\frac{1}{2}}, \end{aligned} \quad (4)$$

and, according to Ref. [7], for the form given below for $G_{\mu\nu}^\alpha$,

$${}^\lambda G \approx {}^x G. \quad (5)$$

The distinct cases are, for $\mu, \nu, \lambda, \sigma$ on centre A, and δ on centre B:

$$\begin{aligned} {}^x H_{\mu\mu} &= -I_\mu(X_A, Z_\mu^{\text{core}}) + \sum_{B \neq A} X_B \langle \mu | V_B | \mu \rangle + V_A^I, \\ {}^x H_{\mu\nu} &= \sum_{B \neq A} X_B \langle \mu | V_B | \nu \rangle, \\ {}^x H_{\mu\delta} &= \frac{1}{2} [-S_{\mu\delta} I_\mu - S_{\mu\delta} I_\delta + X_A \langle \mu | V_A | \delta \rangle + X_B \langle \mu | V_B | \delta \rangle] \\ &\quad + \sum_{C \neq A, B} X_C \langle \mu | V_C | \delta \rangle + \frac{1}{2} (V_A^I + V_B^I) S_{\mu\delta}, \end{aligned} \quad (6)$$

$$\begin{aligned}
 G_{\mu\mu}^{\alpha} &= \sum_{\lambda,\sigma}^A [P_{\lambda\sigma}(\mu\mu|\lambda\sigma) - P_{\lambda\sigma}^{\alpha}(\mu\lambda|\mu\sigma)] + \sum_{B \neq A} \sum_{\delta}^B P_{\delta\delta}(\text{AA}|\text{BB}), \\
 G_{\mu\nu}^{\alpha} &= \sum_{\lambda,\sigma}^A [P_{\lambda\sigma}(\mu\nu|\lambda\sigma) - P_{\lambda\sigma}^{\alpha}(\mu\lambda|\nu\sigma)], \\
 G_{\mu\delta}^{\alpha} &= -P_{\mu\delta}^{\alpha}(\text{AA}|\text{BB}).
 \end{aligned} \tag{7}$$

In the above

$$\begin{aligned}
 S_{\mu\delta} &= \int \chi_{\mu}(1) \chi_{\delta}(1) \, dv_1, \\
 (\mu\nu|\lambda\sigma) &= \iint \chi_{\mu}(1) \chi_{\nu}(1) r_{12}^{-1} \chi_{\lambda}(2) \chi_{\sigma}(2) \, dv_1 \, dv_2,
 \end{aligned}$$

and (AA|BB) is the weighted average (taken over all orbitals on each centre) Coulomb repulsion between an electron in any χ_{μ} on A with an electron in any χ_{δ} on B.

$$P_{\mu\nu}^{\alpha} = \sum_i^{\alpha} n_i^{\alpha} C_{i\mu}^{\alpha} C_{i\nu}^{\alpha}, \quad n^{\alpha} \text{ being the occupation number (1 or 0) for } \phi_i^{\alpha}, \text{ and}$$

$$P_{\mu\nu} = P_{\mu\nu}^{\alpha} + P_{\mu\nu}^{\beta}.$$

$X_B \langle \mu_A | V_B | \mu_A \rangle$ is the potential energy for an electron in orbital χ_{μ} on A, owing to the presence of centre B of core charge X_B .

Z_{μ} is the effective (screened) nuclear charge as seen by an electron in valence orbital χ_{μ} on that centre.

I_{μ} is the ionization potential of an electron in χ_{μ} . It arises because we invoke the Goepfert-Mayer-Sklar approximation [11]

$$\langle \mu_A | -\frac{1}{2} \nabla^2 + X_A V_A(r) | \mu_A \rangle = -I_{\mu}. \tag{8}$$

The value of I_{μ} is obtained from atomic spectral data [12] as a function of the core charge X_A , and the effective nuclear charge, Z_{μ} .

Since the anionic clusters or complexes are studied experimentally as part of a predominantly ionic crystal, the (considerable) effect of the electrostatic potential of the lattice upon the electronic structure of the cluster was incorporated by computing the potential by the Ewald method and including it in the Hamiltonian as described by Brown, O'Dwyer, and Roby [13]. In Eqs. (6), V_A^1 is the electrostatic potential of all "extra-cluster" ions in the lattice at centre A. All "extra-cluster" ions have attributed to them the current ionic charges each iteration, of the appropriate ion within the cluster¹, with the exception that alkali metal ions in these crystals are assumed unipositive throughout. All crystal structure data was taken from [14].

Basis Set

While some more accurate atomic orbital functions are available, the single exponent Slater type orbitals (STO's) were chosen in this work, to enable use of the Variable-Electronegativity Self Consistent Field (VESCF) technique [7, 13].

¹ For the homogeneous crystals investigated.

The VESCF method involves adjustment of orbital effective nuclear charges, Z_μ , (and hence their exponents, and radial distribution) as atomic charges and orbital occupations on each centre vary in the iterative approach to self consistency, by means of the formula [13]

$$Z_\mu = Z_\mu^{\text{core}} - (P_{\mu\mu} - 1)\sigma_{\mu\mu} - \sum_{v \neq \mu} P_{\nu\nu}\sigma_{\mu\nu}. \quad (9)$$

Z_μ^{core} is the core charge, reduced by the screening effect of all inner shell electrons. The use of this formula can accommodate different radial characteristics for AO basis functions belonging to the same atomic subshell but different molecular symmetry species; we have, however, constrained all basis functions of a particular atomic subshell to assume identical exponents and radial distribution. A limited VE approach was employed, in that only monocentric integrals were made VE parameters. Multicentre integrals were kept fixed to reduce the complexity of the computation; all these multicentre integrals were evaluated for the clusters MF_6^{n-} with exponents derived from an assumed $M^{+1} : \text{F}^{-(n+1)/6}$ charge distribution.

Deficiencies in the STO's themselves were in part allayed [15] by the use of Burns's [16] rules to determine the screening constants, $\sigma_{\mu\nu}$, of Eq. (9). With these rules, Hartree-Fock type radial dependence could be well reproduced away from the nucleus, but inaccurate values are produced for integrals depending on the region close to the nucleus. For this reason the GMS approximation was used (Eq. (8)) and for this reason all transition ion monocentric repulsion integrals were scaled with average scaling factors [17] obtained by comparing Burns STO integrals with those of Hartree-Fock functions for the ionic species (M^{+1}) assumed for two centre integral evaluation. A similar but empirically based ($I - A$) scaling factor was applied to fluorine monocentric two electron integrals.

The ability to use the VE procedure with STO's effectively allowing the atomic orbital basis functions to adjust to the molecular environment provides the greatest justification apart from the simplicity of integral evaluation, for this choice of basis function, the assumptions involved in the use of *free ion* functions thus being avoided.

The actual basis set was chosen for each octahedral cluster to represent transition ion $3d$, $4s$, and $4p$ orbitals, and fluorine $2p$ orbitals. Since we were predominantly interested in the prediction of spin properties, the $4s$ and $4p$ functions were included to study the effects of exchange stabilization of the lower a type MO's of some $4s$ and $4p$ character on the spin distribution within each complex. Inclusion of the fluorine $2p$ orbitals enabled estimates of the spin density transferred from the central ion to these orbitals to be obtained, this p -type spin distribution around each fluorine contributing to the anisotropic part of the fluorine hyperfine interaction tensor A . The isotopic part of A arising from a non zero spin distribution at each fluorine nucleus was not studied. Watson and Freeman [18] have indicated that both fluorine $1s$ and $2s$ orbitals make comparable contributions to this interaction, and the inclusion of both fluorine $1s$ and $2s$ functions for the cluster, a further 12 basis functions, would be beyond our present computation facilities. We have not, as yet, investigated the effect of inclusion of just fluorine $2s$ functions.

For interpretation of cluster wavefunctions in terms of the STO atomic orbital basis, the Löwdin eigenvectors from the SCF procedure were transformed to the STO basis, and the resulting eigenvectors subjected to a Mulliken population analysis [19].

Cluster Charge Distribution

For the seven systems studied in this work, K_2MnF_6 , Cs_2MnF_6 , K_2NaCrF_6 , K_2NaFeF_6 , $KMnF_3$, $RbMnF_3$ and $KNiF_3$, there is a crystallographic distinction that can be made, with reference to the octahedral cluster approximation that we have employed, between members of this series. In the first four systems isolated octahedral clusters do in fact exist in the lattices, whereas for the latter three systems, being perovskite lattices, individual fluorines taken to be associated with a particular cluster are in reality shared between two such clusters. We shall refer to these different groups as "isolated cluster", and "shared cluster" type lattices. However several general observations can be made on our results for the series of systems, without explicit regard for this distinction.

From the atomic-orbital occupancy for these systems, as derived by a Mulliken population analysis of our cluster wavefunctions (Tables 1 and 2) it appears firstly that the transition metal $4p$ orbitals are consistently occupied to a negligible extent, and are therefore not involved in bonding within these complexes. However a common feature of each calculation was the significant occupation of the central ion $4s$ orbitals (up to ~ 0.4 electrons), from which one can infer substantial involvement of the $4s$ orbital in the bonding of the octahedral fluoride complexes. These results would indicate that nothing but heuristic importance should be attached to the concept of effective bonding arising from d^2sp^3 hybrid orbitals in those systems, though the higher transition ion orbitals above the d orbitals cannot be disregarded.

It was found that the fluorine ligand $2p\pi$ orbitals were consistently almost completely occupied ($> 98\%$) consistent with the accepted non π -bonding characteristics of the fluorine ligand, covalent bonding occurring predominantly through the $2p\sigma$ orbitals. That the $2p$ subshells of each fluorine ion are almost completely filled (at most only ~ 0.4 electrons short of this) does indicate that the lower $2s$ subshell on each fluorine would remain almost completely occupied and so would not be appreciably involved in bonding and can be considered as "inner shell". However that does not preclude the $2s$ (or $1s$) subshells from contributing to the spin properties of the systems because substantial isotropic hyperfine interaction arises from differences in the *spatial* characteristics at the fluorine nucleus of the ϕ^a and ϕ^b in which these orbitals are involved.

In the complexes existing in perovskite lattices, predicted ionic charges on the intra-cluster ions indicate that these systems are predominantly ionic (Table 2), with central transition-ion charges being slightly lower ($< \sim 0.5$ protonic unit) than the "ionic" crystal field values, as one expects for lattices of this type. However for the other systems studied K_2MnF_6 , Cs_2MnF_6 , K_2NaCrF_6 (all d^3), and K_2NaFeF_6 (d^5) (Table 1), a combination of higher transition-metal oxidation

Table 1. Effect of lattice on cluster charge distributions in "Isolated-Cluster" type lattices (individual orbital occupations from Mulliken analysis)

	$MnF_6^{2-} (d^3)$		$CrF_6^{3-} (d^3)$		$FeF_6^{3-} (d^5)$	
	isolated	K_2MnF_6	isolated	K_2NaCrF_6	isolated	K_2NaFeF_6
M-F distance	1.74	1.74	1.933	1.933	1.910	1.910
Unit cell dimension	8.28	8.266	8.323
4s	0.134	0.139	0.168	0.172	0.360	0.366
4p	-0.011	-0.011	-0.005	-0.004	-0.000	0.000
3d σ	0.855	0.861	0.700	0.705	1.192	1.195
3d π	1.181	1.184	1.101	1.102	1.047	1.048
Total metal charge	+1.645	+1.621	+1.144	+1.124	+2.116	+2.100
2p σ	1.692	1.690	1.738	1.736	1.876	1.874
2p π	1.958	1.957	1.976	1.956	1.988	1.988
Total fluorine charge	-0.608	-0.604	-0.691	-0.687	-0.853	-0.850

Table 2. Effect of lattice on cluster charge distribution in "Shared-Cluster" type lattices (individual orbital occupations from Mulliken Analysis)

	$MnF_6^{4+} (d^5)$		$NiF_6^{4-} (d^6)$	
	isolated	$KMnF_3$	$RbMnF_3$	isolated
M-F distance	2.093	2.093	2.121	2.006
Unit cell dimension	4.186	4.242	4.012
4s	0.318	0.334	0.342	0.373
4p	0.006	0.006	0.008	0.023
3d σ	1.072	1.075	1.066	1.017
3d π	1.012	1.013	1.010	2.000
Total metal charge	+1.486	+1.459	+1.471	+1.524
2p σ	1.923	1.919	1.921	1.933
2p π	1.996	1.995	1.995	1.994
Total fluorine charge	-0.914	-0.910	-0.912	-0.921

states and the existence in these lattices of isolated octahedral anions, implying that such units are relatively stable internally, one expects covalency to play a greater part in bonding. This is borne out by our results. For the d^3 complexes transition ion charges are around 2 protonic units below the "ionic" values, though for FeF_6^{3-} , a d^5 complex, one finds less transfer of electronic charge from ligand to metal, consistent with the "extra stability of the half filled $3d$ subshell". However in this case the Fe $4s$ orbital is occupied to more than twice the extent of the corresponding orbital in the d^3 complexes.

That the predicted central ion charges in the d^3 systems are significantly lower than respective "ionic" charges, as compared to the d^5 and d^8 systems, is readily rationalized as being due to the non-occupancy of antibonding majority-spin molecular orbitals involving the σ bonding $d\sigma$ orbitals. When both the bonding and antibonding molecular orbitals involving the $d\sigma$ orbitals associated with a particular spin (i.e. $e_g^\alpha, e_g^{\alpha*}$) are occupied, no nett transfer of charge can of course occur from metal to ligand by way of electrons of that spin. For the d^3 systems, only the e_g^α bonding MO's are occupied, allowing extensive ligand-to-metal charge transfer through the σ bonding system, whereas for the d^5 and d^8 systems, since e_g^α and $e_g^{\alpha*}$ are both occupied, no such transfer can occur through the σ bonding majority-spin MO's.

Effect of Lattice on Cluster Charge Distributions

It can be seen from Tables 1 and 2 that the inclusion of the extra-cluster lattice potentials appropriate to each systems in its crystalline lattice has little effect on the cluster wavefunctions derived on the assumption that the cluster is completely isolated. At least we have demonstrated this for the cubic lattices considered here. In these cases, a large number of highly symmetrically disposed ions surround the clusters and so there is little electrostatic differentiation between central ion and ligand. The actual values of the extra-cluster electrostatic potentials at the central ion, and at the ligand are given in Table 3. Mention of their derivation was made earlier. It appears that for the cubic systems considered the central ion is in fact stabilized slightly with respect to the fluoride ions by the purely electrostatic potential of the surrounding lattice. This has an attendant small influence on the charge distribution. Overall however the

Table 3. SCF electrostatic potentials at cluster ion sites due to extra-cluster lattice (contribution to ${}^xH_{\mu\mu}$)

$\langle \mu V^1 \mu \rangle$ (eV)			
System	Lattice	μ on M	μ on F
MnF_6^{2-}	K_2MnF_6	-11.018	-10.420
	Cs_2MnF_6	-10.484	-10.076
CrF_6^{3-}	K_2NaCrF_6	-16.239	-15.924
FeF_6^{3-}	K_2NaFeF_6	-15.547	-15.216
MnF_6^{4-}	KMnF_3	-21.725	-20.944
	RbMnF_3	-21.398	-20.652
NiF_6^{4-}	KNiF_3	-22.648	-21.845

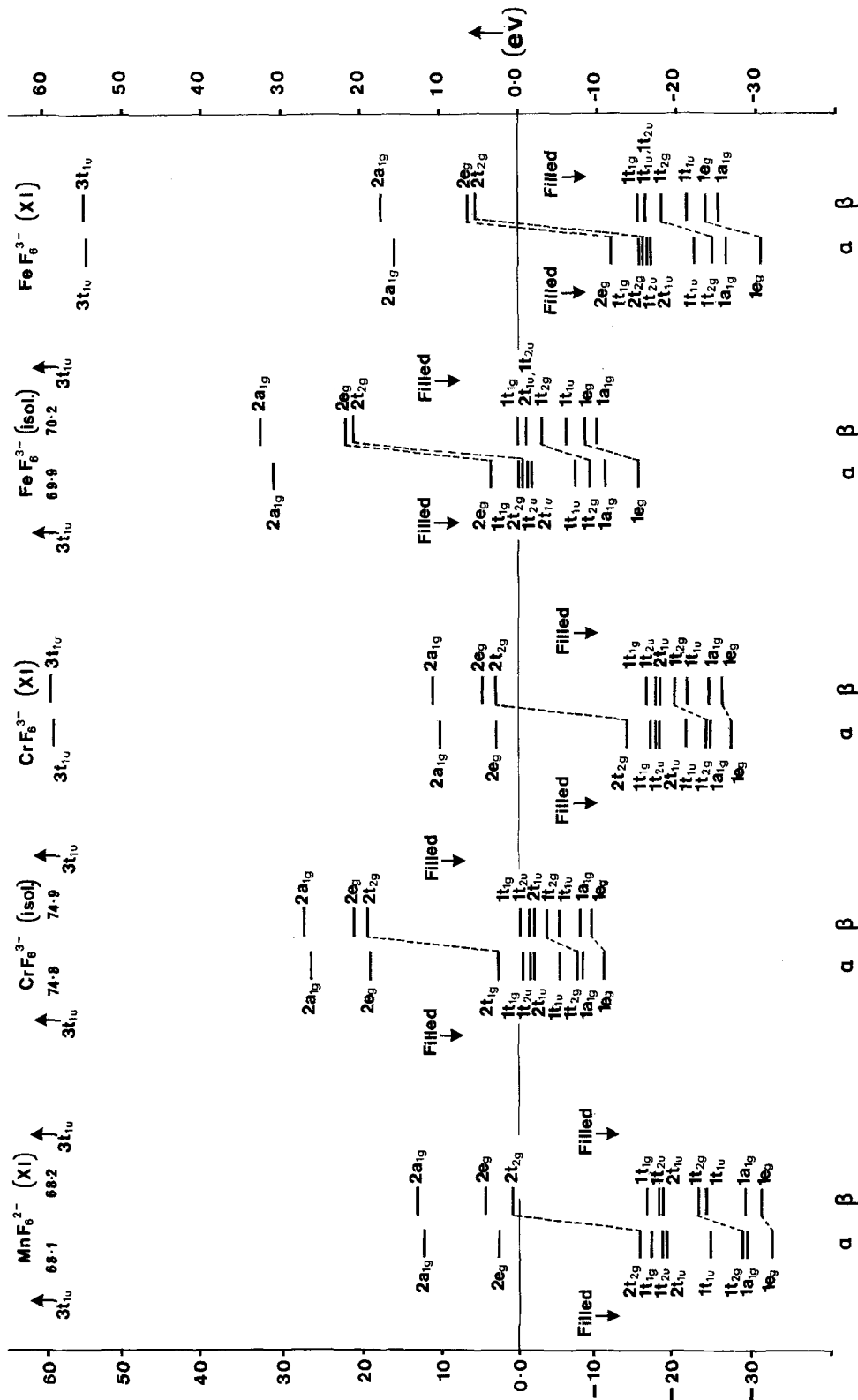


Fig. 1. MO Energy level diagrams for isolated cluster systems

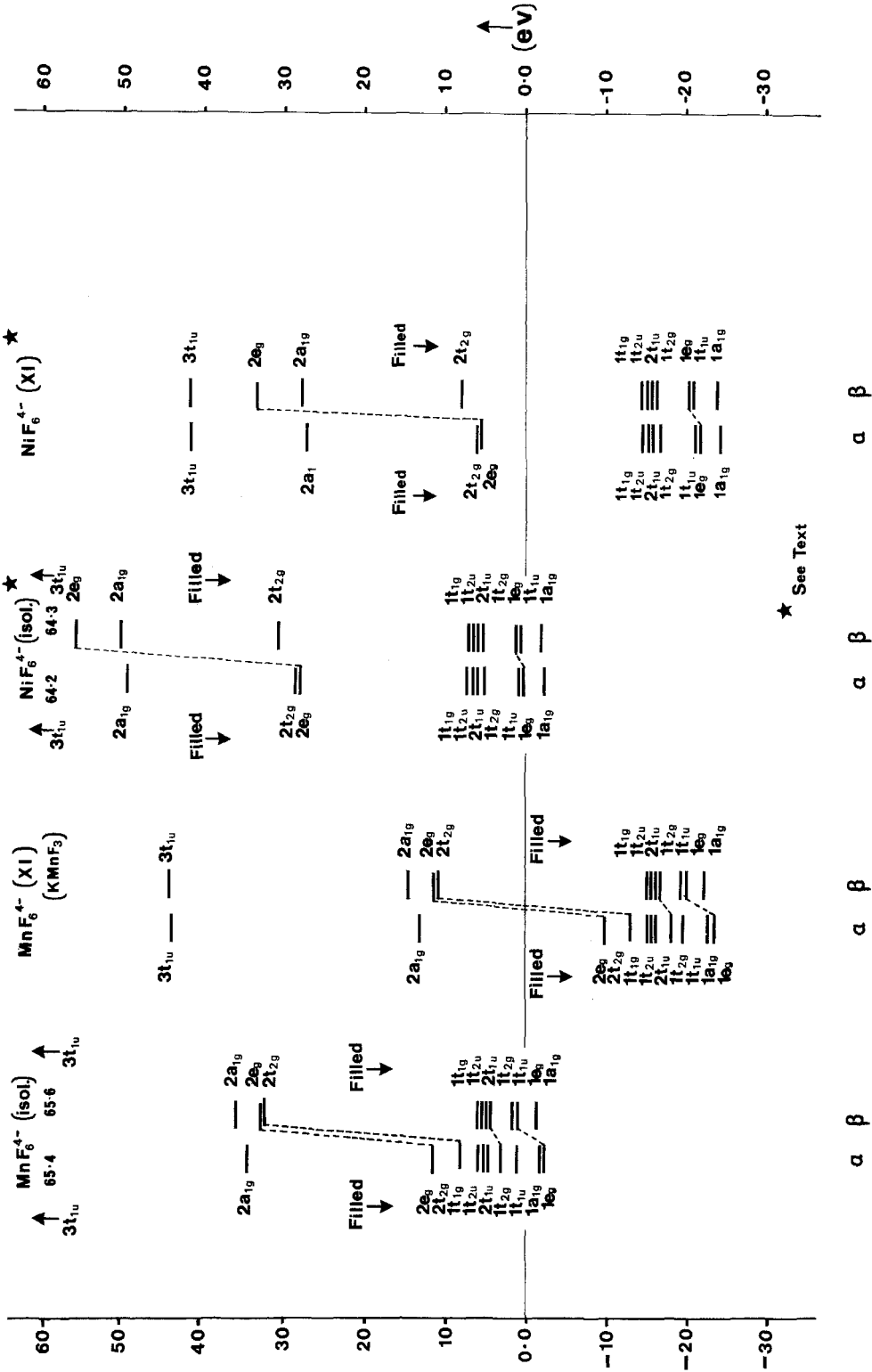


Fig. 2. MO Energy level diagrams for shared-cluster systems

lattice has a powerful stabilizing influence on the electronic structure of the anions (see below and Figs. 1 and 2).

In view of the apparently small effect of the extra-cluster lattice potential, it appears that the cluster itself dominates the behaviour of the component ions in the crystal. For instance, the clusters derived from the perovskite lattices, with high negative overall charges and longer internuclear distances, do yield a much more ionic charge distribution by calculation than the clusters derived from "isolated-cluster" type lattices.

Thus inspection of our predicted cluster charge distributions would indicate that our method does yield results which are in accord with our intuitive ideas on the ionicity of the different types of crystal, the perovskite or shared-cluster, and the isolated-cluster lattices. However we are disappointed that our representation of the extra-cluster lattice potential for the perovskite lattices had so little effect. In these cases (KMnF_3 , RbMnF_3 and KNiF_3), the isolated cluster approximation is an artificiality to the extent that each fluorine of a particular cluster is in reality directly and equally associated with two separate transition metal ions. In an assumed isolated MF_6^- unit therefore the electron donation of each fluorine ion to the single transition ion considered must be over-emphasized. We had hoped that inclusion of the extra-cluster lattice potential would in fact decrease the individual fluorine-to-metal electron transfer to at least in part allow for this artificiality. It would seem that our partitioning of the perovskite lattices is in fact too severe an approximation chemically, or at least that our treatment of the external lattice is inadequate. This point will be returned to in our discussion of cluster spin distributions.

Spin Distributions Derived from Cluster Wave Functions

One feature of our cluster wavefunctions for these high spin systems with from 2 to 5 unpaired electrons is the large exchange stabilization of the bonding majority-spin molecular orbitals compared with the corresponding minority-spin MO's (Fig. 1). The effects of exchange stabilization are large simply because of the large number of unpaired electrons in those systems, as compared to, say, organic radicals. This large preferential stabilization of the bonding majority-spin MO's within these clusters, combined with the significant involvement in these MO's of central ion orbitals that would be unoccupied in the ground state free ion, leads to a substantial excess of majority-spin electrons (Mulliken population) in these higher transition-ion atomic orbitals that are included in the basis set.

The central ion $4p$ atomic orbitals apparently too high in energy to be appreciably involved in the lower bonding MO's, but the $4s$ orbitals, and, for the d^3 systems, the $3d\sigma$ orbitals, show quite large nett majority-spin densities (Tables 4 and 5). Since these orbitals are involved in bonding MO's of local σ symmetry, the excess majority-spin of these orbitals arises from a transfer of positive spin density from the fluorine $2p\sigma$ orbitals, yielding a significant *negative* contribution to the spin density of these fluorine orbitals. This effect is most pronounced in the d^3 cases MnF_6^{2-} , CrF_6^{3-} where the $3d\sigma$ orbitals are close in energy to the highest occupied MO's. The Mulliken analyses reveal quite

Table 4. Effect of lattice on cluster spin distribution in "Isolated-Cluster" type lattices (percentage spin densities per orbital from Mulliken analysis)

	$\text{MnF}_6^{2-} (d^3)$		K_2MnF_6		$\text{CrF}_6^{3-} (d^3)$		K_2NaCrF_6		$\text{FeF}_6^{4-} (d^5)$	
	isolated				isolated				isolated	
$f_{4s} \%$	0.455		0.463	0.467	0.626		0.639		0.961	
$f_{4p} \%$	-0.009		-0.010	-0.010	-0.005		-0.005		0.003	
$f_{3d\sigma} \%$	5.674		5.667	5.662	6.221		6.256		80.807	
$f_{3d\pi} \%$	81.891		81.589	81.448	89.950		89.807		95.213	
Total metal spin (electrons)	2.5745		2.5653	2.5610	2.8290		2.8256		4.4851	
$f_{2p\sigma} \%$	-1.968		-1.966	-1.965	-2.178		-2.192		6.238	
$f_{2p\pi} \%$	4.530		4.605	4.641	2.514		2.550		1.172	
Total fluorine spin (electrons)	0.0709		0.0724	0.0732	0.0285		0.0291		0.0858	
$\langle S^2 \rangle$ Cluster (SUHF function)	a	a		3.756282	3.758229		3.758294		8.750124	
$(f_{\sigma} - f_{\pi}) \%$	-6.497		-6.571	-6.606	-4.692		-4.742		+5.066	

a Not Calculated.

Table 5. Effects of lattice on cluster spin distribution in "Shared-Cluster" type lattices (percentage spin density per orbital from Mulliken analysis)

	$\text{MnF}_6^{4-} (d^5)$		KMnF_3		RbMnF_3		$\text{NiF}_6^{4-} (d^8)$		KNiF_3	
	isolated				isolated		isolated		isolated	
$f_{4s} \%$	1.287		1.332	1.374	1.422		0.563		0.580	
$f_{4p} \%$	0.007		0.007	0.008	0.008		0.011		0.011	
$f_{3d\sigma} \%$	92.809		92.458	93.668	93.367		93.398		98.346	
$f_{3d\pi} \%$	98.816		98.571	99.009	98.956		0.0		0.0	
Total metal spin (electrons)	4.8337		4.8252	4.8576	4.8505		1.9739		1.9731	
$f_{2p\sigma} \%$	2.183		2.292	1.882	1.974		0.440		0.455	
$f_{2p\pi} \%$	0.294		0.311	0.246	0.259		-0.003		-0.003	
Total fluorine spin (electrons)	0.0277		0.0291	0.0237	0.0249		0.0043		0.0045	
$\langle S^2 \rangle$	8.750255		8.750264	8.750286	8.750298		a		2.000043	
$(f_{\sigma} - f_{\pi}) \%$	+1.889		+1.982	+1.636	+1.715		+0.443		+0.457	

a Not Calculated.

large negative (minority-spin) spin densities in the F $2p\sigma$ orbitals, the contribution from exchange stabilization of the $3d\sigma$ orbitals being $\sim -2\%$ to each fluorine $2p\sigma$ orbital. The same effect on the $4s$ central ion orbitals leads to a smaller negative contribution (between -0.1% and -0.2%) to each F $2p\sigma$ orbital spin density, the magnitude of this contribution per orbital depending roughly on the number of unpaired electrons in the cluster, and hence on the magnitude of the exchange stabilization of the lower MO's, a result that has been inferred for some time (see for example Refs. [20a, b]). The exchange stabilization of the central ion $4p$ orbitals is also seen (Table 5) to lead to nett minority spin occupancy of the fluorine $2p\pi$ orbitals in the d^8 case.

Effect of Lattice on Cluster Spin Distributions

When we consider the electronic spin distributions within clusters that are ostensibly similar in isolation, we find that there are essential differences preserved between the various clusters when they are considered in the context of their actual crystalline environments (Tables 4 and 5). Just as in our discussion of the charge distribution in these systems, the extra-cluster lattice potentials again have no great effect on the cluster spin distribution, but the differences in lattice types are maintained by virtue of different characteristics of clusters taken from the two lattice types (higher overall negative charge and longer bondlengths for clusters derived from perovskite lattices). A comparison of the systems FeF_6^{3-} and MnF_6^{4-} in their appropriate lattices reveals the essential difference in behaviour of the covalent (FeF_6^{3-}) and predominantly ionic (MnF_6^{4-}) complexes. The more ionic fluorine ions of the latter, with their $2p$ subshells being almost filled, cannot accommodate a large differentiation between the majority-spin and minority-spin orbitals, and so the nett density to be attributed to each of the orbitals is much less than in the FeF_6^{3-} case. The difference in behaviour of the two classes can be seen further by a comparison of the values of the "spin indicator" for these systems [$(f_\sigma - f_\pi)$, the difference in the spin densities of the fluorine $2p\sigma$ and $2p\pi$ orbitals, a quantity most readily obtainable from experiment] predicted by us, and those obtained experimentally.

Our results are in excellent quantitative agreement with experiment for all of the "isolated-cluster" lattice complexes (the d^3 systems MnF_6^{2-} and CrF_6^{3-} and the d^5 system FeF_6^{3-}). The agreement is not so satisfactory for "shared-cluster" lattices, for reasons discussed below.

It is interesting that early values of this quantity derived from available NMR results generally indicated that for d^3 complexes $(f_\sigma - f_\pi)$ is large and negative, for d^5 complexes $(f_\sigma - f_\pi)$ is small and positive and for d^8 complexes, large and positive, which was rationalized in terms of earlier restricted Hartree Fock theories by the absence of σ bonding in d^3 complexes ($t_{2g}^3 e_g^0 \rightarrow f_\sigma = 0$), the absence of π bonding in d^8 complexes ($t_{2g}^6 e_g^2 \rightarrow f_\pi = 0$) and the effective cancellation of non zero f_σ and f_π values for the d^5 systems.

Aside from the fact that the restricted Hartree Fock theory by no means presents the whole picture [reference the large negative contribution of f_σ to $(f_\sigma - f_\pi)$ in the d^3 complexes], if we examine our results in terms of this

supposed experimental trend, our large positive value for $(f_\sigma - f_\pi)$ for the FeF_6^{3-} (d^5) system must appear anomalous. However our result is in quantitative agreement with experiment for this system².

Despite a lack of quantitative agreement for the perovskite type lattices (Table 6), our method does in fact partially reproduce the substantial decrease in $(f_\sigma - f_\pi)$ on going from K_2NaFeF_6 to KMnF_3 where the two clusters are superficially similar high spin d^5 complexes.

One general point can be made about the spin distribution within all these clusters, by reference to the calculations MnF_6^{2-} in K_2MnF_6 and Cs_2MnF_6 , and the *isolated* complex calculations for MnF_6^{4-} with respective Mn-F distances 2.093 and 2.121 Å. A comparison of the first two calculations, where only the lattice dimension is different but the cluster dimensions remain the same (i.e. different extra-cluster lattice potential) shows that the spin distribution [in particular $(f_\sigma - f_\pi)$] is not sensitive to the external lattice in the "isolated-cluster" lattices. However a comparison of the latter two calculations, where only the internal cluster dimensions are changed (V^l being zero in both cases), does reveal that the cluster spin distribution is very sensitive to small M-F distance changes.

In view of this we consider that our treatment is in fact capable of accounting for the experimentally observable effects of relaxation of fluoride ions of various host lattices on to various substitutional magnetic transition metal ions (T. P. P. Hall *et al.* [2]; Owen and Thornley [23]).

If the metal-ligand distance for these clusters were at an optimum value for the isolated units, on increase of bond distances one would expect the effects of π -type covalency to decrease more rapidly than σ type covalency, and so expect $(f_\sigma - f_\pi)$ to increase slightly. That the change in $f_\sigma - f_\pi$ found for the one instance of this that we investigated was in fact a decrease (1.889% to 1.636%) on going from isolated MnF_6^{4-} (2.093) to MnF_6^{4-} (2.127) is probably a feature of the distorted view of bonding obtained by considering an isolated cluster as being indicative of the bonding in a perovskite-type lattice. However we have not investigated the effects of fluoride ion relaxation for isolated-cluster type lattices as yet.

Comparison of Spin Densities with Experiment: Interpretation of Experimental Results

The choice of cubic crystals containing high spin d^3 , d^5 and d^8 transition metal ions, where there is an accurately octahedral disposition of fluorine ions around these ions considerably simplifies the data reduction, with corresponding increase in confidence limits of the parameters obtained from ESR and NMR spectra, because many terms in the general phenomenological spin hamiltonians become negligibly small in these cases. Accordingly, this type of system has received extensive study.

² Hall *et al.* [2], some years after the high experimental values for Fe^{3+} were reported [21, 22] reiterated the proposition that $f_\sigma - f_\pi$ should be small for d^5 ions generally and offered little comment on their own Fe^{3+} results.

The data of interest to this work – the elements of the fluorine transferred hyperfine interaction tensor A , which occurs in the spin hamiltonians as a term $S.A.I$ – can be obtained by either method. The isotropic or contact contribution to A arises from the non zero nett electronic spin at the fluorine nuclei (in particular that associated with fluorine 1s and 2s orbitals), whereas the anisotropic contribution to A arises from the dipolar interaction with the nuclear spin of the unpaired electronic spin associated with the p orbitals of that centre (A_σ, A_π, A'_π), and from similar interaction of the central ion “3d” electronic spin with the fluorine nucleus, A_D . These contributions are of comparable magnitude. The (smaller) interactions of p type spin distributions on other fluorines with the particular nucleus considered, are generally neglected (but see [24]).

Individual contributions from the three $2p$ orbitals on each fluorine cannot be determined experimentally since the dipolar tensor is traceless. For this reason experimental studies are carried out on systems where each fluorine has tetragonal symmetry, so that the dipolar contribution to A of the fluorine spin can be expressed by quantities $A_\sigma - A_\pi$ and $A_\pi - A'_\pi = 0$. However to obtain $A_\sigma - A_\pi$ one must first make allowance for the $3d$ dipolar contribution A_D : Several simple ways of estimating A_D have been proposed [1, 3, 24] differing in detail. The different possibilities in evaluating A_D may largely account for the discrepancies in $f_\sigma - f_\pi$ values quoted by various authors. Owen and Thornley [23] have summarized experimental results using a simplified but standardized method of data reduction, and their quoted values serve as a general indication of the range of $(f_\sigma - f_\pi)$ values encountered in these systems.

However for purposes of comparison of our results with experiment, we consider that the results of Helmholz *et al.* [21, 22, 24] are most significant since they have investigated the systems MnF_6^{2-} , CrF_6^{3-} , FeF_6^{3-} by standard ESR methods but using host lattices for these ions where the intra-cluster M–F distances are as close as possible to those of the corresponding pure crystal clusters, which data we have used in our calculations. This is important since reference to Table 6 will reveal a marked dependence of $(f_\sigma - f_\pi)$ on host lattice M–F distances, even though some relaxation of the fluoride octahedra onto the substituted magnetic atom undoubtedly occurs. They have also taken account of the central metal dipolar contribution to A in a detailed manner.

We have converted their $A_\sigma - A_\pi$ values to percentage spin densities using the method employed by Hall *et al.* [2], with $\langle r^{-3} \rangle$ for the fluorine orbitals taken to be that of the fluorine ion F^- (Froese [25]), this value being most appropriate to the highly charged fluorine ions occurring in these systems.

Spin densities calculated, and those that we have derived from Helmholz's data, together with those of Owen and Thornley are summarized in Table 6.

In view of all the approximations involved in obtaining $f_\sigma - f_\pi$ values from experiment and from theory, the somewhat remarkable agreement of our results with those of Helmholz for very similar isolated cluster systems may well be fortuitous, but in any case our method appears to produce good results for these systems, and it seems likely that it will provide realistic spin distributions for any transition element systems where the isolated cluster approximation is crystallographically valid.

Table 6. Comparison of calculated values of fluorine transferred hyperfine interaction parameter ($f_\sigma - f_\pi$) % with experiment

	Experimental				Calculated r
	M-F/a Å ^d	NMR ^a	ESR ^b	ESR ^{c,e}	
Mn: K ₂ MnF ₆	1.74/8.28				-6.606
Mn: Cs ₂ MnF ₆	1.74/8.92				-6.571
Mn: Cs ₂ GeF ₆	1.77/9.009		-9.2	-6.12	
Cr: K ₂ NaCrF ₆	1.933/8.266	-4.90	-4.9		-4.74
Cr: K ₂ NaGaF ₆	1.90/8.20		-5.3	-2.90	
Cr: KMgF ₃	1.994		-4.9		
Fe: K ₂ NaFeF ₆	1.910/8.323				+5.14
Fe: K ₂ NaGaF ₆	1.90/8.20		+3.4	+7.63	
Fe: KMgF ₃	1.994		+3.4		
Mn: KMnF ₃	2.093	+0.19	+0.2		(+1.98) ^e
Mn: RbMnF ₃	2.121		+0.3		(+1.72) ^e
Mn: KMgF ₃	1.994		+0.3, 1.2		
Mn: KF	2.673		+2.1		
Ni: KNiF ₃	2.006	+3.30	+3.8		(+0.46) ^e

^a NMR data of R. G. Shulman and K. Knox taken from Ref. [2].

^b Standardized data of Ref. [23].

^c ESR data of Ref. [22, 24].

^d Structural data of Ref. [14].

^e See text.

^f Data from Mulliken analysis of spin unrestricted wavefunctions.

We mention again that we do not consider our treatment of the extra-cluster lattice in perovskite lattices as having only a simple electrostatic effect on the cluster is sufficient. If the "shared-cluster" calculations are viewed in a slightly different light, the results on spin distribution may not be as poor as they seem. The results Hall *et al.* [26] quote for magnetic ions in various host lattices reveal that, say, a substitutional Mn²⁺ in the more expanded non-magnetic lattices (e.g. NaF and KF) does in fact produce a rather large ($f_\sigma - f_\pi$) constant on each fluorine as compared to the more compact and magnetic perovskite lattices. If one disregards the shared-cluster calculations with extra-cluster potentials included, and one looks at the isolated "shared-cluster" results as being indicative of the situation where the fluoride ions of an exploded non-magnetic host lattice have relaxed to a pseudo-equilibrium distance³ from the substituted ion then our values of ($f_\sigma - f_\pi$) for this system are by no means at odds with the results for Mn⁺² in NaF and KF. Our results for NiF₆⁴⁻ remain unsatisfactory however, though this is almost certainly due to the lack of explicit core ionization potential data (used to obtain $-I_n$) for the cases Ni⁺⁸ 3d¹ → 3d⁰, 4s¹ → 4s⁰ and 4p¹ → 4p⁰. Values that we used were extrapolated from the preceding isoelectronic transition ion series and our estimate may have been even 10 eV out for the three cases. Likewise, only estimates of Burns to Hartree-Fock scaling factors were obtained for monocentric nickel ion repulsion integrals. It can be seen (Fig. 2) that uncertainties in these two areas for this case lead to an unsatisfactory MO energy level structure. Undoubtedly,

³ Taken to be the M-F distance of the pure perovskite lattice.

empirical ionization potentials could be varied, as well as the monocentric repulsion integral scaling, to obtain a satisfactory MO level structure, but we include the original NiF_6^{4-} cluster calculations as an indication of the sensitivity of the method to these parameters, and as a contrast to all other calculations, where straightforward application of our method led to very satisfactory results.

Molecular Orbital Energies

The calculated molecular orbital energy values are shown in Figs. 1 and 2. The stabilization of the majority-spin orbitals, and particularly the large effect for e_g and t_{2g} orbitals (those incorporating the central atom $3d$ orbitals) is noteworthy. It is also evident that the electrostatic field of the lattice, although having only a slight effect on the charge distributions and the spin densities, has a large stabilizing effect on the energy of the anion (as expected from the values quoted in Table 3). The anions have substantial stability in the lattice but the implication of Figs. 1 and 2 is that they would be highly unstable in isolation in vacuo.

Merits of Spin Annihilation

There has been much discussion in the literature about the relative merits of the spin-unrestricted Hartree-Fock method as a means of obtaining meaningful estimates of spin densities for open-shell systems. The major criticism of the SUHF function is that it is not an eigenfunction of \hat{S}^2 , though by construction it is an eigenfunction of \hat{S}_z . Amos and Snyder [26] proposed annihilation of the major spin contaminant (the contribution to the ground state SUHF function of the lowest energy higher spin multiplet for the system) and subsequent reinvestigation of spin properties for this new wavefunction. Sando and Harriman [27] compared SUHF function before and after annihilation with the comparatively more exact spin extended HF function and concluded that the SUHF wavefunction yields negative spin densities too large in magnitude, while annihilation seems to over-compensate for this.

The SUHF results before and after single annihilation or projection do however appear to bound the results of the more exact method and experiment, with closest agreement with experiment being afforded by the unprojected SUHF results.

We have investigated the effects of spin annihilation for wavefunctions for these high-spin systems (Table 7), and our results are completely in accord with those obtained for the smaller hydrocarbon radicals. For our systems of high multiplicity, our values of $\langle \hat{S}^2 \rangle$ before and after annihilation reveal that spin contamination of the SUHF function arises almost completely from a contribution from the next highest spin multiplet. We find that spin annihilation invariably has the effect of reducing the effects of exchange stabilization (or spin polarization) in the MO's to which the higher central ion $4s$ (and $4p$) orbitals contribute (and in the d^3 case, the d_σ orbitals), lowering the positive spin of these higher metal orbitals, and consequently reducing the nett negative spin of the fluorine $2p\sigma$ orbitals to which they are bonded.

Table 7. Effect of spin annihilation of SUHF wavefunctions, as monitored by fluorine orbital spin densities, f_σ and f_π . $\langle \hat{S}^2 \rangle$ refers to each cluster as a whole

	SUHF wavefunction			After annihilation			$(f_\sigma - f_\pi)\%$
	$\langle \hat{S}^2 \rangle$	f_σ	f_π	$\langle \hat{S}^2 \rangle$	f_σ	f_π	
K_2MnF_6	3.756282	-1.965	-4.641	3.750011	-0.543	4.630	-5.174
K_2NaCrF_6	3.758294	-2.192	2.550	3.750020	-0.592	2.543	-3.135
K_2NaFeF_6	8.750122	6.336	1.196	8.749998	6.441	1.196	+5.244

Table 8. Comparison of UHFMCZDO results with those derived with a simplified core matrix element evaluation scheme

	Simplified		UHFMCZDO	
	Central ion charge	$(f_\sigma - f_\pi)\%$	Central ion charge	$(f_\sigma - f_\pi)\%$
Cs_2MnF_6	+2.132	-2.331	+1.621	-6.571
K_2NaCrF_6	+1.648	-1.390	+1.124	-4.742
K_2NaFeF_6	+1.700	+1.523	+2.100	+5.140

We are unable to conclude which set of spin densities is more in accord with experiment⁴ due to the rather small effects of annihilation in all but the d^3 cases, and the rather large uncertainties in the quoted "experimental" values, which were referred to earlier.

We also note that spin annihilation does not appreciably affect the charge distributions of these systems.

Conclusion

Our method is applicable to the majority of the systems investigated by ESR techniques, and yields realistic and fairly reliable quantitative information of the spin and charge distributions within the cluster approximation approach to these systems. However the treatment of periodic magnetic lattices such as the perovskites is not entirely satisfactory, and further investigation of these systems will only be of value once the octahedral-cluster approximation is discarded, perhaps in favour of the solution of the periodic MF_3^- system.

Appendix

Comparative calculations were run for several crystals using a simplified technique for evaluating H (the CNDO procedure of Brown, James and O'Dwyer [13]). The results obtained (Table 8) were clearly inferior to those obtained by the method described in the next, when the hyperfine interaction parameter ($f_\sigma - f_\pi$) is considered.

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⁴ Nakatsuji *et al.* [28] have in fact exposed a definite relationship between the two.

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