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Analysis of transferred spin densities in the 3d³ | VF₆ | ⁴⁻ complex, through L.C.A.O.-M.O. calculations

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Abstract. — We use different models, within the L.C.A.O.-M.O. framework to calculate the transferred spin densities for the (t²g)³ | VF₆ | ⁴⁻ complex in the KZnF₃ host. The results which are obtained for 03BB03C0 are not very sensitive to the choice of the method. In comparison with previous works on the (t²g)⁶ (e₉)² | NiF₆ | ⁴⁻ complex, the present work may constitute a step towards the (t²g)³ (e₉)² | MnF₆ | ⁴⁻ or | FeF₆ | ³⁻ complexes in which σ and π spin transfers are still ambiguous.

1. Introduction. — It has been recently shown, for (3d)⁵ (Mn²⁺ F₆⁻) or (Fe³⁺ F₆⁻) octahedral clusters in fluorides, that the different techniques : N.M.R., R.P.E., neutron diffraction on an antiferromagnet [1], E.N.D.O.R. [2, 3, 4], P.A.C. [5], which are used to estimate spin densities on the ligands, lead to conflicting [4] or curious results [5]. The reason for that lies in the fact that a single technique cannot decide both for σ and π transfers. A couple of appropriate techniques have to be used : neutron diffraction and N.M.R. on ligands [1], hyperfine field measurements at distant nuclei by E.N.D.O.R. or P.A.C. and at ligand nuclei by E.P.R. or N.M.R. [3, 4, 5], for instance.

Theoretical models, based upon the L.C.A.O. framework, and overlap considerations are used to convert experimental results into terms of spin densities, i.e. into a quantitative insight on the electronic wave function. Actually, it is not astonishing that discrepancies, due to an over simplification of the theoretical models, occur by using a couple of techniques or another. A direct theoretical calculation of the L.C.A.O.-M.O.'s can be useful to cast some light on the problem. Unhappily, a L.C.A.O.-M.O. calculation on a (3d³)F₆⁻ | cluster needs to deal correctly with a two open shells problem (t²g)³ (e₉)² [6], and it seems reasonable to begin by testing theoretical models on simpler systems.

In this field AMF₃ hosts for (3d)ⁿ ions have been widely used, and many experimental results are available. A sequence with Ni²⁺ : (t²g)⁶ (e₉)², V²⁺ : (t²g)³, Mn²⁺ : (t²g)³ (e₉)² ions at the M²⁺ site of the host permits to treat both experimentally and theoretically single (e₉)² and (t²g)³ open shells before going to the (3d³) ions. In crystals doped with these ions, the actual ionic distances in the cluster do not differ too much from the half lattice parameter since a divalent ion substitutes for another divalent ion. Moreover, the outer crystal field which acts on the cluster is rather flat in this structure.

Since much work has been devoted to the Ni²⁺ ion [7] we study in this paper the V²⁺ F₆⁻ cluster. E.P.R. investigations permit to reveal an isotropic superhyperfine interaction which evidences either polarization of doubly occupied orbitals or a configuration interaction, complementary to the normal π transfer within the (t²g)³ configuration. We have searched for a simple calculation scheme, with a decent computer time consumption, able to account for the superhyperfine interaction (s.h.f.). Preliminary results have been reported elsewhere [8, 9, 10].

(*) E.R.A. 682.
2. Generalities and theoretical background. —

2.1 THEORETICAL BACKGROUND. — In the L.C.A.O.-M.O. framework for $\text{MF}_6$ complexes, electrons occupy a set of:

- antibonding M.O. $\Psi_i^A = N_i^A[\phi_i - \lambda_i \chi_i]$,
- bonding M.O. $\Psi_i^B = N_i^B[\chi_i + \gamma_i \phi_i]$ (2.1)

completed by a set of non bonding M.O. The index $i$ holds for the symmetry $t_2g$ ($\zeta_j$, $\eta_j$, $\zeta_j$) or $e_g$ ($u$, $v$). The $\phi_i$'s are (3d) metal orbitals. The $\chi_i$'s are linear combinations of 2s and 2p $F^-$ orbitals. They are usually labelled $\chi_d$ for $t_2g$ symmetry and $\pi$ bonding, $\chi_a$ and $\chi_b$ for $e_g$ symmetry and $\sigma$ or $b$ bonding. Their expressions can be found in reference [11]. The $N_i$'s are normalization constants. We shall admit that all inner A.O.'s and nuclei can be treated within a core approximation. The M.O.'s are assumed to be eigenfunctions of a S.C.F. hamiltonian:

$$h(r_1) \Psi_i(r_1) = \epsilon_i \Psi_i(r_1).$$ (2.2)

All bonding orbitals are doubly occupied with up and down spin electrons. Corresponding orthogonal antibonding orbitals are doubly occupied, empty or singly occupied with up spin, depending on the $(3d)^8$ configuration under investigation.

In that last case, the quantity of physical interest for spin transfers and superhyperfine interactions is [12]:

$$f_i \approx | \gamma_i |^2 + 2 S_i \gamma_i \downarrow + S_2^2 | \times k_i$$

in which $S_i$ is the overlap integral $\langle \phi_i | \chi_i \rangle$,

$$k_i = \frac{1}{4} \text{ for } i = t_2g \text{ or } k_i = \frac{1}{3} \text{ for } i = e_g.$$

Actually, within a restricted S.C.F. model built from orthogonal M.O.'s, this quantity does not differ from $k_i(\lambda_i \uparrow)$ which characterizes the singly occupied antibonding orbitals [1]. Therefore we may calculate either $\lambda_i \uparrow$ through an hamiltonian $h^A$ appropriate to antibonding orbitals or $\gamma_i \downarrow$ through and hamiltonian $h^B$ appropriate to bonding orbitals. Initially, Sugano and Shulman [13] (S.S.) developed an approximate S.C.F. hamiltonian $h^A$ for $| \text{NiF}_6 \rangle$ which gave satisfactory agreement with N.M.R. and optical measurements. The agreement was not significantly improved, later, by more rigorous and more sophisticated calculations (see table 1 of reference [7]).

In part 3 of this paper we apply a similar calculation to $| \text{VF}_6 \rangle$ for $t_2g$ antibonding orbitals.

Later Watson and Freeman (W.F.) used an approximate hamiltonian $h^A$ for $\gamma_i \downarrow$ and $\gamma_i \uparrow$ and $\gamma_i \downarrow$ in $| \text{NiF}_6 \rangle$ [12], and failed to account for experimental results. Nevertheless, in parts 4.1 and 4.2 of this paper we have used nearly the same calculation for $t_2g$ bonding orbitals of $| \text{VF}_6 \rangle$. The calculation suffers from applying an Hartree-Fock hamiltonian to unoccupied states. An attempt to correct this defect of the model, lead us to propose a simplified configuration interaction treatment in part 4.3.

Actually, the hamiltonians $h^A$ or $h^B$, derived from the pioneering works of S.S. and W.F., are not adapted to deal rigorously with a $(t_2g)^3$ open shell. In part 6 of the paper we have used an ionic approximation of a Hartree-Fock Roothaan procedure (H.F.R.).

The superhyperfine interaction cannot be fully interpreted with a simple $\pi$ bonding scheme for the unpaired electrons, since a negative isotropic interaction arising from a negative 2s spin densities $f_i^s$ has to be invoked to interpret E.P.R. measurements on the $| \text{VF}_6 \rangle$ $\uparrow$ cluster [20].

In part 5 and in part 6, we estimate the polarization of $e_g$ bonding orbitals which could be responsible for negative $f_i^s$ and $f_i^s$ spin densities.

2.2 NUMERICAL CALCULATION OF MATRIX ELEMENTS. — For the sake of simplicity we have used the Richardson's [17] 3d atomic orbitals for $V^{2+}$, built from two Slater components, and a fit of Froese's results [16] given by S.S. [13] for 2s and 2p orbitals of $F^-$. The one electron orbital energies for the free metal ion, $\epsilon_{i,M}$, have been calculated by following Richardson [11] and by using the free ion Racah's parameters given by Watson [15].

The nuclei and the inner electrons of $V^{2+}$, 1s to 3p, treated within a core approximation, were responsible for a potential $V_M^{\text{core}}$:

$$V_M^{\text{core}}(r_1) = - \frac{a + b e^{-ar_1}}{r_1}$$

with $a = 5$, $b = 16.03$, $\alpha = 3.17$, when one uses atomic units [18].

As a preliminary, one of us (J.E.) has established programs [18, 19] to compute any molecular integral appearing in the matrix elements, up to three centre integrals. Let us define the Coulomb interaction operator:

$$(f_{(i)} \parallel f_{(j)}) = \int dV_{ij} f^*(r_2) \left(1 - P_{12} \right) f(r_2)$$ (2.3)

Table I. — Matrix elements used in model A for the $t_2g \uparrow$ antibonding orbitals.

<table>
<thead>
<tr>
<th>$\phi_{1s}$</th>
<th>$e_A 1s_2 \uparrow$</th>
<th>$V^{2+}$</th>
<th>-1.12148</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_{1s}$</td>
<td>$\uparrow \parallel V_L \phi_{1s}$</td>
<td>1.47592</td>
<td></td>
</tr>
<tr>
<td>$\phi_{1s}$</td>
<td>$\uparrow \parallel V_L \chi_2 \uparrow$</td>
<td>0.72434 $\times 10^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$\phi_{1s}$</td>
<td>$\uparrow \parallel V_L \chi_a \uparrow$</td>
<td>0.16691</td>
<td></td>
</tr>
<tr>
<td>$\phi_{1s}$</td>
<td>$\uparrow \parallel \chi_a \uparrow \parallel \chi_a \uparrow$</td>
<td>0.12294</td>
<td></td>
</tr>
<tr>
<td>$\phi_{1s}$</td>
<td>$\parallel \chi_a \uparrow \parallel \chi_a \uparrow$</td>
<td>0.25286</td>
<td></td>
</tr>
</tbody>
</table>
Table II. — Experimental and calculation results. \( f'(\beta, \gamma) \) and \( f' \) were directly deduced from measurements. \( f_a \) was evaluated by assuming \( f_a = 3 f' \).

<table>
<thead>
<tr>
<th>Case</th>
<th>A</th>
<th>B1</th>
<th>B2</th>
<th>C</th>
<th>D</th>
<th>exp. [20]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_1 \uparrow \lambda_1 \uparrow )</td>
<td>0.334</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( N_1 \downarrow \gamma_1 \downarrow )</td>
<td></td>
<td>-0.1519 \times 10^{-2}</td>
<td>0.103</td>
<td>0.104</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular orbital coefficients</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( N_1 \uparrow )</td>
<td></td>
<td></td>
<td></td>
<td>0.991 1</td>
<td>0.982 4</td>
<td>0.996 9</td>
</tr>
<tr>
<td>( N_1 \downarrow )</td>
<td></td>
<td></td>
<td></td>
<td>0.993 3</td>
<td>0.986 1</td>
<td>0.997 0</td>
</tr>
<tr>
<td>( N_1 \uparrow )</td>
<td></td>
<td></td>
<td></td>
<td>0.984 3</td>
<td>0.932 0</td>
<td>0.982 4</td>
</tr>
<tr>
<td>( N_1 \downarrow )</td>
<td></td>
<td></td>
<td></td>
<td>0.987 8</td>
<td>0.942 7</td>
<td>0.985 1</td>
</tr>
<tr>
<td>( N_1 \uparrow \gamma_1 \uparrow )</td>
<td>( 0.3816 \times 10^{-4} )</td>
<td>-0.3250 \times 10^{-4}</td>
<td>0.2916 \times 10^{-1}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( N_1 \downarrow \gamma_1 \downarrow )</td>
<td>-0.3588 \times 10^{-4}</td>
<td>0.1610 \times 10^{-4}</td>
<td>0.3469 \times 10^{-1}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( N_1 \uparrow \gamma_1 \uparrow )</td>
<td>-0.2798 \times 10^{-1}</td>
<td>-0.152 \times 10^{-1}</td>
<td>0.1361 \times 10^{-1}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( N_1 \downarrow \gamma_1 \downarrow )</td>
<td>-0.2031 \times 10^{-1}</td>
<td>-0.182 \times 10^{-1}</td>
<td>0.1660 \times 10^{-1}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Results

| \( f_a \% \) | 2.84 | 0.7 |
| \( f'_a \% \) | -0.22 | -0.67 | -0.38 | -0.3 \pm 0.2 |
| \( f''_a \% \) | -0.12 | -0.22 | -0.02 | -0.1 \pm 0.01 |

where \( P_{12} \) is the permutation operator of electrons 1 and 2. For three centre integrals

\[
(f_A \mid (f_C \| f_C) \| f_B), \quad \text{the operator } (f_C \| f_C)
\]

with \( f_C \) centred on \( C \) was reduced to \( 1/r_C \) as

\[
(f_A \mid (f_C \| f_C) \| f_B) \approx \left( f_A \mid \frac{1}{r_C} \right) (f_B).
\]

Neglecting covalency \((\lambda, \lambda)\) and overlap

\[
S_i = (\varphi_i \mid \lambda_i)
\]

one obtains

\[
h_i(r_i) = -\frac{A_i}{2} + \sum_{jM} (\varphi_{jM} \mid \varphi_{jM}) + \sum_{k} (\lambda_{k} \mid \lambda_{k}) + V_{core}(r_i) + V_{\text{crst}}(r_i) \tag{3.2}
\]

\( \beta \) runs over all ligand nuclei, \( V_{\text{core}} \) is due to inner electrons and nuclei \( jM \) and \( i \) runs over valence electrons.

A further simplification was done by neglecting overlap between fluorine A.O's centred on different \( F^- \) nuclei, and the operators \((\lambda_i \mid \lambda_i)\) in (3.3) were expressed in terms of \((\phi_{a,b} \mid \phi_{a,b})\) (see 3.4). At last, to calculate an antibonding orbital \( \Psi^A \), mainly centred on the metal, S.S. replaced the ionic hamiltonian \( h_1 \) the corresponding self energy operator \((\phi_i \mid \phi_i)\).

The final antibonding hamiltonian was:

\[
h_i^A(r_i) = -\frac{A_i}{2} + V_{M}^{core}(r_i) + V_{\text{crst}}(r_i) + \sum_{jM \neq i} (\varphi_{jM} \mid \varphi_{jM}) + V_{\text{crst}}(r_i) \tag{3.4}
\]

\( k \) runs over all occupied \( F^- \) 2s and 2p orbitals.
Whatever are the approximation used to simplify numerical calculations, the hamiltonian used by S. S. can be seen as obtained from a closed shell Hartree-Fock hamiltonian $h(r_1)$

$$h^*(r_1) = h'(r_1) - (\phi_i \mid \phi_i)$$

where $h'(r_1)$ is an ionic approximation of $h(r_1)$.

To make the largest use of free ion S.C.F. calculation, we have assumed the following relations for up spin:

$$\begin{align*}
(\phi_i \mid h^A \mid \phi_i) &= \epsilon_i^M + (\phi_i \mid V_L \mid \phi_i) \\
(\phi_i \mid h^B \mid \chi_i) &= \epsilon_i^M \phi_i + (\phi_i \mid V_L \mid \chi_i) \\
(\chi_i \mid h^A \mid \chi_i) &= \left( \epsilon_i \frac{A_1}{2} + V_L \right) \chi_i + \\
&+ (\chi_i \mid V_M \mid \chi_i) - (\chi_i \mid \phi_i \mid \phi_i) \mid \chi_i \right). 
\end{align*}$$

In these relations the hamiltonian $h'$ was separated into terms arising from the metal $V_M$ or from the ligand $V_L$. The $\epsilon_i^M$ are the mean values of the S.C.F. Hartree-Fock free ion hamiltonian for the metal. $F^-$ free ion orbital energies were used to evaluate the matrix elements:

$$\begin{align*}
\epsilon_i \frac{A_1}{2} + V_L \chi_i.
\end{align*}$$

Without entering the details, the numerical values of matrix elements for model A are listed in table I. The parameter $\lambda^+_s \uparrow$ was obtained by solving the trinomial equation initially given by W. F. We have found $N_s \uparrow \lambda^+_s = 0.334$ (Table II). In table II we have also indicated the values obtained by a conventional analysis of E.P.R. measurements, where one assumes the relation $f^+_s = 3f^-_s$ [20]. The agreement between the observed value and the calculated value for $N_s \uparrow \lambda^+_s \uparrow$ is excellent.

4. Calculation of down spin bonding M.O. : models B and C. — 4.1 Model B1. — For the $(t_2g \downarrow)$ bonding orbital, an approximate hamiltonian similar to $h^A \uparrow$, can be written by starting from the closed shell Hartree-Fock hamiltonian simplified by a ionic approximation and by omitting the self energy term:

$$h^B_{t_2g\downarrow} = h' - (\chi_{t_2g\downarrow} \mid \chi_{t_2g\downarrow}).$$

In a first step we have admitted the following relations:

$$\begin{align*}
(\phi_i \mid h^A \mid \phi_i) &= (\phi_i \mid h^B \mid \phi_i) - (\phi_i \mid \chi_i \mid \phi_i) \\
(\phi_i \mid h^B \mid \chi_i) &= (\phi_i \mid h^A \mid \chi_i) \\
(\chi_i \mid h^A \mid \chi_i) &= (\chi_i \mid h^B \mid \chi_i).
\end{align*}$$

The second relation will be discussed below (4.2). The numerical values of matrix elements are listed in table III. In comparison with table I, the free metal ion orbital energy is relevant for an unoccupied state. Finally we have found $\gamma^+_s = -0.15 \times 10^{-2}$ (Table II). The negative value conflicts with the usual scheme for bonding M.O.'s characterized by an in phase combination of A.O.'s.

The very low value of $|\gamma_s \downarrow|$ would essentially mean an ionic bonding in which the spin transfers would be dominated by overlap in contradiction with experiment (Table II).

4.2 Model B2. — Actually, the relation (3.6) used above to estimate

$$\begin{align*}
(\phi_{t_2g\downarrow} \mid h^B \mid \chi_{t_2g\downarrow})
\end{align*}$$

has the interest of using the orbital energies and the Racah's parameters previously calculated by Watson [15]. It suffers from dealing with an unoccupied orbital $(\phi_{t_2g\downarrow})$ in the $^{4}A_{2g}(t_{2g}^3)$ ground state which conflicts with the fundamentals of a Hartree-Fock calculation. As previously done by W.F. for $|NiF_6^{4-}$ we have conducted a direct calculation of

$$\begin{align*}
(\phi_{t_2g\downarrow} \mid h^B \mid \chi_{t_2g\downarrow})
\end{align*}$$

In this way, we have obtained

$$\gamma_s = 0.103$$

and $f_s = 1.82\%$ (Table II).

With respect to the calculation in 4.2, the calculation in 4.1 illustrates the trouble which may arise from an incorrect use of free ion results. Indeed, the difference between $\epsilon_{t_2g\uparrow}$ and $\epsilon_{t_2g\downarrow}$ is approximatively given by the mean value of the exchange operator $K_N$ on the metal, i.e. by approximatively 1 a.u.:

$$\epsilon_{t_2g\downarrow} = \epsilon_{t_2g\uparrow} + \langle K_N \rangle \text{ with } K_N \sim 1 \text{ a.u.}$$

So

$$S_n \epsilon_{t_2g\downarrow} \approx S_n \epsilon_{t_2g\uparrow} + S_n$$

but $(\phi_{t_2g\downarrow} \mid K_N \mid \chi_{t_2g\downarrow}) \sim 4S^2$ by a direct calculation.

Nevertheless for $\epsilon_{t_2g\downarrow}$ orbitals the exchange energy is weaker since it involves $B$ and $C$ Racah parameters instead of $A$ for $t_{2g}$ orbitals. The results in table IV, evidences the error which arises from the simple approximation used in (3.6) and (4.3).
4.3 MODEL C. — Since the calculation through \( hB \uparrow \downarrow \) leads to low values both for \( f_\sigma \) in \((t_2g)^3 \) \( V_2^+ \) and \( f_\sigma \) in \((t_2g)^2 \) \( V_2^+ \) [12], we have attempted an empirical correction to the model, based upon the following remark : in the bonding orbitals, the transfer from ligand to the metal tends to the ionization scheme :

\[
V_2^+ \rightarrow \text{F}^-(\text{F}^+)\]

Consequently we have used a modified bonding hamiltonian \( h^{B*} \) defined by

\[
\begin{align*}
a) & \quad \langle \phi | h^{B*} | \phi \rangle = \varepsilon_0(V^+) + \langle \phi | V_{L,i} | \phi \rangle \\
b) & \quad \langle \phi | h^{B*} | \chi \rangle = \varepsilon_0(V^+) S' + \langle \phi | V_{L,i} | \chi \rangle \\
c) & \quad \langle \chi | h^{B*} | \chi \rangle = \langle \chi | h^{B} | \chi \rangle.
\end{align*}
\]

\( \varepsilon_0(V^+) \) is the \((3d)\) free ion energy of \( V^+ \) in the ground state. \( V_{L,i} \) is given by :

\[
V_{L,i} = V_L - \frac{1}{6} \sum_{\alpha=1}^{6} \langle \phi_{i,\alpha} \| \phi_{i,\alpha} \rangle.
\]

5. Core polarization of the \( e_g \) bonding closed shell. — The doubly occupied \( | \text{VF}_6 \rangle \) \( e_g \) bonding orbitals are expressed by

\[
\psi_{e_g,k} = N_k [x_{e_g,k} + \gamma_k \varphi_{e_g} + \gamma_{k'} x_{e_g,k'}]
\]

\( k, k' = \sigma, \sigma^\uparrow, \sigma^\downarrow \) or \( \sigma, \sigma^\uparrow, \sigma^\downarrow \).

Within an unrestricted S.C.F. model, the different parameters for up spin and down spin result in negative transferred densities :

\[
\begin{align*}
a) & \quad f_\sigma^+ = \frac{1}{3} [(N_\sigma \uparrow)^2 - (N_\sigma \downarrow)^2 + (N_\sigma \uparrow + \gamma_{e_g})^2 - (N_\sigma \downarrow + \gamma_{e_g})^2] \\
b) & \quad f_\sigma^- = \frac{1}{3} [(N_\sigma \uparrow)^2 - (N_\sigma \downarrow)^2 + (N_\sigma \uparrow + \gamma_{e_g})^2 - (N_\sigma \downarrow + \gamma_{e_g})^2]
\end{align*}
\]

we have calculated the parameters \( \gamma_{e_g}, \gamma_{e_g}, \gamma_\sigma \) and \( \gamma_\sigma \) by using

\[
\begin{align*}
\gamma_{e_g} = & \quad \chi_{\sigma} \| \chi_{\sigma} \\
\chi_{\sigma} = & \quad \text{a} \| \text{a} \\
\end{align*}
\]

In that way we were able to make an advance towards the configuration interaction method, without much rigor but without modifying our computation scheme.

Matrix elements are listed in table V. Finally we have found \( f_\sigma = 2.14 \% \) (Table II).
4.3 with a modified bonding hamiltonian $h_B'$. Matrix elements are listed in table VII and the calculated values for the $\gamma_s$ are indicated in table II. The corresponding values for $f_s'$ and $f_s''$ are indicated in table II (models B or model C).

Table VII. — Matrix elements used in the « ionization scheme » model C for $e_g \uparrow$ and $e_g \downarrow$ bonding orbitals.

$$
\begin{align*}
(\varphi_{e_g \uparrow} | V'_{Lx} | \varphi_{e_g \uparrow}) &= 1.06215 \\
(\varphi_{e_g \uparrow} | V'_{Ls} | \varphi_{e_g \uparrow}) &= 1.05204 \\
(\varphi_{e_g \uparrow} | V'_{Lx} | \chi_o \downarrow) &= -0.314003 \times 10^{-2} \\
(\varphi_{e_g \uparrow} | V'_{Ls} | \chi_o \downarrow) &= -0.920460 \times 10^{-4} \\
\epsilon_M(e_g \downarrow, 3E_g) V^+ &= -0.559121 \\
\epsilon_M(e_g \uparrow, 3E_g) V^+ &= -0.567551
\end{align*}
$$

6. Approximate Hartree-Fock Roothaan procedure, model D. — The methods developed above do not take into account the difficulties of open shell calculations which have to be treated within the Hartree-Fock Roothaan (H.F.R.) procedure, the effect of which is to insure the orthogonality constraints [6].

An H.F.R. hamiltonian is obtained through a closed shell type H.F. hamiltonian completed by coupling operators [6]. For a half closed shell, as the $(t_2g)^{3}$ shell in the ground state of $V^{2+}$, this operator on the $(\varphi_{t_{2g}}', \chi_{t_{2g}})$ basis can be approximated by the exchange operator on the metal ion, when one neglects the overlap between metal ion and ligand orbitals (ionic approximation).

Within a restricted H.F. calculation in which $S$ stays a good quantum number, the H.F.R. hamiltonian is expressed by

$$
F = h + \Omega
$$

$h$ has been previously defined and

$$
\Omega = 2 M_e + 2 M_0 - K_0
$$

$$
K_0 = f \sum_i K_i = \int \Psi_i^\lambda(r_2) \frac{P_{21}}{r_{12}} \Psi_i^\lambda(r_2) dV_2
$$

$$
M_e | \phi > = \sum_k | \Psi_k^R > < \Psi_k^R | K_0 | \phi > + \\
+ < \phi | \Psi_k^B > K_0 | \Psi_k^B >
$$

$$
M_0 | \phi > = f \sum_i | \Psi_i^\lambda > < \Psi_i^\lambda | K_0 | \phi > + \\
+ < \Psi_i^\lambda | \phi > K_0 | \Psi_i^\lambda >
$$

$i$ runs over the $t_{2g}$ antibonding orbitals and $f$ is the fractional occupation of the corresponding open shell : $f = 1/2$. $k$ runs over the $t_{2g}$ bonding closed shell.

Then, within an ionic approximation, $h$ is reduced to $h'$ as above and the matrix elements between $t_{2g}$ metal and ligand orbitals are given by

$$
(\varphi_s | \Omega | \varphi_s) = (\varphi_s | K_0 | \varphi_s)
$$

$$
(\varphi_s | \Omega | \chi_o) = 2(\varphi_s | K_0 | \chi_o)
$$

$$
(\chi_o | \Omega | \chi_o) = 3(\chi_o | K_0 | \chi_o).
$$

The coefficients $\lambda_\alpha$ and $\gamma_\alpha$ were calculated by diagonalizing the overlap matrix and diagonalizing the Hamiltonian $F$ on the orthonormal ($t_{2g}$) basis.

One has found $\lambda_\alpha = 0.318$ in good agreement with the experimental result.

On the other hand, the $e_g$ bonding closed shell have been treated separately within an Unrestricted H.F. calculation, by diagonalizing $h'$ and the overlap matrix for the $e_g$ symmetry. We have found $f_s' = -0.38\%$ and $f_s'' = -0.02\%$ (Table II, case D).

7. Discussion and conclusion. — We have reviewed different methods to calculate the molecular orbitals of the $\mid VF_{6} \uparrow \downarrow$ complex, in order to interpret the s.h.f. interaction which has been measured in KZnF$_3$ : $V^{2+}$ and expressed in terms of transferred spin densities $f_{s'}$, $f_{s''}$.

We have deliberately used a restricted and simple L.C.A.O. basis, and simplified one electron hamiltonians, within an ionic approximation. Such hamiltonians, have been previously developed by (S.S.) and (W.F.).

A calculation of the $t_{2g} \uparrow$ antibonding orbitals (case A) with the help of a S.S. hamiltonian permits to account for the measured $f_s$ spin densities, when one assumes no contribution from the bonding $t_{2g} \downarrow$ orbitals.

Moreover, a calculation of the $e_g \uparrow$ and $e_g \downarrow$ bonding orbitals (case B$_2$) evidences a polarization of these orbitals. The corresponding values of the negative spin densities ($f_s'$ and $f_s''$) agree with those which have been proposed from E.P.R. measurements. On the other hand, when one admits that the spin transfers depend on the $t_{2g} \downarrow$ bonding orbital, as W.F. did, the corresponding calculation give a poor result (case B$_1$). The result can be considerably altered when one uses approximate relations (3.6) for matrix elements which involve cross terms, with unoccupied states (case B$_1$). We have developed a method to take into account a configuration interaction with the help of a modified W.F. calculation which tends to deal with occupied states only (case C). Then the results are in satisfactory agreement with experiment.

At last we have attempted to treat correctly the open shell problem by using an ionic approximation of the Hartree-Fock Roothaan procedure (case D) and obtained a satisfactory result for $f_s'$. In comparison with case B$_2$, the calculation of the polarization of $e_g$ bonding orbitals differs by taking into account the self energy term in the closed shell Hartree-
Fock hamiltonian. The effect is to increase the negative $f'_0$ density and to spoil agreement with experiment for $f'_0$.

Although the orders of magnitude are generally quite good, none of the 5 calculations proves to be much better than all the others, by yielding a satisfactory agreement with experiment for the three parameters $f_0$, $f_0'$ and $f'_0$ simultaneously. The restricted atomic basis which has been used cannot insure exact values of the electronic wave function at the ligand nuclei. Therefore we cannot hope to account for the isotropic s.h.f. interaction, i.e. for $f'_0$, accurately. Then the more serious test is the ability to account for $(f'_0 - f_0)$, and calculations A, C, D give nearly the same results. Nevertheless the calculation C leads to an important contribution of polarization on the s.h.f. interaction.

Our work may help to establish a reliable one electron hamiltonian, within a simple L.C.A.O.-M.O. framework, and within a moderate computer time consumption, in order to elucidate the mechanisms of s.h.f. interaction and spin transfers for $(3d)^{10}$ ions in ionic crystals.

Particularly, for the $(3d)^5 |MnF_6|^{4-}$ ions, one has to decide if $f_0$ is about $1\%$ as deduced from initial measurements by neutron and E.P.R., or is about $4\%$ deduced from more recent investigations by E.N.D.O.R. and P.A.C... The influence of bond length and of the host crystal on spin transfers has also to be known to draw a conclusion on the covalency contribution to the zero field splitting [21, 22]. Moreover, within the same $3d^4$ configuration (Cr$^{3+}$ and V$^{2+}$, Mn$^{2+}$ and Fe$^{3+}$ for instance), spin transfers and s.h.f. interaction are different for divalent and trivalent ions. Bond length and overlap considerations do not seem sufficient to interpretate this difference and L.C.A.O.-M.O. calculation can bring some light on the problem.

References