A Study of the Cubic Field Splitting Parameter 10Dq
by Means of One-Center Expansion of Complex MO

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ABSTRACT. MO's of a complex are expanded in terms of the set of Shull-Löwdin functions
based on a single point, the nucleus of central metal ion, and the result was interpreted from the
viewpoint of perturbation theory. We find that even in the case of [NiF₆]⁴⁻, which has relatively
small covalency, excited configurations with high orbital angular momentum are considerably mixed
into e_g and t₂g orbitals of central metal ion, and that the distortions in these orbitals differ from
each other. Therefore it is concluded that the energy difference between e_g and t₂g orbitals
evaluated in the MO scheme has little meaning of the unique parameter 10Dq in the crystal field
theory, and that such a unique parameter cannot be defined in a rigorous sense in the MO scheme.

1. INTRODUCTION

In the scope of crystal field theory, the gap between any two energy levels of the central
ion perturbed by the coordination of ligands can be expressed in terms of some parameters. For
the complexes of d⁹ configurations cubic crystal field splitting parameter Dq, inter-electron
repulsion parameter F₂ and F₄, spin-orbit interaction parameter ₓₛ, etc. are used. In most
applications these parameters are replaced by the empirical values. Attempts to calculate
these parameters from first principles have led to results that disagree considerably with the empirically deduced values. One defect inherent in the crystal field theory is that one can know noting but the symmetry of the effective potential resulting from ligations. The usual models for this potential neglect the details of chemical nature of bonding between the central metal and ligands. The other reason for the failure is the defect of the assumptions premised in defining above parameters. We shall give a brief survey on this point in the following section.

An essential turning point was made by Sugino and Shulman who performed a molecular orbital calculation of both "10Dq" and LCAO wave functions of [NiF₄]⁻ ion. They obtained excellent results which agrees well with experiments. However, one has not been able to derive the relations which express the energy eigenvalue spectrum of complex molecules in terms of above parameters within the framework of MO method. The "10Dq" so calculated with the MO scheme could not have the meaning of 10Dq defined in the crystal field theory, and it might be illegitimate to adapt the MO results for the parametric relations from crystal field theory. The purpose of present work is to examine this point.

2. CUBIC CRYSTAL FIELD SPLITTING PARAMETER

(1) 10 Dq in the Primitive Crystal Field Theory. The crystal field potential for an octahedral complex can be expanded as follows:

\[ V_L = R_0(\vec{r}) Y_l(\theta, \phi) + R_4(\vec{r}) Y_4(\theta, \phi) + \cdots \]  

where the summation is over all electrons of central metal ion, and \( Y_l(\theta, \phi) \) is the symmetry-adapted linear combination (SALC) of spherical harmonics of order \( l \) which belongs to \( A_{1g} \) representation of point group \( O_h \).

If the unperturbed d orbitals of free metal ion are given by

\[ \varphi_e = R_{2d}(\vec{r}) Y_2(\theta, \phi) \]
\[ \varphi_r = R_{4d}(\vec{r}) Y_4(\theta, \phi) \]  

where \( Y_2(\theta, \phi) \) and \( Y_4(\theta, \phi) \) are the SALC's of spherical harmonics which belong to \( E_g \) and \( T_{2g} \) representation respectively, then the difference between the first order perturbation energies in these is

\[ \epsilon_l^d - \epsilon_r^d = \langle \varphi_e | V_L | \varphi_e \rangle - \langle \varphi_r | V_L | \varphi_r \rangle = \langle R_0 | R_0 | Y_2 \rangle \langle Y_2 | Y_2 \rangle - \langle Y_4 | Y_4 \rangle \]

\[ = \langle R_0 | R_0 | Y_2 \rangle \cdot K \quad (K:\text{constant}) \]  

The primitive crystal field theory defines this single integral term multiplied by a constant from the angular part integral as 10Dq, and takes its value from experiments.

But the empirical value must be the energy difference resulting from "total perturbation", that is, it includes all the higher order perturbation energy corrections:

\[ \Delta \epsilon_l - \Delta \epsilon_r = (\epsilon_l^{(2)} + \epsilon_r^{(2)} + \cdots) - (\epsilon_l^{(3)} + \epsilon_r^{(3)} + \cdots) = (\epsilon_l^{(2)} + \epsilon_r^{(2)}) - (\epsilon_l^{(3)} + \epsilon_r^{(3)}) = (\epsilon_l^{(2)} - \epsilon_l^{(3)}) + (\epsilon_r^{(2)} - \epsilon_r^{(3)}) \]  

So that above definition of 10Dq bears the assumption

\[ (\epsilon_l^{(2)} - \epsilon_l^{(3)}) \approx (\epsilon_r^{(2)} - \epsilon_r^{(3)}) \]  

But it may be wrong although the general assumptions that \( \langle \varphi_e | \epsilon_l^{(2)} \rangle \) and \( \langle \varphi_r | \epsilon_r^{(2)} \rangle \) are valid.

Actually the failure of theoretical calculation of 10Dq according to Eq. (3) is not only due to the defect of \( R_4 \) given by simple model potential neglecting the covalency but also due to neglecting the higher order perturbation correction. It is conceived that the latter fault...
makes the discrepancy between theoretical and empirical values more significant than the defect of simple model potential, at least in the "ionic" complexes. 14,15 of course, the covalent effect becomes more significant in the "covalent" complexes.

(2) **Effect of Total Perturbation.** If the ϕ₀, ϕ₁ orbitals of free metal ion becomes ϕ₀', ϕ₁' by the perturbation due to ligation, the Integral Hellmann-Feynman theorem 15 gives the total perturbation energy (the sum of the perturbation energies of all order) difference by

\[
\Delta e_{t} - \Delta e_{s} = \frac{\langle \phi_{s}| V_{L} | \phi_{s}' \rangle}{\langle \phi_{s}| \phi_{s}' \rangle} - \frac{\langle \phi_{s}| V_{L} | \phi_{s}' \rangle}{\langle \phi_{s}| \phi_{s}' \rangle}
\]

(6)

Here, if it could be assumed to a good approximation that only the radial part of ϕ₀ and ϕ₁ are distorted by the perturbation and that the radial distortions in these are equal to each other, that is,

\[
\begin{align*}
\psi_{0}' &= R_{s}(r)Y_{0}^{0}(\theta, \phi) \\
\psi_{1}' &= R_{s}(r)Y_{1}^{1}(\theta, \phi) \\
(R_{s}(r) &= \sum_{C, C', R_{s}(r)}),
\end{align*}
\]

(7)

then from Eq. (6) \(\Delta e_{t} - \Delta e_{s}\) is given by single term:

\[
\Delta e_{t} - \Delta e_{s} = \frac{\langle \phi_{s}| V_{L} | \phi_{s}' \rangle}{\langle \phi_{s}| \phi_{s}' \rangle} - \frac{\langle \phi_{s}| V_{L} | \phi_{s}' \rangle}{\langle \phi_{s}| \phi_{s}' \rangle} \cdot K
\]

(8)

This result suggests that the quantity given by Eq. (6) be the actual parameter 10Dq replaced with the empirically deduced value. In fact it can be shown that if above assumption (Eq. (7)) is valid, there results simple scaling of the parameter 10Dq and inter-electron repulsion parameter \(F_{s}\), along the lines suggested above. 16

Now consider the case in which the perturbed wave functions \(\psi_{0}'\) and \(\psi_{1}'\) contain the excited configurations with higher orbital angular momentum than d orbital (angular distortion) and have unequal radial distortions:

\[
\psi_{0}' = R_{d}(r)Y_{0}^{0}(\theta, \phi) + R_{d}(r)Y_{1}^{1}(\theta, \phi) + \cdots
\]

(9)

where \(R_{d}(r) \neq R_{s}(r), R_{s}(r) \neq R_{d}(r)\), and so forth.

In this case,

\[
\Delta e_{t} = \frac{1}{\langle \phi_{s}| V_{L} | \phi_{s}' \rangle} - [\langle \phi_{s}| V_{L} | \phi_{s}' \rangle + \langle \phi_{s}| V_{L} | \phi_{s}' \rangle + \langle \phi_{s}| V_{L} | \phi_{s}' \rangle + \cdots]
\]

(10)

Unfortunately as it is, the value of \(\Delta e_{t} - \Delta e_{s}\) cannot be expressed in a single term as in the previous case. So this value cannot be parameterized to give the energy gaps between other energy levels. That is, it is merely the energy difference between the perturbed states, \(\psi_{0}'\) and \(\psi_{1}'\), and has no more significance.

3. **ONE-CENTER EXPANSION OF LCAOMO OF A COMPLEX ION**

In this section we expand the \(\phi_{s}'\) and \(\psi_{1}'\) orbitals of [NiF₄]⁺⁺, which correspond to \(\phi_{s}'\) and \(\phi_{1}'\) respectively, in terms of the set of Shull–Löwdin functions based on a single point, the nucleus of Ni²⁺ ion. The wave functions of [NiF₄]⁺⁺ are given by Sugano and Shulman 13,

\[
\Psi_{s} = N_{s}(\phi_{s} - \lambda_{2}s - \lambda_{2}s), N_{s} = 0.968, \lambda_{2} = 0.113, \lambda_{2} = 0.386
\]

(11)

where \(\phi_{s}\) and \(\phi_{t}\) are the Hartree–Fock atomic orbitals of Ni²⁺ ion,

\[
\phi_{s} = R_{s}(r)Y_{0}^{0}(\theta, \phi), \quad N_{s} = 0.968, \quad \phi_{t} = R_{t}(r)Y_{1}^{1}(\theta, \phi), \quad \lambda_{2} = 0.249
\]

Now consider the case in which the perturbed wave functions \(\psi_{0}'\) and \(\psi_{1}'\) contain the excited configurations with higher orbital angular momentum than d orbital (angular distortion) and have unequal radial distortions:

\[
\phi_{0}' = R_{d}(r)Y_{0}^{0}(\theta, \phi) + R_{d}(r)Y_{1}^{1}(\theta, \phi) + \cdots
\]

(10)

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\[ \psi_i = R_{3d}(r) \left( \frac{-1}{\sqrt{2}} \right) [Y_{5/2}(\theta, \phi) - Y_{-5/2}(\theta, \phi)] \]  
\[ \phi_x = R_{3d}(r) \left( \frac{-i}{\sqrt{2}} \right) [Y_{3/2}(\theta, \phi) - Y_{-3/2}(\theta, \phi)] \]  
with \( R_{3d}(r) = r^2 (3.4096e^{-2.315r} + 45.261e^{-4.589r} + 129.48e^{-8.502r} + 24.071e^{-15.02r}) \) and \( \psi_x, \psi_y, \) and \( \psi_z \) are the SALC's of Hartree–Fock atomic orbitals of \( \text{F}^- \) ions (refer to Fig. 1 which describes the coordinates of each ligand orbital),

\[ \chi_{1a} = \frac{1}{\sqrt{12}} (2\psi_{2s} - 2\psi_{2} - \bar{\psi}_{2s} - \bar{\psi}_2 - \psi_{4s} - \psi_{4}) \]
\[ \chi_{1b} = \frac{1}{\sqrt{12}} (2\psi_{2s} + 2\psi_{2} - \bar{\psi}_{2s} - \bar{\psi}_2 - \psi_{4s} + \psi_{4}) \]
\[ \chi_{1c} = \frac{1}{2} (\psi_{1s} - \psi_{2s} + \psi_{1} - \psi_{2}) \]
\[ \chi_{1d} = \frac{1}{2} (\psi_{1s} - \psi_{2s} - \psi_{1} + \psi_{2}) \]
\[ \chi_{1e} = \frac{1}{2} (\psi_{2s} + \psi_{2} + \psi_{4s} + \psi_{4}) \]
\[ \chi_{1f} = \frac{1}{2} (\psi_{2s} - \psi_{2} - \psi_{4s} + \psi_{4}) \]

Let the Shull–Löwdin functions\(^{17}\) be

\[ \phi_{nlm} = R_{nl}(r) Y_l(\theta, \phi) \]

where \( Y_l(\theta, \phi) \) are the spherical harmonics and \( R_{nl}(r) \) are the radial functions defined by

\[ R_{nl}(r) = \frac{(2\eta)^{3/2}}{(n+l+1)!} \frac{1}{\sqrt{\pi}} \left( \frac{\eta r}{\pi} \right)^{\frac{1}{2}} L_{n+l}^{(2l+1)}(\eta r) \exp(-\eta r) \]

The parameter \( \eta \), usually referred to as the orbital exponent, is a variable scale factor, and the \( L_{n+l}^{(2l+1)}(2\eta r) \) are the \( (2l+2) \)-order associated Laguerre polynomials defined according to the conventions of Pauling and Wilson.\(^{15}\)

Thus \( R_{nl}(r) \) can be written as

\[ R_{nl}(r) = A_{nl} \frac{(2\eta)^{3/2}}{(n+l+1)!} B_{nl} \left( \frac{\eta r}{\pi} \right)^{\frac{1}{2}} L_{n+l}^{(2l+1)}(\eta r) \exp(-\eta r) \]

with

\[ A_{nl} = \left[ (2\eta)^{3/2} (n-l-1)! (n+l+1)! \right]^{1/2} \]

and

\[ B_{nl} = \left[ (-)^k (2\eta)^{k+1} \right] / \left[ (n-l-k)! (2l+2+k)! k! \right] \]

These functions form a complete basis set which is discrete in its entirety. These properties greatly simplify the numerical work, giving fast convergence. First, we expand the unperturbed orbital of free nickel ion for comparison with the expansion of \( \Psi \) and \( \Psi^* \).
The expansion formula is given by
\[
\varphi_i = R_{2d}(r) Y_2^2(\theta, \phi) = \sum D_{2d} \phi_i^d
\]  
(15)
where \( \phi_i^d \) are the SALC's of Shull-Löwdin functions which belong to the irreducible representation denoted by the appropriate superscript, \( x, y, \xi, \eta, \zeta \). The coefficients \( D_{2d} \) are given by
\[
D_{2d} = \langle \phi_i^d | \varphi_d \rangle = \int_0^\infty R_{2d}(r) R_{2d}(r) r^2 dr
\times \int Y_2^2(\theta, \phi) Y_i(\theta, \phi) d\Omega
= A_{2d} \int_0^\infty \int_0^\infty (r^2 e^{-w}) r^2 (3.4906 e^{-2.315 r} 
+ 4.2612 e^{-2.232 r} + 129.45 e^{-2.686 r} 
+ 24.971 e^{-15.91 r}) r^2 dr
\]
(16)
Note that
\[ D_4 = D_3 = D_2 = D_1 = D_0 = D_{-1} = D_{-2} = D_{-3} \]
We choose the value of \( \gamma \) as 3.80, which shows the most fast convergence. The reason for this choice is that the value of \( \gamma \), giving fast convergence in the expansion of \( \varphi_d \), is very likely to give fast convergence in the expansion of \( \varphi_i \), which is not greatly different from \( \varphi_d \). The values of the coefficients \( D_{2d} \) are tabulated in Table 1.

The expansion formula of \( \Phi_i \) is given by
\[
\Phi_i = \sum C_{2d} \phi_i^d
\]
where
\[
\phi_i^d = R_{2d}(r) Y_i(\theta, \phi) = \sum G_{2d} Y_i(\theta, \phi)
\]
(18)
Values of \( G_{2d} \) are tabulated in Tables 2~6. The expansion coefficients \( C_{2d} \) in Eq. (17) are given by
\[
C_{2d} = \langle \phi_i^d | \Phi_i \rangle
\]
(19)
Using the group theory in Ref. 10, it can be shown that
\[
C_4 = C_3 = C_2 \quad \text{and} \quad C_1 = C_0
\]
(20)
Here, \( C_4 \) and \( C_2 \) are calculated more easily than the others.

\begin{table}[h]
\centering
\caption{Expansion of d orbital of free Ni\textsuperscript{2+} ion.}
\begin{tabular}{|c|c|}
\hline
\( n \) & \( D_n \) \\
\hline
3 & 0.9771 \\
4 & 0.0008 \\
5 & 0.2073 \\
6 & 0.0100 \\
7 & 0.0051 \\
8 & 0.0126 \\
9 & 0.0035 \\
10 & 0.0018 \\
11 & 0.0011 \\
12 & 0.0006 \\
13 & 0.0004 \\
14 & 0.0002 \\
15 & 0.0002 \\
16 & 0.0001 \\
17 & 0.0001 \\
18 & 1.0000 \\
\hline
\end{tabular}
\end{table}

\( C_i \)'s are given by
\[
C_i = \langle \phi_i^d | \Phi_i \rangle = N_i \left[ \langle \phi_i^d | \varphi_d \rangle - \lambda_2 \langle \phi_i^d | \chi_{2s} \rangle \right]
\]
(21a)
\[
\langle \phi_i^d | \varphi_d \rangle = D_n \lambda_2 \\
\langle \phi_i^d | \chi_{2s} \rangle = \frac{1}{2} \left[ \langle \phi_i^d | \varphi_{2s} \rangle + \langle \phi_i^d | \varphi_{2p_0} \rangle \\
+ \langle \phi_i^d | \varphi_{2p_1} \rangle + \langle \phi_i^d | \varphi_{2p_2} \rangle \right]
\]
(21b)

From the geometry, it is obvious that
\[
\langle \phi_i^d | \varphi_{2s} \rangle = \langle \phi_i^d | \varphi_{2p_0} \rangle = \langle \phi_i^d | \varphi_{2p_1} \rangle = \langle \phi_i^d | \varphi_{2p_2} \rangle
\]
(21b)

Thus, we are left with
\[
\langle \phi_i^d | \chi_{2s} \rangle = 2 \langle \phi_i^d | \varphi_{2s} \rangle
\]
\[
= 2 \left[ \int R_{2s}(r) Y_i^2(\theta, \phi) \right]^* \left[ R_{2s}(r) \right] \\
= \frac{i}{\sqrt{2}} \left[ Y_2^2(\theta, \phi) + Y_1^0(\theta, \phi) \right] \left[ R_{2s}(r) \right] \\
= 2 \left[ \int R_{2s}(r) \sum G_{2d} Y_i(\theta, \phi) \right]^* \\
\left[ R_{2s}(r) \right] \sqrt{2} \left[ Y_2^2(\theta, \phi) + Y_1^0(\theta, \phi) \right] \left[ R_{2s}(r) \right] \\
= 2 \sqrt{2} G_{2d} \left[ \int R_{2d}(r) Y_i^2(\theta, \phi) \right] \\
\left[ R_{2s}(r) \right] \\
\left[ R_{2s}(r) \right] Y_i^2(\theta, \phi) \\
\left[ R_{2s}(r) \right]
\]
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Table 2. Symmetry adapted linear combinations of spherical harmonics.

\[ Y_l = \sum \lambda_j G_j (Y) \]

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Table 3. Symmetry adapted linear combinations of spherical harmonics.

\[ Y_l = \sum G_j (Y) \]

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</table>

\[ \varphi = 2 \sqrt{G_l} | A_{l, m_1} \rangle \]

\[ C_{l,m} = \langle \psi_l | \varphi \rangle \]

\[ \langle \psi_l | \varphi \rangle = \int \psi_{l-1}^* \psi_{l+1} \psi_l \theta, \phi \rangle \omega \]
Table 4. Symmetry adapted linear combinations of spherical harmonics.

\[ Y_l = \sum G_l Y_l^m = \frac{1}{\sqrt{2}} i \sqrt{2} G_{1\ell} (Y_l^m + Y_l^{-m}) + \sqrt{2} G_{1\ell} (Y_l^m - Y_l^{-m}) + \sqrt{2} G_{1\ell} (Y_l^m + Y_l^{-m}) + \ldots \]

<table>
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<tr>
<th>( l )</th>
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<td>( Y_8^+ )</td>
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<td>0.9865659</td>
</tr>
<tr>
<td>10</td>
<td>( Y_{10}^+ )</td>
<td>0.3766213</td>
<td>0.9933839</td>
</tr>
<tr>
<td>12</td>
<td>( Y_{12}^+ )</td>
<td>0.4154286</td>
<td>0.9864351</td>
</tr>
</tbody>
</table>

Table 5. Symmetry adapted linear combinations of spherical harmonics.

\[ Y_l = \sum G_l Y_l^m = G_l (Y_l^m + Y_l^{-m}) + \sqrt{2} G_{1\ell} (Y_l^m - Y_l^{-m}) + \sqrt{2} G_{1\ell} (Y_l^m + Y_l^{-m}) + \ldots \]

<table>
<thead>
<tr>
<th>( l )</th>
<th>( G_l )</th>
<th>( \sqrt{2} G_{1\ell} )</th>
<th>( \sqrt{2} G_{1\ell} )</th>
<th>( \sqrt{2} G_{1\ell} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>( Y_4^+ )</td>
<td>0.64549722</td>
<td>-0.7657662</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>( Y_6^+ )</td>
<td>0.93541435</td>
<td>0.35365329</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>( Y_8^+ )</td>
<td>-0.3840073</td>
<td>-0.6031514</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>( Y_{10}^+ )</td>
<td>0.34870326</td>
<td>-0.64326752</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>( Y_{12}^+ )</td>
<td>0.76564149</td>
<td>-0.69597055</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>( Y_{14}^+ )</td>
<td>0.77191640</td>
<td>-0.80039433</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>( Y_{16}^+ )</td>
<td>0.83256392</td>
<td>-0.91144345</td>
<td></td>
</tr>
</tbody>
</table>

It is obvious that

\[
\langle \phi_l | \phi_m \rangle = \frac{1}{\sqrt{2}} \left[ 2 \langle \phi_l^+ | \phi_m^+ \rangle + 2 \langle \phi_l^- | \phi_m^- \rangle \right] + \langle \phi_l^0 | \phi_m^0 \rangle + \langle \phi_l^+ | \phi_m^- \rangle + \langle \phi_l^- | \phi_m^+ \rangle + 2 \langle \phi_l^0 | \phi_m^0 \rangle
\]

\[
\langle \phi_l^+ | \phi_m^- \rangle = \langle \phi_l^- | \phi_m^+ \rangle = \langle \phi_l^0 | \phi_m^0 \rangle
\]

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Table 6. Symmetry adapted linear combinations of spherical harmonics.

\[ Y_l^m = \sum G_{lm} Y_l^m = \frac{1}{\sqrt{2}} [\sqrt{2} G_{l0} (Y_l^0 + Y_l^{-0}) + \sqrt{2} G_{l1} (Y_l^1 + Y_l^{-1}) + \sqrt{2} G_{l2} (Y_l^2 + Y_l^{-2}) + \ldots] \]

<table>
<thead>
<tr>
<th>l</th>
<th>( \sqrt{2} G_{l0} )</th>
<th>( \sqrt{2} G_{l1} )</th>
<th>( \sqrt{2} G_{l2} )</th>
<th>( \sqrt{2} G_{l3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( Y_1^0 )</td>
<td>-1</td>
<td>( Y_1^0 )</td>
<td>( Y_1^0 )</td>
</tr>
<tr>
<td>6</td>
<td>( Y_6^0 )</td>
<td>0.55901689</td>
<td>0.82919202</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>( Y_8^0 )</td>
<td>-0.65068202</td>
<td>-0.75935032</td>
<td>0.82919202</td>
</tr>
<tr>
<td>10</td>
<td>( Y_{10}^0 )</td>
<td>0.44497917</td>
<td>0.48820518</td>
<td>0.75935032</td>
</tr>
<tr>
<td>12</td>
<td>( Y_{12}^0 )</td>
<td>-0.51609084</td>
<td>-0.54714937</td>
<td>-0.65068202</td>
</tr>
<tr>
<td>14</td>
<td>( Y_{14}^0 )</td>
<td>0.38376947</td>
<td>0.39917223</td>
<td>0.44497917</td>
</tr>
<tr>
<td>16</td>
<td>( Y_{16}^0 )</td>
<td>-0.43576913</td>
<td>-0.48582019</td>
<td>-0.4999982</td>
</tr>
</tbody>
</table>

From the physical reasoning it is noted that

\[ \langle \phi_{l1}^m | \phi_{l2}^m \rangle = \langle \phi_{l1}^m | \phi_{l2}^m \rangle = \langle \phi_{l1}^m | \phi_{l2}^m \rangle = \langle \phi_{l1}^m | \phi_{l2}^m \rangle \]

(23-c)

From above three relations (23-b), (23-c), (23-d), and an additional relation

\[ \langle \phi_{l1}^m | \phi_{l2}^m \rangle = \langle \phi_{l1}^m | \phi_{l2}^m \rangle = \langle \phi_{l1}^m | \phi_{l2}^m \rangle = \langle \phi_{l1}^m | \phi_{l2}^m \rangle \]

it follows that

\[ \langle \phi_{l1}^m | \phi_{l2}^m \rangle = 2 \langle \phi_{l1}^m | \phi_{l2}^m \rangle \]

(23-f)

The validity of relations (21-b) and (23-f) can be shown explicitly by using the transformation properties of angular momentum eigenvector under finite rotations.

Thus, we are left with

\[ \langle \phi_{l1}^m | \phi_{l2}^m \rangle = \sqrt{3} \langle \phi_{l1}^m | \phi_{l2}^m \rangle \]

(23-e)

\[ = \sqrt{3} \int [R_{l1} (r) Y_l^m (\theta, \phi)]^m \]

\[ \times \int [R_{l2} (r) Y_l^m (\theta, \phi)]^m \]

(23-f)

Computations of two-center overlap integrals in Eq. (21-c), (23-g), and (23-h) are performed on IBM-360, the electronic digital computer of Seoul National University. We have used a new program based on the formula derived by Silver and Ruedenberg. The values of coefficients \( C_{l1} \) and \( C_{l2} \) from Eq. (21) and (23) are in Tables 7 and 8.

4. RESULTS AND DISCUSSION

From Table 7, one may note that nearly...
complete convergence is obtained in the expansion of $t_{ij}^*$ orbital. However, from Table 8, it is noted that the convergence in the expansion of $e_{ij}^*$ orbital appears to halt at 0.9745. One probable reason for this is that excited configurations with higher energy must be mixed judging from the large mixing of ligand atomic orbital in $e_{ij}^*$ orbital than in $t_{ij}^*$ orbital. But the more important reason is the singularity of 2$s$ atomic orbital of $F^-$ contained in $e_{ij}^*$ orbital.
5. CONCLUSION

The energy difference between $\epsilon^*_s$ and $\epsilon^*_d$ orbitals evaluated in the MO method have little meaning of 10Dq defined in the crystal field theory. That is, this value cannot be parameterized to give the energy gaps between other energy levels. In other senses, if the LCAO-MO's of complex ion obtained in the MO scheme are accurate, it is impossible to express the energy eigenvalue spectrum of complexes in terms of limited number of parameters such as 10Dq, F, F', etc.

REFERENCES

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