착물 분자궤도함수의 일점 전개에 의한 입방결정장 분열 파라미터 10Dq의 고찰

金鎬澂 · 李相燁

서울대학교 자연과학대학 화학과

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

Hojing Kim and **Sangyoub Lee**

Department of Chemistry, Seoul National University, Seoul, Korea

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요 약. 착물의 분자궤도함수를 중심 금속이온의 핵을 원점으로 하는 함수들을 기저함수 집합으로 하여 일점 전개하고, 그 결과를 섭동론적인 입장에서 해석했다. $KNiF_3$의 결정구조 (perovskite structure) 내에 존재하는 공유결합성이 비교적 작은 $[NiF_6]^{4-}$의 경우에도, 리간드의 배위로 인한 섭동으로 중심 금속이온의 e_g 궤도함수와 t_{2g} 궤도함수에 g 궤도함수 이상의 각운동량을 갖는 들뜬상태 배치가 상당히 크게 섞여 들어온다는 것과, 이들 궤도함수들이 갖는 변형이 서로 다르다는 것을 발견했다. 여기서 MO 계산에 의해 얻어지는 e_g^* 궤도함수와 t_{2g}^* 궤도함수 사이의 에너지차는 결정장 이론에서 정의되는 단일한 파라미터로서의 10Dq의 의미는 갖지 못하며, 엄밀한 입장에선 그와 같은 파라미터는 정의될 수 없음을 밝혔다.

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 $[NiF_6]^{4-}$, which has relatively small covalency, excited configurations with high orbital angular momentum are considerably mixed into e_g and t_{2g} 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 t_{2g}^* 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 senes 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 d^n configurations cubic crystal field splitting parameter Dq, inter-electron repulsion parameter F_2 and F_4, spin-orbit interaction parameter ξ_d, etc. are used. [1~4] In most applications these parameters are replaced by the empirical values. [5~6] Attempts to calculate

these parameters from first principles have led to results that disagree considerably with the empirically deduced values[7~10]. One defect inherent in the crystal field theory is that one can know noting but the smmetry 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 Sugano and Shulman who performed a molecular orbital calculation of both "10Dq" and LCAO wave functions of $[NiF_6]^{4-}$ ion. They obtained excellent results which agrees well with experiments.[11~13] 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:

$$V_L = R_0(r)Y_0^0(\theta,\varphi) + R_4(r)Y_4^0(\theta,\varphi) + R_6(r)Y_6^0(\theta,\varphi) + \cdots \quad (1)$$

where the summation is over all electrons of central metal ion, and $Y_l^0(\theta,\varphi)$ 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

$$\varphi_e = R_{n2}(r)Y_2^e(\theta,\varphi)$$
$$\varphi_t = R_{n2}(r)Y_2^t(\theta,\varphi) \quad (2)$$

where $Y_2^e(\theta,\varphi)$ and $Y_2^t(\theta,\varphi)$ 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

$$\epsilon_e^{(1)} - \epsilon_t^{(1)} = \langle\varphi_e|V_L|\varphi_e\rangle - \langle\varphi_t|V_L|\varphi_t\rangle$$
$$= \langle R_{n2}|R_4|R_{n2}\rangle \{\langle Y_2^e|Y_4^0|Y_2^e\rangle - \langle Y_2^t|Y_4^0|Y_2^t\rangle\}$$
$$= \langle R_{n2}|R_4|R_{n2}\rangle \cdot K \quad (K:\text{constant}) \quad (3)$$

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;

$$\Delta\epsilon_e - \Delta\epsilon_t = (\epsilon_e^{(1)} + \epsilon_e^{(2)} + \epsilon_e^{(3)} + \cdots\cdots)$$
$$- (\epsilon_t^{(1)} + \epsilon_t^{(2)} + \epsilon_t^{(3)} + \cdots\cdots)$$
$$= (\epsilon_e^{(1)} + \epsilon_e^{(h)}) - (\epsilon_t^{(1)} + \epsilon_t^{(h)})$$
$$= (\epsilon_e^{(1)} - \epsilon_t^{(1)}) + (\epsilon_e^{(h)} - \epsilon_t^{(h)}) \quad (4)$$

So that above definition of 10Dq bears the assumption

$$\epsilon_e^{(1)} - \epsilon_t^{(1)} \gg \epsilon_e^{(h)} - \epsilon_t^{(h)} \quad (5)$$

But it may be wong although the general assumptions that $\epsilon_e^{(1)} \gg \epsilon_e^{(h)}$ and $\epsilon_t^{(1)} \gg \epsilon_t^{(h)}$ are valid.

Actually the failure of theortical 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 covalency effect becomes more significant in the "covalent" complexes.

(2) Effect of Total Perturbation. If the φ_e, φ_t orbitals of free metal ion becomes φ_e', φ_t' by the perturbation due to ligation, the Integral Hellmann-Feynman theorem[16] gives the total perturbation energy (the sum of the perturbation energies of all order) difference by

$$\Delta\epsilon_e - \Delta\epsilon_t = \frac{\langle\varphi_e|V_L|\varphi_e'\rangle}{\langle\varphi_e|\varphi_e'\rangle} - \frac{\langle\varphi_t|V_L|\varphi_t'\rangle}{\langle\varphi_t|\varphi_t'\rangle} \quad (6)$$

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

$$\begin{aligned}\varphi_e' &= R_d(r)Y_2^e(\theta,\varphi) \\ \varphi_t' &= R_d(r)Y_2^t(\theta,\varphi) \\ (R_d(r) &= \sum_{n'} C_{n'}R_{n'2}(r)),\end{aligned}\right\} \quad (7)$$

then from Eq. (6) $\Delta\epsilon_e - \Delta\epsilon_t$ is given by single term:

$$\Delta\epsilon_e - \Delta\epsilon_t = \frac{\langle R_{n2}|R_4|R_d\rangle}{\langle R_{n2}|R_d\rangle} \cdot K \quad (8)$$

This result suggests that the quantity given by Eq. (8) 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_n along the lines suggested above.[16]

Now consider the case in which the perturbed wave functions φ_e', and φ_t' contain the excited configurations with higher orbital angular momentum than d orbital (angular distortion) and have unequal radial distortions:

$$\varphi_e' = R_d^e(r)Y_2^e(\theta,\varphi) + R_g^e(r)Y_4^e(\theta,\varphi) + \cdots\cdots$$

$$\varphi_t' = R_d^t(r)Y_2^t(\theta,\varphi) + R_g^t(r)Y_4^t(\theta,\varphi) + \cdots\cdots \quad (9)$$

where $R_d^e(r) \doteqdot R_d^t(r)$, $R_g^e(r) \doteqdot R_g^t(r)$, and so forth.

In this case,

$$\Delta\epsilon_e = \frac{1}{\langle R_{n2}|R_d^e\rangle}[\langle R_{n2}Y_2^e|R_0Y_0^e + R_4Y_4^e|R_d^eY_2^e\rangle \\ + \langle R_{n2}Y_2^e|R_4Y_4^e + R_6Y_6^e|R_t^eY_4^e\rangle \\ + \langle R_{n2}Y_2^e|R_4Y_4^e + R_6Y_6^e + R_8Y_8^e|R_t^eY_6^e\rangle \\ + \cdots\cdots]$$

$$\Delta\epsilon_t = \frac{1}{\langle R_{n2}|R_d^t\rangle}[\langle R_{n2}Y_2^t|R_0Y_0^e + R_4Y_4^t|R_d^tY_2^t\rangle \\ + \langle R_{n2}Y_2^t|R_4Y_4^e + R_6Y_6^e|R_t^tY_4^t\rangle + \cdots\cdots] \quad (10)$$

Unfortunate as it is, the value of $\Delta\epsilon_e - \Delta\epsilon_t$ 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, φ_e' and φ_t', and has no more significance.

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

In this section we expand the e_t^* and t_{2g}^* orbitals of $[NiF_6]^{4-}$, which correspond to φ_e' and φ_t' respectively, in terms of the set of Shull-Löwdin functions based on a single point, the nucleus of Ni^{2+} ion. The wave functions of $[NiF_6]^{4-}$ are given by Sugano and Shulman[13],

$$\begin{aligned}&\Psi_e^* = N_e(\varphi_e - \lambda_s\chi_s - \lambda_\sigma\chi_\sigma), \quad N_e = 0.968, \\ &\qquad \lambda_s = 0.113, \quad \lambda_\sigma = 0.396 \\ &\Psi_t^* = N_t(\varphi_t - \lambda_\pi\chi_\pi), \quad N_t = 0.988, \quad \lambda_\pi = 0.249\end{aligned}$$

$$\quad (11)$$

where φ_e and φ_t are the Hartree-Fock atomic orbitals of Ni^{2+} ion,

$$\varphi_e : \varphi_u = R_{3d}(r)Y_2^0(\theta,\varphi) \qquad (3z^2-r^2)$$

$$\varphi_v = R_{3d}(r)\left(\frac{1}{\sqrt{2}}\right)[Y_2^2(\theta,\varphi) + Y_2^{-2}(\theta,\varphi)]$$

$$(x^2-y^2)$$

$$\varphi_t : \varphi_\xi = R_{3d}(r)\left(\frac{i}{\sqrt{2}}\right)[Y_2^1(\theta,\varphi) + Y_2^{-1}(\theta,\varphi)]$$

$$(yz)$$

$$\varphi_\eta = R_{3d}(r)\left(\frac{-1}{\sqrt{2}}\right)[Y_2^1(\theta,\varphi) - Y_2^{-1}(\theta,\varphi)]$$
$$(xz)$$

$$\varphi_\zeta = R_{3d}(r)\left(\frac{-i}{\sqrt{2}}\right)[Y_2^2(\theta,\varphi) - Y_2^{-2}(\theta,\varphi)]$$
$$(xy)$$

with $R_{3d}(r) = r^2(3.4096e^{-2.315r} + 45,261e^{-4.523r} + 129.48e^{-8.502r} + 24.071e^{-15.01r})$ and χ_u, χ_σ, and χ_π are the SALC's of Hartree-Fock atomic orbitals of F⁻ ions (refer to *Fig.* 1 which describes the cordinates of each ligand orbital),

$$\chi_{us} = \frac{1}{\sqrt{12}}(2\varphi_{3,s} + 2\varphi_{6,s} - \varphi_{1,s} - \varphi_{2,s} - \varphi_{4,s} - \varphi_{5,s})$$

$$\chi_{u\sigma} = \frac{1}{\sqrt{12}}(2\varphi_{3,z} + 2\varphi_{6,z} - \varphi_{1,z} - \varphi_{2,z} - \varphi_{4,z} - \varphi_{5,z})$$

$$\chi_{vs} = \frac{1}{2}(\varphi_{1,s} - \varphi_{2,s} + \varphi_{4,s} - \varphi_{5,s})$$

$$\chi_{v\sigma} = \frac{1}{2}(\varphi_{1,z} - \varphi_{2,z} + \varphi_{4,z} - \varphi_{5,z})$$

$$\chi_{\xi\pi} = \frac{1}{2}(\varphi_{2,x} + \varphi_{3,y} + \varphi_{5,y} + \varphi_{6,x})$$

Fig. 1. Coordinate system used to describe the atomic orbitals of the six ligand atoms and the central metal ion.
(x_i, y_i, z_i) ---coordinates with origin at the nucleus of the *i*-th ligand atom
(x, y, z) ---coordinates with origin at the nucleus of the centaral metal ion

$$\chi_{\eta\pi} = \frac{1}{2}(\varphi_{1,y} + \varphi_{3,x} + \varphi_{4,x} + \varphi_{6,y})$$

$$\chi_{\zeta\pi} = \frac{1}{2}(\varphi_{1,x} + \varphi_{2,y} + \varphi_{4,y} + \varphi_{5,x})$$

with

$$\varphi_{i,s} = R_{2s}(r_i)Y_0^0(\theta_i,\varphi_i) = (-11,156e^{-8.70r_i} + 10.805r_ie^{-2.425r_i})Y_0^0(\theta_i,\varphi_i)$$

$$\varphi_{i,z} = R_{2p}(r_i)Y_1^0(\theta_i,\varphi_i) = r_i(15.671e^{-3.7374r_i} + 1.5742e^{-1.3584r_i})Y_1^0(\theta_i,\varphi_i)$$

$$\varphi_{i,x} = R_{2p}(r_i)\left(\frac{-1}{\sqrt{2}}\right)[Y_1^1(\theta_i,\varphi_i) - Y_1^{-1}(\theta_i,\varphi_i)]$$

$$\varphi_{i,y} = R_{2p}(r_i)\left(\frac{i}{\sqrt{2}}\right)[Y_1^1(\theta_i,\varphi_i) + Y_1^{-1}(\theta_i,\varphi_i)]$$

Let the Shull-Löwdin functions[17] be

$$\psi_{nlm} = \bar{R}_{nl}(r)Y_l^m(\theta,\varphi) \tag{12}$$

where $Y_l^m(\theta,\varphi)$ are the spherical harmonics and $\bar{R}_{nl}(r)$ are the radial functions defined by

$$\bar{R}_{nl}(r) = -\frac{(2\eta)^{3/2}}{(n+l+1)!}\sqrt{\frac{(n-l+1)!}{(n+l+1)!}} \times (2\eta r)^l L_{n+l+1}^{2l+2}(2\eta r)\exp(-\eta r) \tag{13}$$

The parameter η, usually referred to as the orbital exponent, is a variable scale factor, and the $L_{n+l+1}^{2l+2}(2\eta r)$ are the $(2l+2)$-order associated Laguerre polynomials defined according to the conventions of Pauling and Wilson.[18]

Thus $\bar{R}_{nl}(r)$ can be written as

$$\bar{R}_{nl}(r) = A_{nl}\sum_{k=0}^{n-l-1}B_{nl}^k r^{l+k}e^{-\eta r} \tag{14}$$

with

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

and

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

These functions form a complete basis set which is discrete in its entirety. These properties greatly simplify the the numerical work, giving fast convergence. First, we expand the unperturbed dorbital of free nickel ion for comparison with the expansion of Ψ_γ^e and Ψ_γ^e.
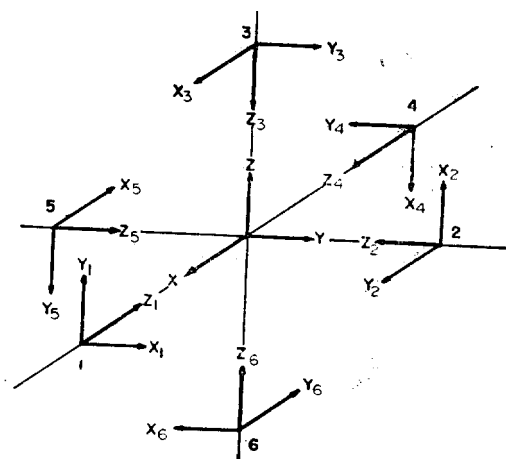
The expansion formula is given by

$$\varphi_\lambda = R_{3d}(r)Y_2^\lambda(\theta,\varphi) = \sum_n D_{n2}^\lambda \psi_{n2}^\lambda \qquad (15)$$

where ψ_{n2}^λ are the SALC's of Shull-Löwdin functions which belong to the irreducible representation denoted by the appropriate superscript, u, v, ξ, η, ζ. The coefficients D_{n2}^λ are given by

$$D_{n2}^\lambda = \langle \psi_{n2}^\lambda | \varphi_\lambda \rangle = \int_0^\infty R_{n2}^*(r)R_{3d}(r)r^2 dr$$
$$\times \int Y_2^{\lambda*}(\theta,\varphi)Y_2^\lambda(\theta,\varphi)d\Omega$$
$$= A_{n2}\sum_{k=0}^{n-3} B_{n2}^k \int_0^\infty (r^{2+k}e^{-\eta r})r^2(3.4096e^{-2.315r}$$
$$+45.261e^{-4.523r} + 129.48e^{-8.502r}$$
$$+24.071e^{-15.01r})r^2 dr \qquad (16)$$

Note that

$$D_{n2}^\xi = D_{n2}^\eta = D_{n2}^\zeta = D_{n2}^u = D_{n2}^v \equiv D_{n2}$$

We choose the value of η as 3.80, which shows the most fast convergence. The reason for this choice is that the value of η, giving fast convergence in the expansion of φ_λ, is very likely to give fast convergence in the expansion of Ψ_λ^i, which is not greatly different from φ_λ. The values of the coefficients D_{n2} are tabulated in *Table* 1.

The expansion formula of Ψ_λ^i is given by

$$\Psi_\lambda^i = \sum_{nl} C_{nl}^\lambda \psi_{nl}^\lambda$$

where

$$\psi_{nl}^\lambda = \bar{R}_{nl}(r)Y_l^\lambda(\theta,\varphi) = \bar{R}_{nl}(r)\sum_m G_{lm}^\lambda Y_l^m(\theta,\varphi) \qquad (18)$$

Values of G_{lm}^λ are tabulated in *Tables* 2~6. The expansion coefficients C_{nl}^λ in Eq. (17) are given by

$$C_{nl}^\lambda = \langle \psi_{nl}^\lambda | \Psi_\lambda^i \rangle \qquad (19)$$

Using the group theory[19], it can be shown that

$$C_{nl}^\xi = C_{nl}^\eta = C_{nl}^\zeta \quad \text{and} \quad C_{nl}^u = C_{nl}^v \qquad (20)$$

Here, C_{nl}^ξ and C_{nl}^u are calculated more easily than the others.

Table 1. Expansion of d orbital of free Ni^{2+} ion. $\varphi_\lambda = \sum_n D_{n2}\psi_{n2}^\lambda$.

n	D_{n2}
3	0.9771
4	0.0008
5	0.2073
6	0.0100
7	0.0501
8	0.0126
9	0.0128
10	0.0052
11	0.0035
12	0.0018
13	0.0011
14	0.0006
15	0.0004
16	0.0002
17	0.0002
18	0.0001
$\sum_n |D_{n2}|^2$	1.0005

C_{nl}^ξ's are given by

$$C_{nl}^\xi = \langle \psi_{nl}^\xi | \Psi_\xi^i \rangle$$
$$= N_\xi[\langle \psi_{nl}^\xi | \varphi_\xi \rangle - \lambda_\pi \langle \psi_{nl}^\xi | \chi_{\xi\pi} \rangle] \qquad (21)$$
$$\langle \psi_{nl}^\xi | \varphi_\xi \rangle = D_{n2}\delta_{l2} \qquad (21\text{-}a)$$
$$\langle \psi_{nl}^\xi | \chi_{\xi\pi} \rangle = \frac{1}{2}[\langle \psi_{nl}^\xi | \varphi_{2,x} \rangle + \langle \psi_{nl}^\xi | \varphi_{3,y} \rangle$$
$$+ \langle \psi_{nl}^\xi | \varphi_{5,y} \rangle + \langle \psi_{nl}^\xi | \varphi_{6,x} \rangle]$$

From the geometry, it is obvious that

$$\langle \psi_{nl}^\xi | \varphi_{2,x} \rangle = \langle \psi_{nl}^\xi | \varphi_{3,y} \rangle = \langle \psi_{nl}^\xi | \varphi_{5,y} \rangle = \langle \psi_{nl}^\xi | \varphi_{6,x} \rangle \qquad (21\text{-}b)$$

Thus, we are left with

$$\langle \psi_{nl}^\xi | \chi_{\xi\pi} \rangle = 2\langle \psi_{nl}^\xi | \varphi_{3,y} \rangle$$
$$= 2\int [\bar{R}_{nl}(r)Y_l^\xi(\theta,\varphi)]^*[R_{2p}(r_3)$$
$$\times \frac{i}{\sqrt{2}}\{Y_1^1(\theta_3,\varphi_3) + Y_1^{-1}(\theta_3,\varphi_3)\}]dv$$
$$= 2\int [\bar{R}_{nl}(r)\sum_m G_{lm}^\xi Y_l^m(\theta,\varphi)]^*$$
$$[R_{2p}(r_3)\frac{i}{\sqrt{2}}\{Y_1^1(\theta_3,\varphi_3) + Y_1^{-1}(\theta_3,\varphi_3)\}]dv$$
$$= 2\left| \sqrt{2}G_{11}^\xi \right| \int \{\bar{R}_{nl}(r)Y_1^1(\theta,\varphi)\}^*$$
$$\{R_{2p}(r_3)Y_1^1(\theta_3,\varphi_3)\}dv$$

Table 2. Symmetry adapted linear combinations of spherical harmonics.

$$Y_l^\xi = \sum_m G_{lm}^\xi Y_l^m = \frac{i}{\sqrt{2}}\left[\frac{\sqrt{2}}{i}G_{l1}^\xi(Y_l^1+Y_l^{-1})+\frac{\sqrt{2}}{i}G_{l3}^\xi(Y_l^3+Y_l^{-3})+\cdots\cdots+\frac{\sqrt{2}}{i}G_{l,l-1}^\xi(Y_l^{l-1}+Y_l^{-l})\right]$$

1		$\frac{\sqrt{2}}{i}G_{l1}^\xi$	$\frac{\sqrt{2}}{i}G_{l3}^\xi$	$\frac{\sqrt{2}}{i}G_{l5}^\xi$	$\frac{\sqrt{2}}{i}G_{l7}^\xi$	$\frac{\sqrt{2}}{i}G_{l9}^\xi$	$\frac{\sqrt{2}}{i}G_{l,11}^\xi$
4	Y_4^ξ	0.35355339	−0.93541435				
6	Y_6^ξ	0.90138782	0.32889676	0.28165036			
	$Y_6^{\xi\prime}$	0	−0.65044364	0.75955453			
8	Y_8^ξ	0.47598582	−0.55781092	−0.51929370	−0.43888328		
	Y_8^ξ	0	−0.23671604	0.76282144	−0.60172167		
10	Y_{10}^ξ	0.86376719	0.27958166	0.26792725	0.24701672	0.20721504	
	$Y_{10}^{\xi\prime}$	0	−0.13317195	0.43130904	−0.73793823	0.50168208	
	$Y_{10}^{\xi\prime\prime}$	0	−0.75376510	0	0.45703723	0.47218126	
12	Y_{12}^ξ	0.52384546	−0.42500507	−0.41303069	−0.39287055	−0.36007180	−0.30060490
	$Y_{12}^{\xi\prime}$	0	−0.37304625	0.67662665	0.14938000	0.01611959	−0.61679709
	$Y_{12}^{\xi\prime\prime}$	0	0.08576491	0	−0.63399655	0.74573696	−0.18592778

Table 3. Symmetry adapted linear combinations of spherical harmonics.

$$Y_l^\eta = \sum_m G_{lm}^\eta Y_l^m = -\frac{1}{\sqrt{2}}\left[-\sqrt{2}G_{l1}^\eta(Y_l^1-Y_l^{-1})-\sqrt{2}G_{l3}^\eta(Y_l^3-Y_l^{-3})-\cdots\cdots-\sqrt{2}G_{l,l-1}^\eta(Y_l^{l-1}-Y_l^{-l})\right]$$

1		$-\sqrt{2}G_{l1}^\eta$	$-\sqrt{2}G_{l3}^\eta$	$-\sqrt{2}G_{l5}^\eta$	$-\sqrt{2}G_{l7}^\eta$	$-\sqrt{2}G_{l9}^\eta$	$-\sqrt{2}G_{l,11}^\eta$
4	Y_4^η	0.35355339	0.93541435				
6	Y_6^η	0.90138782	−0.32889676	0.28165036			
	$Y_6^{\eta\prime}$	0	0.65044364	0.75955453			
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	$Y_{10}^{\eta\prime}$	0	0.13317195	0.43130904	0.73793823	0.50168208	
	$Y_{10}^{\eta\prime\prime}$	0	0.75376510	0	−0.45703723	0.47218126	
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	$Y_{12}^{\eta\prime}$	0	0.37304625	0.67662665	−0.14938000	0.01611959	0.61679709
	$Y_{12}^{\eta\prime\prime}$	0	−0.08576491	0	0.63399655	0.74573696	0.18592778

$$\equiv 2|\sqrt{2}G_{l1}^\xi|A_{nl}\sum_{k=0}^{n-l-1}B_m^k[15.671\ \mathcal{J}(l+k+1,$$
$$l,\ 1,\ 2,\ 1;\eta,\ 3.\ 7374,\ R)$$
$$+1.5742\mathcal{J}(l+k+1,l,1,2,1;\eta,1.3584,R)]$$

(21-c)

where

$$\mathcal{J}(\bar{n},l,m,\bar{n}',l';\eta,\eta',R)=\int[r^{\bar{n}-1}e^{-\eta r}Y_l^m(\theta,\varphi)]^*$$

$$\times[r_3^{\bar{n}'-1}e^{\eta'r_3}Y_{l'}^{m'}(\theta_3,\varphi_3)]dv$$

(22)

and the internuclear distance R between Ni^{2+} and F^- ions is 3.7927 a. u.

C_{nl}^s's are given by

$$C_{nl}^s=\langle\psi_{nl}^s|\mathcal{F}_s^s\rangle$$
$$=N_e[\langle\psi_{nl}^s|\varphi_u\rangle-\lambda_s\langle\psi_{nl}^s|\chi_{us}\rangle-\lambda_\sigma\langle\psi_{nl}^s|\chi_{u\sigma}\rangle]$$

(23)

Table 4. Symmetry adapted linear combinatioms of spherical harmonics.

$$Y_l^\tau = \sum_m G_{lm}^\tau Y_l^m = \frac{-i}{\sqrt{2}}[i\sqrt{2}G_{l2}^\tau(Y_l^2 - Y_l^{-2}) + i\sqrt{2}G_{l6}^\tau(Y_l^6 - Y_l^{-6}) + i\sqrt{2}G_{l10}^\tau(Y_l^{10} - Y_l^{-10}) + \cdots]$$

l		$i\sqrt{2}G_{l2}^\tau$	$i\sqrt{2}G_{l6}^\tau$	$i\sqrt{2}G_{l10}^\tau$
4	Y_4^ζ	−1		
6	Y_6^ζ	0.21926450	0.97566545	
	$Y_6^{\zeta'}$	0.97566545	−0.21926450	
8	Y_8^ζ	−0.27464711	−0.96154509	
	$Y_8^{\zeta'}$	−0.96154509	0.27464711	
10	Y_{10}^ζ	0.10966095	0.35946213	0.92669383
	$Y_{10}^{\zeta'}$	0.96450533	−0.26379921	−0.01180837
	$Y_{10}^{\zeta''}$	0.24021644	0.89509606	−0.37563161
12	Y_{12}^ζ	−0.13880607	−0.44154838	−0.88643551
	$Y_{12}^{\zeta'}$	−0.60008533	−0.67455251	0.42997268
	$Y_{12}^{\zeta''}$	−0.78780103	0.59161977	−0.17133472

Table 5. Symmetry adapted linear combinations of spherical harmonics.

$$Y_l^\alpha = \sum_m G_{lm}^\alpha Y_l^m = G_{l0}Y_l^0 = \frac{1}{\sqrt{2}}[\sqrt{2}G_{l4}^\alpha(Y_l^4 + Y_l^{-4}) + \sqrt{2}G_{l8}^\alpha(Y_l^8 + Y_l^{-8}) + \sqrt{2}G_{l12}^\alpha(Y_l^{12} + Y_l^{-12}) + \cdots]$$

l		G_{l0}^α	$\sqrt{2}G_{l4}^\alpha$	$\sqrt{2}G_{l8}^\alpha$	$\sqrt{2}G_{l12}^\alpha$	$\sqrt{2}G_{l16}^\alpha$
4	Y_4^α	0.64549722	−0.76376262			
6	Y_6^α	0.93541435	0.35355339			
8	Y_8^α	0.69597055	−0.39400753	−0.60031914		
	$Y_8^{\alpha'}$	0	0.83601718	−0.54870326		
10	Y_{10}^α	0.91144345	0.26465658	0.31500433		
	$Y_{10}^{\alpha'}$	0	0.76564149	−0.64326752		
12	Y_{12}^α	0.71852352	−0.30406127	−0.33728553	−0.52679140	
	$Y_{12}^{\alpha'}$	0	0.70456649	0.33875374	−0.62356392	
14	Y_{14}^α	0.89795050	0.22431543	0.24070991	0.29227764	
	$Y_{14}^{\alpha'}$	0	0.86035454	−0.32402604	−0.39344274	
	$Y_{14}^{\alpha''}$	0	0	0.77191640	−0.63572406	
16	Y_{16}^α	0.73194689	−0.25680265	−0.27041397	−0.30493124	−0.48187069
	$Y_{16}^{\alpha'}$	0	0.67239780	0.09018452	0.36306158	−0.63869729
	$Y_{16}^{\alpha''}$	0	0	0.85174236	−0.49801831	−0.16282728

$$\langle \psi_{nl}^*|\varphi_u\rangle D_{n2}\delta_{l2} \qquad (23\text{-a})$$

$$\langle \psi_{nl}^*|\chi_{us}\rangle = \frac{1}{\sqrt{12}}[2\langle \psi_{nl}^*|\varphi_{3,s}\rangle + 2\langle \psi_{nl}^*|\varphi_{6,s}\rangle$$
$$- \langle \psi_{nl}^*|\varphi_{1,s}\rangle - \langle \psi_{nl}^*|\varphi_{2,s}\rangle - \langle \psi_{nl}^*|\varphi_{4,s}\rangle$$
$$- \langle \psi_{nl}^*|\varphi_{5,s}\rangle]$$

It is obvious that

$$\langle \psi_{nl}^*|\varphi_{3,s}\rangle = \langle \psi_{nl}^*|\varphi_{6,s}\rangle \qquad (23\text{-b})$$

and

Table 6. Symmetry adapted linear combinations of spherical harmonics.

$$Y_l^v = \sum_m G_{lm}^v Y_l^m = \frac{1}{\sqrt{2}}[\sqrt{2}G_{l2}^v(Y_l^2+Y_l^{-2}) + \sqrt{2}G_{l6}^v(Y_l^6+Y_l^{-6}) + \sqrt{2}G_{l10}^v(Y_l^{10}+Y_l^{-10})+) +\cdots]$$

1		$\sqrt{2}G_{l2}^v$	$\sqrt{2}G_{l6}^v$	$\sqrt{2}G_{l10}^v$	$\sqrt{2}G_{l14}^v$
4	Y_4^v	-1			
6	Y_6^v	0.55901699	0.82915620		
8	Y_8^v	-0.65068202	-0.75935032		
	$Y_8^{v'}$	-0.75935032	0.65068202		
10	Y_{10}^v	0.44497917	0.48620518	0.75206254	
	$Y_{10}^{v'}$	0.39845247	-0.85957253	0.31995420	
12	Y_{12}^v	-0.51600908	-0.54714937	-0.65906160	
	$Y_{12}^{v'}$	-0.83033957	0.13051364	0.54175861	
14	Y_{14}^v	0.38276947	0.39917223	0.44709882	0.70303037
	$Y_{14}^{v'}$	0.38861700	-0.19799798	-0.80094175	0.41020232
	$Y_{14}^{v''}$	0.31287505	-0.86005276	0.39772861	0.06504153
16	Y_{16}^v	-0.43975013	-0.45389219	-0.49098594	-0.59961196
	$Y_{16}^{v'}$	-0.77436940	-0.22198134	0.48752039	0.33674944
	$Y_{16}^{v''}$	-0.36008422	0.47572496	-0.66531451	0.44875575

$$\langle\psi_{nl}^*|\varphi_{1,s}\rangle=\langle\psi_{nl}^*|\varphi_{2,s}\rangle=\langle\psi_{nl}^*|\varphi_{4,s}\rangle=\langle\psi_{nl}^*|\varphi_{5,s}\rangle \tag{23-c}$$

From the physical reasoning it is noted that

$$\langle\psi_{nl}^u+\psi_{nl}^v|\varphi_{1,s}\rangle=\langle\psi_{nl}^u+\psi_{nl}^v|\varphi_{2,s}\rangle$$
$$=\cdots\cdots=\langle\psi_{nl}^u+\psi_{nl}^v|\varphi_{6,s}\rangle \tag{23-d}$$

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

$$\langle\psi_{nl}^v|\varphi_{1,s}\rangle=\langle\psi_{nl}^v|\varphi_{2,s}\rangle=\langle\psi_{nl}^v|\varphi_{4,s}\rangle=\langle\psi_{nl}^v|\varphi_{5,s}\rangle \tag{23-e}$$

it follows that

$$\langle\psi_{nl}^*|\varphi_{3,s}\rangle=2\langle\psi_{nl}^*|\varphi_{1,s}\rangle \tag{23-f}$$

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.[20]

Thus, we are left with

$$\langle\psi_{nl}^*|\chi_{ws}\rangle=\sqrt{3}\langle\psi_{nl}^*|\varphi_{3,s}\rangle$$
$$=\sqrt{3}\int[\bar{R}_{nl}(r)Y_l^v(\theta,\varphi)]^*$$
$$\times[R_{2s}(r_3)Y_0^0(\theta_3,\varphi_3)]dv$$

$$=\sqrt{3}G_{l0}^v\int[\bar{R}_{nl}(r)Y_l^0(\theta,\varphi)]^*$$
$$\times[R_{2s}(r_3)Y_0^0(\theta_3,\varphi_3)]dv$$
$$=\sqrt{3}G_{l0}^v A_{nl}\sum_{k=1}^{n-l-1}B_{nl}^k[-11.156\,\mathrm{c}^3\,(l+k+1,$$
$$l,0,1,0;\eta,8.70,R)+10.805\mathrm{c}^3(l+k+1,l,$$
$$0,2,0;\eta,2.425,R)] \tag{23-g}$$

Similarly

$$\langle\psi_{nl}^*|\chi_{wo}\rangle=\sqrt{3}\,G_{l0}^v\sum_{k=1}^{n-l-1}B_{nl}^k\,[15.671\mathrm{c}^3(l+k+1,$$
$$l,0,2,1;\eta,3.7374,R)+1.5742\;\mathrm{c}^3\;(l+k+1,$$
$$l,0,2,1;\eta,1.3584,R)] \tag{23-h}$$

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.[21] The values of coefficients C_{nl}^u and C_{nl}^v from Eq. (21) and (23) are in Tables 7 and 8.

4. RESULTS AND DISCUSSION

From Table 7, one may note that nearly

Table 7. Expansion of Ψ'_t. $\Psi^a_t = \sum C'_{nl} \phi'_{nl}$ $\sum |C'_{nl}|^2 = 0.9967$

l \ n	2	4	6	8	10	12
3	0.9575					
4	0.0210					
5	0.1663	−0.0051				
6	0.0696	0.0141				
7	−0.0276	−0.0280	−0.237			
8	0.0941	0.352	0.0577			
9	−0.0560	−0.0348	−0.0837	−0.0212		
10	0.0492	0.0236	0.0752	0.0380		
11	−0.0191	−0.0097	−0.0345	−0.0333	−0.0526	
12	0.0151	0.0031	−0.0007	0.0086	0.0573	
13	−0.0104	−0.0039	0.0025	0.0081	−0.0120	−0.0339
14	0.0082	0.0042	0.0099	−0.0022	−0.0205	0.0142
$\sum |C'_{nl}|^2$	0.9657	0.0040	0.0179	0.0031	0.0066	0.0014

Table 8. Expansion of Ψ^a_e. $\Psi^a_e = \sum C^e_{nl} \psi^a_{nl}$ $\sum |C^e_{nl}|^2 = 0.9745$

l \ n	2	4	6	8	10	12	14	16
3	0.9202							
4	0.0639							
5	0.0918	−0.0189						
6	0.1497	0.0448						
7	−0.0740	−0.0610	−0.0342					
8	0.0521	0.0397	0.0560					
9	0.0810	0.0217	−0.0258	−0.0242				
10	−0.1163	−0.0754	−0.0526	0.0120				
11	0.0847	0.0671	0.0962	0.0347	−0.0155			
12	−0.0131	−0.0139	−0.0468	−0.0537	−0.0283			
13	0.0067	−0.0100	−0.0226	0.0104	0.0537	0.0047		
14	−0.0319	−0.0127	0.0135	0.0263	−0.0041	−0.0321		
15	0.0235	0.0213	0.0290	−0.0015	−0.0328	0.0077	0.0188	
16	0.0084	0.0030	−0.0125	−0.0217	−0.0041	0.0235	−0.0213	
17	−0.0032	−0.0091	−0.0199	−0.0033			−0.0209	0.0159
18	−0.0136	−0.0084	−0.0001					0.0013
$\sum |C^e_{nl}|^2$	0.9192	0.0193	0.0213	0.0061	0.0051	0.0017	0.0012	0.0003

complete convergence is obtained in the expansion of t^*_{2g} orbital. However, from Table 8, it is noted that the convergence in the expansion of e^*_g 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^*_g orbital than in t^*_{2g} orbital. But the more important reason is the singularity of 2s atomic orbital of F^- contained in e^*_g orbital.
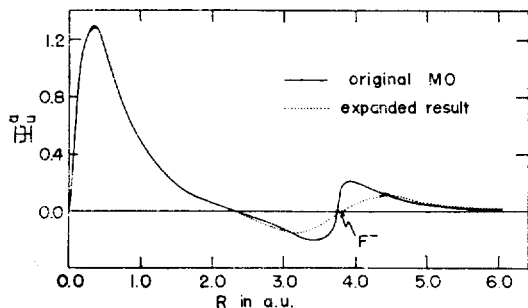
Fig. 2. Convergence in the expansion of Ψ.
This figure shows that the slow convergence is
due to the singularity of the 2s wave function
at the F⁻nucleus.

Linear combinations of wave functions based on
only one point, the nucleus of Ni^{2+}, cannot
treat these singularities at F⁻ nuclei.[22] Fig. 2
shows this point clearly. Extensive adjustment
of the scale factor to a better optimum value
for the basis function of each l-value might
give better convergence, but it involves some
difficulties in practice.

However, comparison of results in Table 7
and Table 8 with that of Table 1 shows the
following facts clearly.

We can consider the e_g^* and t_{2g}^* orbital as
the perturbed d orbitals of free metal ion. And
the result of the perturbation is that excited
configurations with higher orbital angular mo-
mentum than d orbital are considerably mixed
into the perturbed d orbital of metal ion
(angular distortion). The extent of this
angular distortion is greater in e_g^* orbital
than in t_{2g}^* orbital. Accordingly the radial
distortions in these orbitals are different from
each other.

To summarize, the e_g^* and t_{2g}^* orbital ob-
tained in the MO scheme are such wave
functions as explained in Eq. (9). So we
should say that the "10Dq" of MO scheme is
not the 10Dq defined in the extended crystal
field theory.[16]

5. CONCLUSIOM

The energy difference between e_g^* and t_{2g}^*
orbitals evaluated in the MO method have little
meaning of 10Dq defined in the crystal field
theory. That is, this value cannot be para-
meterized 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 para-
meters such as 10Dq, F_2, F_4, etc.

REFERENCES

1. H. Bethe, Ann. Physik., 3, 133 (1929).
2. J. H. Van Vleck, Phys. Rev., 41, 208 (1932).
3. C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill Book Company, Inc., 1962.
4. J. S. Griffith, "The Theory of Transition Metal Ions", Cambridge at the University Press, 1971.
5. Belford, Calvin and Belford, J. Chem. Phys., 26, 1165 (1957).
6. D. G. Homes and D. S. McClure, J. Chem. Phys., 26, 1686 (1957).
7. J. C. Phillips, J. Phys. Chem. Solids, 11, 226 (1959).
8. W. H. Kleiner, J. Chem. Phys., 20, 1784 (1952).
9. A. J. Freeman and R. E. Watson, Phys. Rev., 120, 1254 (1960).
10. C. A. Hutchison and E. Y. Wong, J. Chem. Phys., 29, 754 (1958).
11. R. G. Shulman and S. Sugano, Phys. Rev., 130, 506 (1963).
12. K. Knox, R. G. Shulman, and S. Sugano, Phys. Rev., 130, 512 (1963).
13. S. Sugano and R. G. Shulman, Phys. Rev., 130,
14. H. Kim and C. Lee, Pro. Coll. Natur. Sci.,

SNU, **1**, 93 (1976).

15. H. Kim and D. Lee, *J. Korean Chem. Soc.*, **21**, 23 (1977).

16. H. Kim, *J. Korean Chem. Soc.*, **20**, 198 (1976)

17. H. Shull and P. O. Löwdin, *J. Chem. Phys.*, **23**, 1362 (1955).

18. L. Pauling and E. B. Wilson, "Introduction to Quantum Mechnics", McGraw-Hill, 1935.

19. M. Tinkham, "Group Theory and Quantum Mechanics", McGraw-Hill, 1974.

20. M. E. Rose, "Elementary Theory of Angular Momentum", John Wiley & Sons, Inc., 1966.

21. M. E. Rose, "Elementary Theory of Anguler Momentum", John Wiley & Sons, Inc., 1966.

22. D. M. Silver and K. Ruedenberg, *J. Chem. Phys.*, **49**, 4301 (1968).

23. S. Hagstrom and H. Shull, *J. Chem. Phys.*, **30**, 1314 (1959).