

## 점전하 모형에 의한 $10Dq$ 에서의 배치간 작용의 영향

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## The Effect of the Configuration Interaction on $10Dq$ in a Point Charge Model

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**요약.** Octahedral symmetry를 지닌 리간드에 의한 영향 아래있는 하나의  $d$  전자를 갖는 금속 착물을 대상으로, 결정장 분리계수  $10Dq$ 를 결정장이론에 의하여 이론적으로 계산하였다. 점전하 모형을 쓰되, Shull-Löwdin 함수를 사용하여 배치간 작용을 고려하고, Integral Hellmann-Feynman Theorem을 써서 고차섭동의 영향을 추출하였다. 고차섭동의 영향이 일차섭동의 약 50%가 됨을 알았다. Octahedral potential에 의해  $3d$  함수의 각 성분의 변화가 없고,  $E_g$ 와  $T_{2g}$  상태에서, 동경성분의 변화가 일정하므로  $10Dq$ 는 유일한 파라미터로 남을 것이라는 결론을 얻었다.

**ABSTRACT.** For the metal complex of  $d^1$  configuration with the octahedrally coordinated ligands, the crystal field parameter,  $10Dq$ , is calculated from first principles within the framework of the crystal field theory. With the point charge model, the configuration interaction is introduced by use of the Shull-Löwdin functions. Through the Integral Hellmann-Feynman Theorem, the higher order effect is visualized. It is found that the higher order effect on  $10Dq$  is about 50% of the first order effect. Since  $3d$  function is angularly undistorted and radially equally distorted in  $E_g$  and  $T_{2g}$  states, due to the octahedral potential, the calculated  $10Dq$  is still the unique parameter for the splitting.

### 1. INTRODUCTION

The crystal field theory of Bethe<sup>1</sup> and Van Vleck<sup>2</sup>, which has been successful in explaining the magnetic properties and the spectra of the transition metal complexes, is based on the assumption that the metal ion feels a purely electrostatic field with point group symmetry of the ligands. According to the theory, it is possible

to express the gaps between any two energy levels of the metal ion by a single parameter, usually denoted by  $10Dq$ , and it corresponds to the radial integral of the first order splitting<sup>3</sup>. However, in practice, the integral is replaced by the empirical value<sup>4~6</sup>. Attempts to calculate  $10Dq$  from first principles have led to results that disagree considerably with the empirically deduced values<sup>7</sup>.

One of the reasons of the failure is that one can know nothing but the symmetry of the crystal field potential. Therefore, in the theoretical calculations, a model of the potential is employed. The other is that the higher order energy was not included. Theoretically, the difference of the first order perturbation energies is parameterized, but in practice, this very parameter is replaced by empirical values which are, by definition, the difference of the sum of the perturbation energies of all order (hereafter we call total perturbation energy). Therefore, even if the explicit form of the crystal field potential can be known,  $10Dq$  cannot be calculated from the first order energies, as long as the higher order correction contributes remarkably to the splitting. If, however, one uses the Integral Hellmann-Feynman Theorem (IHF)<sup>8</sup>, the formulations of the first order energy in the classical crystal field theory can be replaced by that of the total perturbation energy.

We analyzed the calculation of  $10Dq$  of  $[\text{Ni F}_6]^{4-}$  by Sugano and Shulman<sup>9</sup>, which is essentially the SCF MO method and thus employs relatively explicit potential. We became convinced that at least for that complex, the contribution of the higher order effect is dominant and that even the sign of  $10Dq$  disagrees with the empirical value if solely the first order energy is taken into account<sup>19</sup>.

One of the purposes of the present work is to check the higher order effect in the situation where single  $d$  electron is placed in the center of octahedrally coordinated point charges. From a logical point of view, the result of the calculation should merely reflect the defects of the potential. If IHF is used, the wave functions obtained from the variational scheme can be used in the total perturbation energy expression as if they were the perturbation functions. We employ the set of the Shull-Löwdin functions<sup>10</sup>, by which integrals converge very rapidly, as a

common basis set in the zero order and the perturbed states. The use of a common basis set guarantees the equality<sup>8</sup>,  $\langle \phi | \Delta V | \Psi \rangle \langle \phi | \Psi \rangle^{-1} = \langle \Psi | H | \Psi \rangle - \langle \phi | H^0 | \phi \rangle$ , where  $\Delta V = H - H^0$ , and  $\phi$  and  $\Psi$  are the variational function of  $H^0$  and  $H$ , respectively.

The secondary objective of the work is to examine the nature of the angular and the radial distortions. The existence of the unique parameter,  $10Dq$ , depends on the nature of these distortions, when the configuration interaction prevails.

## 2. FORMULATION

Let the Shull-Löwdin functions<sup>10</sup> be

$$\phi_{nlm} = \bar{R}_{nl}(r) Y_l^m(\theta, \phi) \quad (1)$$

where  $Y_l^m(\theta, \phi)$  are the spherical harmonics<sup>3,11</sup>, and  $\bar{R}_{nl}(r)$  are the radial functions defined by

$$\bar{R}_{nl}(r) = \frac{(2Q)^{3/2}}{(n+l+1)!} \sqrt{\frac{(n-l-1)!}{(n+l+1)!}} (2Qr)^l L_{n+l+1}^{2l+2}(2Qr) \exp(-Qr) \quad (2)$$

$Q$  is the effective nuclear charge of the metal ion, and  $L_n^l(x)$  are the associated Laguerre polynomials. Thus,

$$\begin{aligned} \bar{R}_{nl}(r) &= (2Q)^{3/2+l} \sqrt{(n+l+1)!(n-l-1)!} r^l \cdot \\ &\exp(-Qr) \sum_{k=0}^{n-l-1} \frac{(-2Q)^k}{(n-l-1-k)!(2l+2+k)!k!} r^k \\ &\equiv A_{nl} \sum_{k=0}^{n-l-1} B_{nl}^k \exp(-Qr) r^{l+k} \end{aligned} \quad (3)$$

where definitions of  $A_{nl}$  and  $B_{nl}^k$  are obvious. These radial functions form an orthonormal complete set, that is,

$$\int_0^\infty \bar{R}_{nl}(r) \bar{R}_{n'l'}(r) r^2 dr = \delta_{nn'} \quad (4)$$

Since the expectation values of the hydrogenic Hamiltonian increase rapidly as  $n$  increases, these functions are also expected to make other expectation values converge more rapidly than the hydrogenic wave functions, which are not complete until the wave functions for the con-

tinuum are taken into full account. If the zero order Hamiltonian<sup>12</sup> is

$$H^0 = -\frac{1}{2}p^2 - \frac{Q}{r} \quad (5)$$

and the kinetic energy operator  $K_l$  is

$$K_l = \frac{1}{2r^2} \left[ l(l+1) - \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) \right] \quad (6)$$

then the matrix elements are

$$\begin{aligned} & \langle \psi_{ilm} | H^0 | \psi_{jl'm'} \rangle \\ &= \delta_{ll'} \delta_{mm'} \left[ \int_0^\infty \bar{R}_{il} K_l \bar{R}_{jl} r^2 dr - Q \int_0^\infty \bar{R}_{il} \bar{R}_{jl} r dr \right] \quad (7) \end{aligned}$$

It can be shown that<sup>12</sup>,

$$\begin{aligned} & \langle \psi_{ilm} | H^0 | \psi_{jl'm'} \rangle \\ &= \delta_{ll'} \delta_{mm'} Q^2 \left[ \frac{1}{2} \delta_{ij} + \left( \frac{\epsilon_{jl}}{\epsilon_{il}} \right) \left\{ (1 - \delta_{ij}) + \frac{2(j-l-1)}{2l+3} \right. \right. \\ & \quad \left. \left. - \frac{1}{l+1} \right\} \right] \quad (8) \end{aligned}$$

where  $\epsilon_{nl} = \sqrt{\frac{(n+l+1)!}{(n-l-1)!}}$  and  $i \geq j$ .

Given the zero order Schrödinger equation

$$H^0 \phi_k = E_k^0 \phi_k \quad (9)$$

one may obtain approximations to  $\phi_k$  (denoted by  $\tilde{\phi}_k$ )

$$(\tilde{\phi}_1, \tilde{\phi}_2, \dots, \tilde{\phi}_{20}) = (\phi_{3d}, \phi_{4d}, \dots, \phi_{13d}, \phi_{5g}, \dots, \phi_{13g}) \quad (10)$$

from a limited set of the Shull-Löwdin functions

$$(\phi_1, \phi_2, \dots, \phi_{20}) = (\phi_{3d}, \phi_{4d}, \dots, \phi_{13d}, \phi_{5g}, \dots, \phi_{13g}) \quad (11)$$

through variation. That is,

$$\tilde{\phi}_k = \sum_{i=1}^{20} \phi_i \alpha_{ik} \quad (12)$$

The lowest eigenvalue obtained from the secular equation is close approximation to the exact hydrogenic  $3d$  energy, and the corresponding eigenvector  $\phi_{3d}$  is an approximation to the hydrogenic  $3d$  wave function. For instance, when the effective nuclear charge of the metal ion is 1, the lowest eigenvalue is  $-0.55496 \times 10^{-1}$  a. u., while the exact hydrogenic  $3d$

energy is  $-0.55556 \times 10^{-1}$  a. u. We were not able to use the wave functions higher than  $14d$ , due to the loss of the significant figures in the radial integrals.

If six point charges (ligands) are placed around the metal ion as in Fig. 1, the potential<sup>13</sup>,  $\Delta V$ , is given by

$$\Delta V = \sum_{i=1}^6 \frac{Z}{|\vec{R} - \vec{r}_i|} \quad (13)$$

On the other hand,

$$\frac{1}{|\vec{R} - \vec{r}_i|} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_l^m(\theta, \varphi) \quad (14)$$

Substituting Eq. (14) into Eq. (13),

$$\begin{aligned} \Delta V &= \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} \left[ \sum_{i=1}^6 Y_l^{m*}(\theta_i, \varphi_i) \right] \cdot \\ & \quad Y_l^m(\theta, \varphi) \\ &= 6\sqrt{4\pi} \frac{r_{<}^0}{r_{>}^1} Y_0^0 + \frac{7}{2} \sqrt{\frac{4\pi}{9}} \frac{r_{<}^4}{r_{>}^5} \cdot \\ & \quad \left[ Y_4^0 + \sqrt{\frac{5}{14}} (Y_4^4 + Y_4^{-4}) \right] + \dots \\ &\equiv 6\sqrt{4\pi} R^{03} \omega^{00} + \frac{7}{2} \sqrt{\frac{4\pi}{9}} R^{04} \omega^{04} + \dots \quad (15) \end{aligned}$$

Let the Schrödinger equation of the perturbed

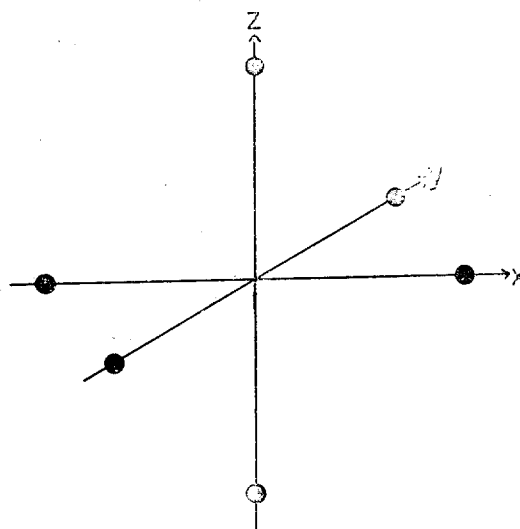


Fig. 1. Coordinates used to describe the regular octahedron of the point charges. (metal-ligand distance =  $R$  in a. u., metal charge =  $Q$ , and ligand charge =  $Z$ ).

states be

$$H\Psi_k = E_k\Psi_k \quad (16)$$

with

$$H = H^0 + \Delta V \quad (17)$$

The eigenvectors,  $\Psi_k$ , can be approximated with  $\tilde{\Psi}_k$ ,

$$\tilde{\Psi}_k = \sum_{i=1}^{20} \tilde{\phi}_i \beta_{ik} \quad (18)$$

The Schrödinger equations for  $E_g$  and  $T_{2g}$  are given by, respectively,

$$H\Psi_k^{eg} = E_k^{eg}\Psi_k^{eg} \quad (19)$$

$$H\Psi_k^{t2g} = E_k^{t2g}\Psi_k^{t2g} \quad (20)$$

And by the definition of  $10Dq$ ,

$$10Dq \equiv \Delta = E_1^{eg} - E_1^{t2g} \quad (21)$$

The matrix elements of  $H$  are

$$\begin{aligned} \langle \tilde{\phi}_i | H | \tilde{\phi}_j \rangle &= \langle \tilde{\phi}_i | H^0 + \Delta V | \tilde{\phi}_j \rangle \\ &= \langle \tilde{\phi}_i | H^0 | \tilde{\phi}_j \rangle \delta_{ij} + \langle \tilde{\phi}_i | \Delta V | \tilde{\phi}_j \rangle \end{aligned} \quad (22)$$

since  $\tilde{\phi}_i$  are diagonal with respect to  $H^0$ .

Taking  $\tilde{\phi}_i \equiv R_{nl}^i \omega_{lm}^i$ , then one has

$$\begin{aligned} \langle \tilde{\phi}_i | \Delta V | \tilde{\phi}_j \rangle &= 6\sqrt{4\pi} \langle R_{nl}^i | R^{00} | R_{n'l'}^j \rangle \cdot \\ &\quad \langle \omega_{lm}^i | \omega^{00} | \omega_{l'm'}^j \rangle \\ &\quad + \frac{7}{2} \sqrt{\frac{4\pi}{9}} \langle R_{nl}^i | R^{04} | R_{n'l'}^j \rangle \cdot \\ &\quad \langle \omega_{lm}^i | \omega^{04} | \omega_{l'm'}^j \rangle \end{aligned} \quad (23)$$

from Eq. (15). By use of Eq. (12), the integrals of the radial parts may be expressed as

$$\begin{aligned} \langle R_{nl}^i | R^{00} | R_{n'l'}^j \rangle &= \sum_{k=1}^{20} \sum_{k'=1}^{20} \alpha_{ki} \alpha_{k'j} \cdot \\ &\quad \langle \bar{R}_{kl} | R^{00} | \bar{R}_{k'l'} \rangle \end{aligned} \quad (24)$$

$$\begin{aligned} \langle R_{nl}^i | R^{04} | R_{n'l'}^j \rangle &= \sum_{k=1}^{20} \sum_{k'=1}^{20} \alpha_{ki} \alpha_{k'j} \cdot \\ &\quad \langle \bar{R}_{kl} | R^{04} | \bar{R}_{k'l'} \rangle \end{aligned} \quad (25)$$

It can be shown that<sup>18</sup>

$$\begin{aligned} F^n(p, a) &\equiv \int_0^\infty r^p \exp(-ar) \frac{r^{<n}}{r^{>n+1}} dr \\ &= \frac{1}{R^{n+1}} \int_0^R r^{p+n} \exp(-ar) dr + \\ &\quad R^n \int_R^\infty r^{p-n-1} \exp(-ar) dr \end{aligned}$$

$$\begin{aligned} &= \exp(-aR) \left[ \frac{(p+n)!}{a^{p+n+1} R^{n+1}} \cdot \right. \\ &\quad \left. \sum_{l=p+n+1}^\infty \frac{(aR)^l}{l!} + R^n \frac{(p-n-1)!}{a^{p-n}} \right. \\ &\quad \left. \sum_{l=0}^{p-n-1} \frac{(aR)^l}{l!} \right] \end{aligned} \quad (26)$$

According to Eqs. (3) and (26), the integrals in Eqs. (24) and (25) may be expressed as

$$\langle \bar{R}_{kl} | R^{00} | \bar{R}_{k'l'} \rangle = A_{kl} A_{k'l'} \sum_{i=0}^{k-l-1} \sum_{i'=0}^{k'-l'-1} B_{kl}^{i'}$$

$$\begin{aligned} B_{kl}^{i'} \exp(-2QR) &\times \left[ \frac{p!}{(2Q)^{p+1} R} \cdot \right. \\ &\quad \left. \sum_{q=p+1}^\infty \frac{(2QR)^q}{q!} + \frac{(p-1)!}{(2Q)^p} \sum_{q=0}^{p-1} \frac{(2QR)^q}{q!} \right] \end{aligned} \quad (27)$$

$$\langle \bar{R}_{kl} | R^{04} | \bar{R}_{k'l'} \rangle = A_{kl} A_{k'l'} \sum_{i=0}^{k-l-1} \sum_{i'=0}^{k'-l'-1} B_{kl}^{i'}$$

$$\begin{aligned} B_{kl}^{i'} \exp(-2QR) &\times \left[ \frac{(p+4)!}{(2Q)^{p+5} R^5} \cdot \right. \\ &\quad \left. \sum_{q=p+5}^\infty \frac{(2QR)^q}{q!} + \frac{R^4(p-5)!}{(2Q)^{p-4}} \sum_{q=0}^{p-5} \frac{(2QR)^q}{q!} \right] \end{aligned} \quad (28)$$

where  $p = t + t' + l + l' + 2$ , and  $B_{kl}^t$  and  $B_{k'l'}^{t'}$  are alternating series. The positive and the negative terms of the series are calculated separately in order to minimize the loss of significant figures.

From the Schrödinger equation of Eqs. (9) and (16), one can immediately write down

$$\langle \phi_l | H^0 + \Delta V | \Psi_l \rangle = E_l \langle \phi_l | \Psi_l \rangle \quad (29)$$

or

$$\langle \phi_l | \Delta V | \Psi_l \rangle = (E_l - E_l^0) \langle \phi_l | \Psi_l \rangle \quad (30)$$

Thus one has

$$E_l - E_l^0 = \frac{\langle \phi_l | \Delta V | \Psi_l \rangle}{\langle \phi_l | \Psi_l \rangle} \quad (31)$$

which is the Integral Hellmann-Feynman Theorem<sup>8</sup>. Eq. (31) does hold even with approximations  $\tilde{\phi}_k$  and  $\tilde{\Psi}_l$  only if they are made of a common basis set<sup>8</sup>.

From Eq. (21)

$$\Delta = (E_1^{eg} - E_1^0) - (E_1^{t2g} - E_1^0) \quad (32)$$

According to Eqs. (18) and (31)

$$\Delta = \frac{\langle \tilde{\phi}_1^{eg} | \Delta V | \tilde{\Psi}_1^{eg} \rangle}{\langle \tilde{\phi}_1^{eg} | \tilde{\Psi}_1^{eg} \rangle} - \frac{\langle \tilde{\phi}_1^{t2g} | \Delta V | \tilde{\Psi}_1^{t2g} \rangle}{\langle \tilde{\phi}_1^{t2g} | \tilde{\Psi}_1^{t2g} \rangle}$$

$$\begin{aligned}
& \frac{\langle \tilde{\phi}_1^{eg} | \Delta V | \sum_k \beta_{k1}^{eg} \tilde{\phi}_k^{eg} \rangle}{\langle \tilde{\phi}_1^{eg} | \sum_k \beta_{k1}^{eg} \tilde{\phi}_k^{eg} \rangle} \\
& - \frac{\langle \tilde{\phi}_1^{t2g} | \Delta V | \sum_k \beta_{k1}^{t2g} \tilde{\phi}_k^{t2g} \rangle}{\langle \tilde{\phi}_1^{t2g} | \sum_k \beta_{k1}^{t2g} \tilde{\phi}_k^{t2g} \rangle} \\
& = [\langle \tilde{\phi}_1^{eg} | \Delta V | \tilde{\phi}_1^{eg} \rangle - \langle \tilde{\phi}_1^{t2g} | \Delta V | \tilde{\phi}_1^{t2g} \rangle] \\
& + [\langle \tilde{\phi}_1^{eg} | \Delta V | \sum_{k=2} \nu_{k1}^{eg} \tilde{\phi}_k^{eg} \rangle \\
& - \langle \tilde{\phi}_1^{t2g} | \Delta V | \sum_{k=2} \nu_{k1}^{t2g} \tilde{\phi}_k^{t2g} \rangle] \quad (33)
\end{aligned}$$

where  $\nu_{k1} = \beta_{k1}/\beta_{11}$ . The first term on the right of Eq. (33) corresponds to the  $10Dq$  of the classical crystal field theory. The second term corresponds to the higher order correction on  $10Dq$ , coming from the mixing of excited configurations.

### 3. RESULTS AND DISCUSSION

Computations are performed on IBM-360, the electronic digital computer of the Seoul National University. For the comparison, the empirically deduced value of  $10Dq$  of  $\text{TiF}_6^{3-}$ , 15,500 $\text{cm}^{-1}$ ,<sup>15</sup> is referred. Thus the calculations are performed for the metal-ligand distance  $R=3.7, 3.8, 3.9$ ,

and 4.0 atomic units, and for the effective nuclear charge of the metal ion  $Q=4.0, 5.7, 5.9$ , and 6.3.  $Q=4.0$  corresponds to the completely screened nuclear charge by the inner electrons, and  $Q=5.9$  is calculated from the Slater rule. The ligand charge  $Z$  is varied from  $-0.50$  to  $-1.20$ .

It is noticeable that the higher order effect on  $10Dq$  is remarkable when  $R=3.8$  a. u. and  $Q=5.9$ . (see Table 1 and 2) The effect of the higher order correction is visually presented in Fig. 2.

The contributions of each excited configuration to the higher order, which are calculated from Eq. (33), are shown in Table 3 and the situation is more visually shown in Fig. 3. The equielectron density curve of  $d_{xz}$  and  $d_{x^2-y^2}$  in  $xz$  plane ( $\varphi=0^\circ$ ) are represented in Fig. 4 and Fig. 5, respectively. And when  $\theta$  is  $20^\circ$  and  $45^\circ$  in  $xz$  plane, the probability distributions along the distance from the metal ion are shown in Fig. 6 and Fig. 7, respectively. These probability distribution lines are not normalized. In Table 4, one finds that the fraction of the

Table 1.  $10Dq$  ( $\text{cm}^{-1}$ ) dependence upon the ligand charge  $Z$  and the metal charge  $Q$  (metal-ligand distance  $R=3.8$  a. u.).

Q		Ligand charge (Z)				
		-0.50	-0.72	-0.90	-1.00	-1.20
4.0	First*	13,100	18,800	23,600	26,200	31,400
	Higher	300	900	1,400	1,900	2,600
	Total	13,400	19,700	25,000	28,100	34,000
5.7	First	4,910	7,070	8,840	9,820	11,800
	Higher	-80	-160	-230	-270	-300
	Total	4,830	6,910	8,610	9,550	11,500
5.9	First	4,330	6,230	7,790	8,650	10,400
	Higher	1,370	2,760	4,210	4,850	6,400
	Total	5,700	8,990	11,900	13,500	16,800
6.3	First	3,370	4,850	6,070	6,740	8,090
	Higher	-40	-80	-130	-150	-210
	Total	3,330	4,770	5,940	6,590	7,880

\*First;  $10Dq$  calculated from the first order approximation, Higher; higher order correction on  $10Dq$ , Total;  $10Dq$  including higher order correction.

Table 2.  $10Dq$  ( $\text{cm}^{-1}$ ) dependence upon the ligand charge  $Z$  and the metal-ligand distance  $R$  in a. u. (metal charge  $Q=5.9$ ).

$R$		Ligand charge ( $Z$ )				
		-0.50	-0.72	-0.90	-1.00	-1.20
3.7	First*	4,900	7,060	8,820	9,800	11,800
	Higher	-70	-140	-210	-250	-400
	Total	4,830	6,920	8,610	9,550	11,400
3.8	First	4,330	6,230	7,790	8,650	10,400
	Higher	1,370	2,760	4,210	4,850	6,400
	Total	5,700	8,990	11,900	13,500	16,800
3.9	First	3,820	5,510	6,880	7,650	9,180
	Higher	-50	-120	-160	-200	-270
	Total	3,770	5,390	6,720	7,450	8,910
4.0	First	3,380	4,870	6,090	6,770	8,120
	Higher	-40	-90	-140	-170	-230
	Total	3,340	4,780	5,950	6,600	7,890

\*First;  $10Dq$  calculated from the first order approximation, Higher; higher order correction on  $10Dq$ , Total;  $10Dq$  including higher order correction.

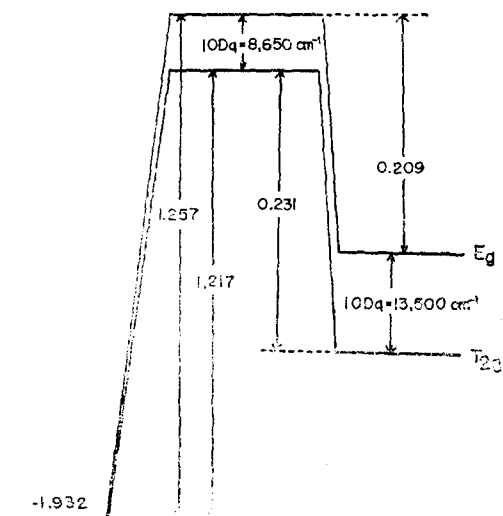


Fig. 2. Energy-level diagram showing the higher order effect on  $10Dq$ . (unit=atomic unit, metal-ligand distance  $R=3.8$  a. u., metal charge  $Q=5.9$ , and ligand charge  $Z=-1.00$ ).

radial integrals inside the ligands are dominant, and the phenomenon coincides with that observed by Karplus *et al.*<sup>17</sup> It means that the radial integrals are affected only by the inner functions.

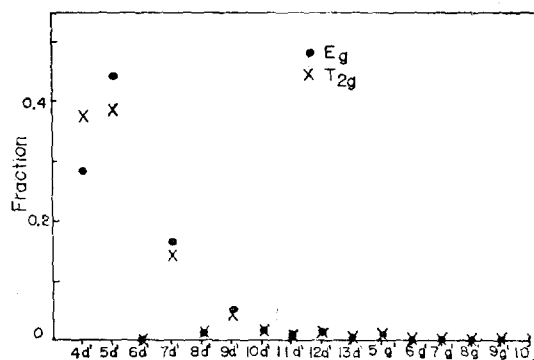


Fig. 3. Contributions of each excited configuration to the higher order effect (metal-ligand distance  $R=3.8$  a. u., metal charge  $Q=5.9$ , and ligand charge  $Z=-1.00$ ).

In Table 1 and Table 2, the calculated values agree, in order of magnitude, with the empirically deduced value at  $Q=5.9$  and  $R=3.8$  a. u. This implies that the point charge model is fairly realistic at least for this complex. The calculated values of  $10Dq$  are very sensitive to  $Q$  and  $Z$ . The fact implies that  $10Dq$  itself sensitively depends on the bond formations

Table 3. Contributions of each excited configuration to the higher order (metal-ligand distance is 3.8 a.u., metal charge is 5.9, and ligand charge is -1.0).

	$T_{2g}$		$E_g$	
	$\nu_{k1}{}^{t2g*}$	$\langle \tilde{\phi}_1{}^{t2g}   \Delta V   \nu_{k1}{}^{t2g} \tilde{\phi}_k{}^{t2g} \rangle$	$\nu_{k1}{}^{eg**}$	$\langle \tilde{\phi}_1{}^{eg}   \Delta V   \nu_{k1}{}^{eg} \tilde{\phi}_k{}^{eg} \rangle$
4d	$-2.97 \times 10^{-1}$	$-8.76 \times 10^{-2}$	$-2.54 \times 10^{-1}$	$-6.02 \times 10^{-2}$
5d	$2.21 \times 10^{-1}$	$-8.82 \times 10^{-2}$	$2.26 \times 10^{-1}$	$-9.33 \times 10^{-2}$
6d	$-2.00 \times 10^{-3}$	$-8.88 \times 10^{-6}$	$-7.45 \times 10^{-4}$	$-3.47 \times 10^{-6}$
7d	$8.04 \times 10^{-2}$	$-3.38 \times 10^{-2}$	$7.95 \times 10^{-2}$	$-3.34 \times 10^{-2}$
8d	$-1.75 \times 10^{-2}$	$-2.75 \times 10^{-3}$	$-1.73 \times 10^{-2}$	$-2.54 \times 10^{-3}$
9d	$-2.47 \times 10^{-2}$	$-1.02 \times 10^{-2}$	$-2.70 \times 10^{-2}$	$-1.00 \times 10^{-2}$
10d	$-1.23 \times 10^{-2}$	$-3.42 \times 10^{-3}$	$-1.21 \times 10^{-2}$	$-3.36 \times 10^{-3}$
11d	$7.05 \times 10^{-3}$	$-1.97 \times 10^{-3}$	$6.93 \times 10^{-3}$	$-1.93 \times 10^{-3}$
12d	$-5.97 \times 10^{-3}$	$-2.65 \times 10^{-3}$	$-5.68 \times 10^{-3}$	$-2.60 \times 10^{-3}$
13d	$8.58 \times 10^{-4}$	$-1.56 \times 10^{-4}$	$8.42 \times 10^{-4}$	$-1.53 \times 10^{-4}$
<hr/>				
5g	$1.47 \times 10^{-2}$	$-3.15 \times 10^{-4}$	$-2.65 \times 10^{-2}$	$-1.13 \times 10^{-3}$
6g	$1.89 \times 10^{-3}$	$-8.11 \times 10^{-6}$	$-2.35 \times 10^{-2}$	$-2.02 \times 10^{-4}$
7g	$1.24 \times 10^{-4}$	$1.09 \times 10^{-7}$	$-5.62 \times 10^{-4}$	$9.84 \times 10^{-7}$
8g	$2.29 \times 10^{-5}$	$4.24 \times 10^{-10}$	$-1.17 \times 10^{-4}$	$4.33 \times 10^{-9}$
9g	$-1.43 \times 10^{-6}$	$-3.26 \times 10^{-10}$	$2.97 \times 10^{-5}$	$-1.36 \times 10^{-8}$
10g	$3.75 \times 10^{-5}$	$-2.65 \times 10^{-8}$	$-6.16 \times 10^{-5}$	$-8.75 \times 10^{-8}$
11g	$1.95 \times 10^{-5}$	$-1.25 \times 10^{-8}$	$-3.19 \times 10^{-5}$	$-4.08 \times 10^{-8}$
12g	$-7.74 \times 10^{-6}$	$-3.90 \times 10^{-9}$	$1.91 \times 10^{-5}$	$-1.93 \times 10^{-8}$
13g	$3.36 \times 10^{-6}$	$-1.72 \times 10^{-9}$	$-5.70 \times 10^{-6}$	$-5.39 \times 10^{-9}$

\* $\nu_{k1}{}^{t2g} = \beta_{k1}{}^{t2g} / \beta_{11}{}^{t2g}$ , \*\* $\nu_{k1}{}^{eg} = \beta_{k1}{}^{eg} / \beta_{11}{}^{eg}$ .

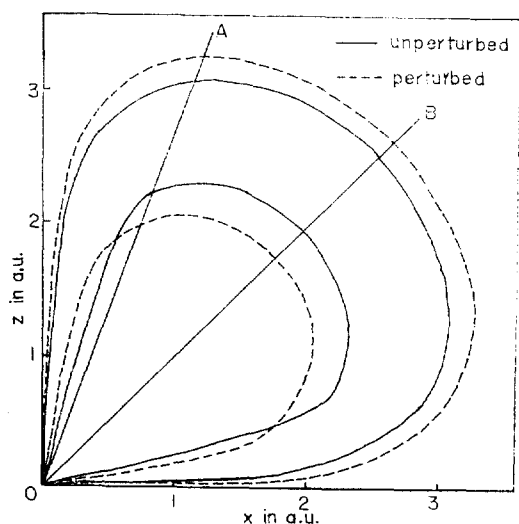


Fig. 4. Equipotential density curve of  $d_{xx}$  in  $xz$  plane ( $\varphi=0$ ) (metal-ligand distance  $R=3.8$  a.u., metal charge  $Q=5.9$ , and ligand charge  $Z=-1.00$ ).

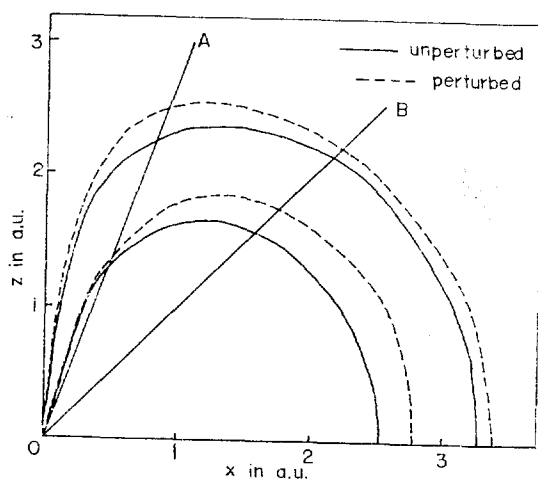


Fig. 5. Equipotential density curve of  $d_{x^2-y^2}$  in  $xz$  plane ( $\varphi=0$ ) (metal-ligand distance  $R=3.8$  a.u., metal charge  $Q=5.9$ , and ligand charge  $Z=-1.00$ ).

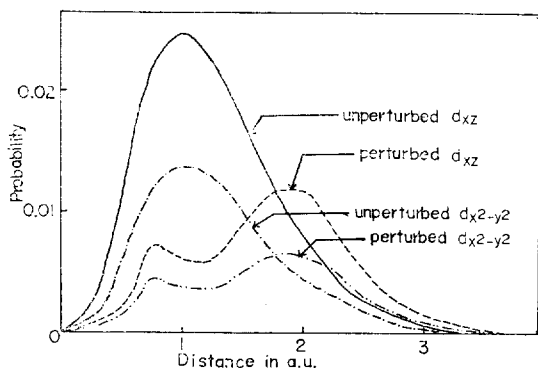


Fig. 6. Electron density distribution along the line A in Fig. 4 and Fig. 5 ( $\varphi=0$ ,  $\theta=20^\circ$ ).

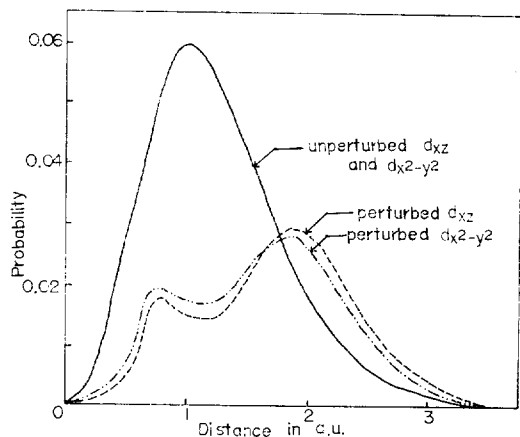


Fig. 7. Electron density distribution along the line B in Fig. 4 and Fig. 5 ( $\varphi=0$ ,  $\theta=45^\circ$ ).

between the metal ion and ligands, and on the interaction between the inner electrons and the valence electrons of the metal ion. The higher order effect is about one half of the first order effect in  $10Dq$ . Thus, the higher order correction is essential in the calculation of  $10Dq$  from first principles. The parameter  $10Dq$ , of which the classical expression is given by

$$10Dq = \langle \phi_1^{eg} | \Delta V | \phi_1^{eg} \rangle - \langle \phi_1^{t2g} | \Delta V | \phi_1^{t2g} \rangle \quad (34)$$

may be replaced by the empirical value. However, in the theoretical calculations, even if the

Table 4. Fractions of the radial integrations inside the ligands (metal-ligand distance  $R=3.8$  a. u., and metal charge  $Q=5.9$ ).

$n$	$\langle \bar{R}_{n2}   R^{00}   \bar{R}_{n2} \rangle$	$\langle \bar{R}_{n2}   R^{04}   \bar{R}_{n2} \rangle$	$\langle \bar{R}_{n4}   R^{00}   \bar{R}_{n4} \rangle$	$\langle \bar{R}_{n4}   R^{04}   \bar{R}_{n4} \rangle$
3	1.000	1.000		
4	1.000	1.000		
5	1.000	1.000	1.000	1.000
6	1.000	1.000	1.000	1.000
7	1.000	1.000	1.000	1.000
8	1.000	0.998	1.000	0.999
9	0.998	0.989	0.999	0.996
10	0.989	0.951	0.994	0.971
11	0.949	0.841	0.968	0.892
12	0.854	0.629	0.890	0.712
13	0.738	0.385	0.767	0.455

precise form of the crystal field potential is given, the first order approximation may not agree with the empirically deduced values. In fact, according to the analysis of the  $[\text{NiF}_6]^{4-}$  calculation by Sugano and Shulman, where a relatively explicit potential is employed, even the sign of the first order disagrees with the empirical  $10Dq$  value.<sup>19</sup>

From Table 3, one finds that the effects of  $g$ -functions are negligible (no angular distortion), and each excited configuration contributes nearly equally, in  $E_g$  and  $T_{2g}$  states, to the higher order correction. The phenomenon of the equal radial distortion is also seen in Fig. 4 through Fig. 7. It means that there exists the sole radial integral which can be parameterized. Thus,  $10Dq$  should be recognized as a unique parameter at least in the present model.<sup>8</sup>

#### 4. CONCLUSIONS

From the observations obtained from the present work, one may conclude that, in the  $10Dq$ , the higher order effect is as important as the first order. The simple point charge model is fairly realistic for the description of the crystal field potential of  $\text{TiF}_6^{3-}$  ion.



Since the introduction of the excited configuration mixing does not alter the angular dependence of the zero order functions, and causes the equal radial distortion to the  $E_g$  and  $T_{2g}$  states, the  $10Dq$  so obtained still remains as a unique parameter.

Thus, only if the model potential is refined, one may calculate the  $10Dq$  from first principles, within the framework of the crystal field theory, by introducing the extensive configuration.

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