

## Integral Hellmann-Feynman Approach 에 의한 $\text{KNiF}_3$ 의 Cubic Crystal Field Splitting $10 Dq$ 의 계산

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## Calculation of the Cubic Crystal Field Splitting $10 Dq$ in $\text{KNiF}_3$ . An Integral Hellmann-Feynman Approach

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**要 約.** Integral Hellmann-Feynman formula를 사용하여  $\text{KNiF}_3$ 의 cubic crystal field splitting  $10 Dq$ 를 first principle로 부터 계산하였다. Covalency parameter들과 필요한 적분치들은 Sugano와 Shulman의 계산치를 사용하였다. 계산치  $7100 \text{ cm}^{-1}$ 는 실험치  $7250 \text{ cm}^{-1}$ 와 대단히 잘 일치하였다. 고차섭동에너지 보정치는  $10 Dq$  자체와 같은 order of magnitude를 가지며 따라서 first principle로 부터  $10 Dq$ 를 계산하는데 있어서 반드시 고려되어야 할 몫이라는 것을 발견하였다. 또한 point charge potential이 crystal field potential의 압도적인 부분을 차지하는 것을 발견하였다.

**Abstract.** By use of an Integral Hellmann-Feynman formula, the cubic crystal field splitting  $10 Dq$  in  $\text{KNiF}_3$  is calculated from first principles. Numerical values of covalency parameters and necessary integrals are quoted from Sugano and Shulman. The result,  $7100 \text{ cm}^{-1}$ , is in excellent agreement with the observed value,  $7250 \text{ cm}^{-1}$ . It is found that higher order perturbation energy correction is of the same order of magnitude as  $10 Dq$  itself and is, therefore, essential in calculating  $10 Dq$  from first principles. It is also found that the point charge potential is the dominant part of the crystal field potential.

### 1. Introduction

The Bethe<sup>1</sup> and Van Vleck<sup>2</sup> crystal field theory has been successfully applied to the interpretation of a wide range of experimental data such as optical absorbance and paramagnetic

resonance, for example. To establish the validity of the theory, the need for the calculation of the crystal field splitting  $10 Dq$  from first principles appeared demanding. Several attempts have been made to calculate  $10 Dq$  in chrome alum from first principles in the framework of

ionic model. Though first attempts seemed successful,<sup>3,4</sup> it soon turned out that serious difficulties were involved in the problem as long as ionic model was retained.<sup>5-8</sup>

An essential turning point was made by Sugano and Shulman (henceforth denoted as S & S) who, supported by NMR data of covalency<sup>9</sup> and optical spectra<sup>10</sup>, performed a molecular orbital calculation from first principles of both  $10 Dq$  and the LCAO wave functions in  $\text{KNiF}_3$ .<sup>11</sup> They obtained excellent numerical value of  $10 Dq$ , but later their calculation was criticized both by Watson and Freeman<sup>12</sup> and by Šimánek and Šroubek.<sup>13</sup>

Several other molecular orbital calculations have been performed on the same molecule.<sup>14-16</sup> Hubbard et. al.<sup>17</sup> undertook configuration interaction approach to explain weak covalency in transition metal salts including  $\text{KNiF}_3$ . All these attempts gave results much smaller than the observed value.

We focus our attention on the fact that the conventional crystal field theory has been confined to the calculation of the first order perturbation energies. We have at hand an Integral Hellmann-Feynman formula of degenerate case recently elucidated by the present authors.<sup>18</sup> It enables us to calculate  $\Delta E$ , the energy change accompanied by a perturbation in Hamiltonian  $\Delta H$ , including higher order perturbation energies when the zeroth state is degenerate as long as the final state wave function is available.

We take, following S&S, the antibonding molecular orbital of  $(\text{NiF}_6)^{4-}$  molecule which is a linear combination of the  $\text{Ni}^{2+}$  and F-Hartree-Fock atomic orbitals as our final state wave function. Numerical values of covalency parameters and necessary integrals are quoted from S&S III.<sup>11</sup> It is shown that the total perturbation energy correction, higher than second order, in the calculation of  $10 Dq$  in

$\text{KNiF}_3$  is of the same order of magnitude as the value of  $10 Dq$  itself and is, therefore, essential in obtaining reasonable value of  $10 Dq$ . It is also found that the point charge model gives excellent value of  $10 Dq$  if higher order energy is included by means of the Integral Hellmann-Feynman formula of degenerate case.

## 2. Formulation

**A. Zeroth State Hamiltonian.** The zeroth state of the  $(\text{NiF}_6)^{4-}$  molecule is represented by non-interacting  $\text{Ni}^{2+}$  ion and six octahedrally coordinated  $\text{F}^-$  ions. The zeroth state Hamiltonian is written as

$$H^0 = H^M(1 \sim 8) + H^{(I)}(9 \sim 16) + H^{(II)}(17 \sim 24) + \dots + H^{(VI)}(49 \sim 56) \quad (2.1)$$

where

$$H^M = \sum_{i=1}^8 \left( -\frac{1}{2} A_i + V^M(i) + \frac{1}{2} \sum_{j \neq i}^8 g(ij) \right) \quad (2.2)$$

$$g(ij) = 1/r_{ij} \quad (2.3)$$

$$V^M(i) = \text{potential due to the nucleus plus } (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6 \text{ core electrons of } \text{Ni}^{2+} \text{ acting on the } i\text{-th } 3d \text{ electron of the } \text{Ni}^{2+} \quad (2.4)$$

$$H^{(VI)} = \sum_{i=49}^{56} \left( -\frac{1}{2} A_i + V^{(VI)}(i) + \frac{1}{2} \sum_{j=49}^6 g(ij) \right) \quad (2.5)$$

$$V^{(VI)}(i) = \text{potential due to the nucleus plus } (1s)^2 \text{ core electrons of the 6-th ligand } \text{F}^- \text{ acting on the } i\text{-th valence electron of the same } \text{F}^- \quad (2.6)$$

Obviously, subscript  $M$  stands for the metal ion and the Roman numbers I~VI stand for the ligand numbering.

**B. Perturbed State Hamiltonian.** In our picture, the zeroth state is perturbed in two separate steps. Ligand-ligand interactions represented by  $\Delta H^A$  are considered first. Metal-ligand interactions represented by  $\Delta H^B$  are applied

hereafter. The perturbed state Hamiltonian is written as

$$H = H^0 + \Delta H^A + \Delta H^B \quad (2.7)$$

where

$$\Delta H^A = \sum_{N=I}^{V,I} \sum_{i=N,M} \left( V^{(N)}(i) + \frac{1}{2} \sum_{j \in N} g(ij) \right) \quad (2.8)$$

$$\Delta H^B = \sum_{j \in M} \sum_{N=I}^{V,I} V^{(N)}(j) + \sum_{i \in M} V^M(i) + \sum_{i \in M} \sum_{j \in M} g(ij) \quad (2.9)$$

Thus, we have

$$H = \sum_{i=1}^{56} \left( -\frac{1}{2} \Delta_i + V^M(i) + \sum_{N=I}^{V,I} V^{(N)}(i) + \frac{1}{2} \sum_{j=1}^{56} g(ij) \right) \quad (2.10)$$

Spin-orbit coupling and other small perturbations are neglected. Let us say that the system is in the intermediate state when  $\Delta H^A$  alone is applied to the zeroth state and in the final state when  $\Delta H^B$  is applied hereafter.

**C. Application of the integral Hellmann-Feynman Formula.** Let us suppose that the following Schrödinger equations are satisfied exactly,

$$H^0 \Phi^0 = E^0 \Phi^0 \quad (2.11)$$

$$(H^0 + \Delta H^A) \Phi' = E' \Phi' \quad (2.12)$$

$$(H^0 + \Delta H^A + \Delta H^B) \Psi = E \Psi \quad (2.13)$$

$\Phi^0$ ,  $\Phi'$ , and  $\Psi$  are the zeroth state, the intermediate state, and the final state wave functions respectively. Then, making use of the Integral Hellmann-Feynman formula, eq. (13) of ref. 17, we can write

$$\begin{aligned} \Delta E &\equiv E - E^0 \\ &= (E - E') + (E' - E) \\ &= \frac{\langle \Phi' | \Delta H^B | \Psi \rangle}{\langle \Phi' | \Psi \rangle} + \frac{\langle \Phi^0 | \Delta H^A | \Phi' \rangle}{\langle \Phi^0 | \Phi' \rangle} \end{aligned} \quad (2.14)$$

Now, let us suppose that the zeroth state is  $g$ -fold degenerate, and that the degeneracy is

maintained to the intermediate state, that is,

$$E_1^0 = E_2^0 = E_3^0 = \dots = E_g^0 \quad (2.15)$$

and

$$E_1' = E_2' = E_3' = \dots = E_g' \quad (2.16)$$

Then, for the energy difference of two configurations,  $\alpha$  and  $\beta$ , in the final state, we have

$$E_\beta - E_\alpha = \Delta E_\beta'' - \Delta E_\alpha'' \quad (2.17)$$

where

$$\Delta E_\beta'' \equiv E_\beta - E_\beta' \quad (2.18)$$

and

$$\Delta E_\alpha'' \equiv E_\alpha - E_\alpha' \quad (2.19)$$

In the light of the Integral Hellmann-Feynman formula, eq. (2.17) can be written as

$$E_\beta - E_\alpha = \frac{\langle \Phi_\beta' | \Delta H^B | \Psi_\beta \rangle}{\langle \Phi_\beta' | \Psi_\beta \rangle} - \frac{\langle \Phi_\alpha' | \Delta H^B | \Psi_\alpha \rangle}{\langle \Phi_\alpha' | \Psi_\alpha \rangle} \quad (2.20)$$

Let us consider the implications of eq. (2.20). The  $g$ -fold degenerate space in eqs. (2.15) and (2.16) represents the  $3d$  energy state of the Ni<sup>2+</sup> both in the zeroth state and in the intermediate state. It is obvious that  $\Delta H^A$  alone will not affect the  $3d$  energy level of the free Ni<sup>2+</sup>. Hence,  $\Delta H^B$  alone appears in eq. (2.20). Another point to mention is that previous calculations of  $10Dq$  have been concerned with the direct evaluation of the difference between the energy of the ground state configuration and that of the excited state configuration. But, our approach as shown in eq. (2.20) appears totally different.

**D. Wave Functions.** Since numerical values of covalency parameters and necessary integrals are quoted from S & S III, the same orbital functions used by S & S will be considered relevant. The normalized radial part of the Ni<sup>2+</sup>  $3d$  function, taken, from Watson's table<sup>19</sup>, is

$$R_{3d}(r) = r^2(3.4096e^{-2.315r} + 45.261e^{-4.523r} + 129.48e^{-8.502r} + 24.071e^{-15.01r}) \quad (2.21)$$

Then, the atomic  $d$  functions with appropriate symmetry are given as follows:

$$\begin{aligned} u &= Y(2, 0)R_{3d} \\ v &= (1/\sqrt{2})[Y(2, 2) + Y(2, -2)]R_{3d} \\ \xi &= (i/\sqrt{2})[Y(2, 1) + Y(2, -1)]R_{3d} \\ \eta &= (-1/\sqrt{2})[Y(2, 1) - Y(2, -1)]R_{3d} \\ \zeta &= (-i/\sqrt{2})[Y(2, 2) - Y(2, -2)]R_{3d} \end{aligned} \quad (2.22)$$

where  $Y(lm)$  is a spherical harmonic defined as  $Y(lm) = \Theta(lm)\Phi(m)$  in Condon and Shortle-<sup>20</sup>.

Froese's numerical values<sup>21</sup> of  $F^-$  radial functions from her Hartree-Fock calculation were fitted by S & S to a two-term analytical function:

$$R_{2p}(r) = r(15.671e^{-3.7374r} + 1.5742e^{-1.3584r}) \quad (2.23)$$

The complete  $F^-$   $2p$  functions are

$$\phi_{2p\sigma} = Y(1, 0)R_{2p} \quad (2.24)$$

$$\phi_{2p\pi\pm} = Y(1, \pm 1)R_{2p} \quad (2.25)$$

For the  $2s$  function, S & S used the Slater function orthogonalized to the  $1s$ -core function:

$$R_{2s}(r) = (-11.156e^{-8.70r} + 10.805e^{-2.425r}) \quad (2.26)$$

The complete  $2s$  function is

$$\phi_{2s} = (4\pi)^{-1/2}R_{2s} \quad (2.27)$$

Symmetry adapted ligand MO's are given in Appendix I where subscript  $i$  of the ligand atomic orbital denotes the ligand position whose numbering is shown in Fig. 1. Atomic  $d$  orbitals given by eq. (2.22) and the ligand MO's of corresponding symmetry type given in Appendix I are combined to give MO's for the  $(\text{NiF}_6)^{4-}$  molecule, which are given in Appendix II.

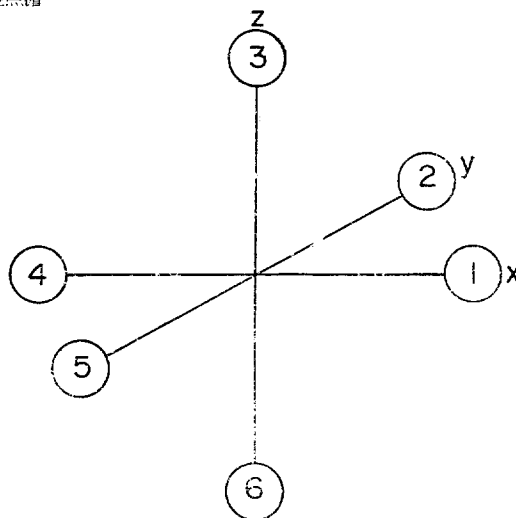


Fig. 1. Coordinates used to describe the regular octahedron of  $F^-$  ions which are numbered 1-6.

### E. Evaluation of the Matrix Elements.

Let  $\alpha$  and  $\beta$  represent the final ground state configuration  $(\xi_{\pm}'\eta_{\pm}'\zeta_{\pm}'u_{\pm}'v_{\pm}')$  and the final excited state configuration  $(\xi_{\pm}'\eta_{\pm}'\zeta_{\pm}'u_{\pm}'v_{\pm}')$  respectively. In order to facilitate the evaluation of matrix elements, the orbitals to accommodate

$i$	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$\phi_i$	$u$	$v$	$\xi$	$\eta$	$\zeta$	$\bar{\xi}$	$\bar{\eta}$	$\bar{\zeta}$	$s\sigma_2$	$p\sigma_2$	$s\sigma_3$	$p\sigma_3$	$p\pi_7$	$p\pi_8$
$\phi_i^{\alpha}$	$u'$	$v'$	$\xi'$	$\eta'$	$\zeta'$	$\bar{\xi}'$	$\bar{\eta}'$	$\bar{\zeta}'$	$s\sigma_2'$	$p\sigma_2'$	$s\sigma_3'$	$p\sigma_3'$	$p\pi_7'$	$p\pi_8'$
	15	16	17	18	19	20	21	22	23	24	25			
	$p\pi_9$	$\bar{s}\sigma_2$	$\bar{p}\sigma_2$	$\bar{s}\sigma_3$	$\bar{p}\sigma_3$	$\bar{p}\pi_7$	$\bar{p}\pi_8$	$\bar{p}\pi_9$	$s\sigma_1$	$p\sigma_1$	$p\pi_1$			
	$p\pi_9'$	$\bar{s}\sigma_2'$	$\bar{p}\sigma_2'$	$\bar{s}\sigma_3'$	$\bar{p}\sigma_3'$	$\bar{p}\pi_7'$	$\bar{p}\pi_8'$	$\bar{p}\pi_9'$						
	26	27	28	29	30	31	32	33	34	35	36	37		
	$p\pi_2$	$p\pi_3$	$s\sigma_4$	$p\sigma_4$	$p\pi_4$	$s\sigma_5$	$p\sigma_5$	$p\pi_5$	$s\sigma_6$	$p\sigma_6$	$p\pi_6$	$p\pi_{10}$		
	38	39	40	41	42	43	44	45	46	47	48	49		
	$p\pi_{11}$	$p\pi_{12}$	$\bar{s}\sigma_1$	$\bar{p}\sigma_1$	$\bar{p}\pi_1$	$\bar{p}\pi_2$	$\bar{p}\pi_3$	$\bar{s}\sigma_4$	$\bar{p}\sigma_4$	$\bar{p}\pi_4$	$\bar{s}\sigma_5$	$\bar{p}\sigma_5$		
	50	51	52	53	54	55	56							
	$\bar{p}\pi_5$	$\bar{s}\sigma_6$	$\bar{p}\pi_6$	$\bar{p}\pi_6$	$\bar{p}\pi_{10}$	$\bar{p}\pi_{11}$	$\bar{p}\pi_{12}$							

(2.28)

the 56 valence electrons of the (NiF<sub>6</sub>)<sup>4-</sup> molecule in the intermediate state and the final state are denoted by  $\phi_i$  and  $\psi_i$  respectively as follows:  $\psi_i$ , the final excited state wave function, is obtained by replacing  $\xi_i$  in  $\phi_i$  by  $\bar{v}_i$ . Orbitals 1 through 8 are antibonding orbitals, 9 through 22 bonding orbitals, and 23 through 56 non-bonding orbitals. For non-bonding orbitals,  $\psi_i$ 's are the same as the corresponding  $\phi_i$ 's because no mixing occurs between the central metal orbitals and the ligand orbitals. Then,  $\Phi'$  and  $\Psi$  can be written as following:

$$\Phi' = \frac{1}{\sqrt{8!}} \cdot \frac{1}{\sqrt{48!}} |\phi_1(1)\phi_2(2)\cdots\phi_7(7)\phi_8(8)| \cdot |\phi_9(9)\phi_{10}(10)\cdots\phi_{55}(55)\phi_{56}(56)| \quad (2.29)$$

$$\Psi = \frac{1}{\sqrt{56!}} |\phi_1(1)\phi_2(2)\cdots\phi_{55}(55)\phi_{56}(56)| \quad (2.30)$$

Using determinantal functions eqs. (2.29) and (2.30) for the intermediate and the final state respectively and employing  $\Delta H^B$  given by eq. (2.9), we get, after some manipulation (see Appendix III), the following:

$$\begin{aligned} \Delta E' &\equiv \frac{\langle \Phi' | \Delta H^B | \Psi \rangle}{\langle \Phi' | \Psi \rangle} \\ &\cong \sum_{k=1}^8 \langle \phi_k | \langle \psi_k \rangle^{-1} [\langle \phi_k | V_\theta(k) \\ &\quad + \sum_{i=9}^{56} \langle \phi_i | \phi_i \rangle^{-1} (J_i - K_i) | \phi_k \rangle] \\ &\quad + \sum_{i=9}^{56} \langle \phi_i | \phi_i \rangle^{-1} \langle \phi_i | V^M(I) | \phi_i \rangle \quad (2.31) \end{aligned}$$

where it is noted that

$$\begin{aligned} V_\theta(k) &\equiv \sum_{N=I}^{V-I} V^{(N)}(k) \\ &= \sum_{N=I}^{V-I} \frac{1}{|\vec{r}_k - \vec{R}_N|} + \sum_{N=I}^{V-I} \frac{-8}{|\vec{r}_k - \vec{R}_N|} \quad (2.32) \end{aligned}$$

The first term in eq. (2.32) is nothing more than the point charge potential,  $V_L^{pt}$ , and the rest is a part of Kleiner's correction.<sup>5</sup>  $J_i$  and  $K_i$  are the Coulomb and the exchange interaction

operators respectively defined by

$$J_i \equiv \int d\tau_2 \phi_i^*(2) g(12) \phi_i(2) \quad (2.33)$$

and

$$K_i \equiv \int d\tau_2 \phi_i^*(2) g(12) \phi_i(1) P_{12} \quad (2.34)$$

In the derivation of eq. (2.31), terms higher than second order are neglected. It is noted that the last term in eq. (2.31) is independent of the  $\alpha$  or  $\beta$  configuration of the final state. Following the conventional definition of 10 Dq and utilizing eqs. (2.20) and (2.31), we have

$$\begin{aligned} 10 Dq &\equiv \Delta E_\beta'' - \Delta E_\alpha'' \\ &\cong \langle \bar{v} | \bar{v}' \rangle^{-1} \langle \bar{v} | V_\theta + \sum_{i=9}^{56} \langle \phi_i | \phi_i \rangle^{-1} \\ &\quad (J_i - K_i) | \bar{v}' \rangle - \langle \xi | \xi' \rangle^{-1} \langle \xi | V_\theta + \\ &\quad \sum_{i=9}^{56} \langle \phi_i | \phi_i \rangle^{-1} (J_i - K_i) | \xi' \rangle \quad (2.35) \end{aligned}$$

### 3. Calculation of 10 Dq.

Numerical values of covalency parameters and necessary integrals quoted from S & S III<sup>11</sup> are given in Table 1. The calculation is made in three steps, each step being characterized by the crystal field potential employed.

#### Step 1. By Use of Point Charge Potential.

In a position to check the validity of the point charge model, it is a good approximation to write

$$\begin{aligned} 10 Dq &\cong \frac{\langle \bar{v} | V_L^{pt} | \bar{v}' \rangle}{\langle \bar{v} | \bar{v}' \rangle} - \frac{\langle \xi | V_L^{pt} | \xi' \rangle}{\langle \xi | \xi' \rangle} \\ &= \frac{\langle \bar{v} | V_L^{pt} | \bar{v} - \lambda_s s \sigma_3 - \lambda_\sigma \bar{p} \sigma_3 \rangle}{\langle \bar{v} | \bar{v} - \lambda_s s \sigma_3 - \lambda_\sigma \bar{p} \sigma_3 \rangle} \\ &\quad - \frac{\langle \xi | V_L^{pt} | \xi - \lambda_\pi \bar{p} \pi_9 \rangle}{\langle \xi | \xi - \lambda_\pi \bar{p} \pi_9 \rangle} \quad (3.1) \end{aligned}$$

$V_L^{pt}$  is the point charge potential given by

$$V_L^{pt} = \sum_{N=I}^{V-I} \frac{1}{|\vec{r} - \vec{R}_N|} \quad (3.2)$$

Substituting numerical values in Table 1 into eq. (3.1), we obtain 8180 cm<sup>-1</sup> for 10 Dq which

Table 1. Numerical values of covalency parameters and integrals quoted from *S* & *S* III.

Covalency parameters	Quoted from <i>S</i> & <i>S</i> III	
$\lambda_s$	0.113	Table VII
$\lambda_\sigma$	0.396	
$\lambda_\pi$	0.249	
$\gamma_s$	0.031	
$\lambda_\sigma$	0.285	
$\gamma_\pi$	0.173	
Normalization factors		
$N_e^{-\frac{1}{2}}$	0.968	Eq. (8.2)
$N_i^{-\frac{1}{2}}$	0.988	
Integrals		
$\langle v s\sigma_3\rangle$	0.08143	Table I
$\langle v p\sigma_3\rangle$	0.11071	
$\langle \zeta p\pi_9\rangle$	0.07556	
$\langle v V_L^{pt} v\rangle$	1.58687	Table II
$\langle \zeta V_L^{pt} \zeta\rangle$	1.58055	
$\langle v V_L v\rangle$	1.5327	
$\langle \zeta V_L \zeta\rangle$	1.5490	
$\langle v V_L^{pt} s\sigma_3\rangle'^*$	0.058109	Table V
$\langle v V_L^{pt} p\sigma_3\rangle'$	0.070939	
$\langle \zeta V_L^{pt} p\pi_9\rangle'$	0.035267	
$\langle v V_L s\sigma_3\rangle$	-0.00099	
$\langle v V_L p\sigma_3\rangle$	0.05782	
$\langle \zeta V_L p\pi_9\rangle$	0.06244	

\*Primed integrals are the two-center integrals.

is approximately 10 % larger than the observed value, 7250 cm<sup>-1</sup>.

### Step 2. By Use of Sugano and Shulman Potential $V_L$ .

Sugano and Shulman expressed the contribution from the six fluoride ions by  $V_L$  which was defined by

$$V_L = V_L^{pt} + V_L^K + V_L^E \quad (3.3)$$

$V_L^K$  is Kleiner's additional potential due to the imperfect screening of the ligand nuclear charge by the ligand electrons, which can be written as

$$V_L^K = -8V_L^{pt} + V_L^{\text{Coulomb}} \quad (3.4)$$

$V_L^E$  is the exchange-interaction operator introduced by Tanabe and Sugano.<sup>6</sup> We notice that

$\langle \phi_i|\phi_i\rangle$ 's in eq. (2.35) are all close to unity and approximate  $\Delta H^B$  by  $V_L$ . Thus we have

$$10 Dq \cong \frac{\langle \bar{v}|V_L|\bar{v}'\rangle}{\langle \bar{v}|\bar{v}'\rangle} - \frac{\langle \bar{\zeta}|V_L|\bar{\zeta}'\rangle}{\langle \bar{\zeta}|\bar{\zeta}'\rangle} \\ = \frac{\langle \bar{v}|V_L|\bar{v} - \lambda_s \bar{s}\sigma_3 - \lambda_\sigma \bar{p}\sigma_3\rangle}{\langle \bar{v}|\bar{v} - \lambda_s \bar{s}\sigma_3 - \lambda_\sigma \bar{p}\sigma_3\rangle} \\ - \frac{\langle \bar{\zeta}|V_L|\bar{\zeta} - \lambda_\pi \bar{p}\pi_9\rangle}{\langle \bar{\zeta}|\bar{\zeta} - \lambda_\pi \bar{p}\pi_9\rangle} \quad (3.5)$$

Numerical values are again substituted into eq. (3.5) to give 6940 cm<sup>-1</sup> for 10  $Dq$  which is only 4 % less than the observed value.

### Step 3. By Means of Eq. (2.35).

If we let  $S$  represent the average value of the 48 overlap integrals, namely  $\langle \phi_i|\phi_i\rangle$ 's, eq. (2.35) can be approximated to give

$$10 Dq \cong \langle \bar{v}|\bar{v}'\rangle^{-1} \langle \bar{v}|V_\theta + S^{-1} \sum_{i=9}^{56} (J_i - K_i)|\bar{v}'\rangle \\ - \langle \bar{\zeta}|\bar{\zeta}'\rangle^{-1} \langle \bar{\zeta}|V_\theta + S^{-1} \sum_{i=9}^{56} (J_i - K_i)|\bar{\zeta}'\rangle \quad (3.6)$$

Combining eqs. (2.33), (2.34), (3.3) and (3.4), we can make the following approximation:

$$\sum_{i=9}^{56} (J_i - K_i) = V_L + 7V_L^{pt} \quad (3.7)$$

Combining eqs. (3.6) and (3.7) and rearranging, we get

$$10 Dq \cong \langle \bar{v}|\bar{v}'\rangle^{-1} \langle \bar{v}|S^{-1}V_L + 7(S^{-1})V_L^{pt}|\bar{v}'\rangle \\ - \langle \bar{\zeta}|\bar{\zeta}'\rangle^{-1} \langle \bar{\zeta}|S^{-1}V_L + 7(S^{-1})V_L^{pt}|\bar{\zeta}'\rangle \quad (3.8)$$

We define  $V_L^H$  as following:

$$V_L^H = S^{-1}V_L + 7(S^{-1} - 1)V_L^{pt} \quad (3.9)$$

Then, we can write

$$10 Dq \cong \frac{\langle \bar{v}|V_L^H|\bar{v}\rangle}{\langle \bar{v}|\bar{v}'\rangle} - \frac{\langle \bar{\zeta}|V_L^H|\bar{\zeta}'\rangle}{\langle \bar{\zeta}|\bar{\zeta}'\rangle} \quad (3.10)$$

The value of  $S$ , 0.99753, is readily calculated from numerical values in Table 1. Eq. (3.8) gives, after substituting necessary values in Table 1 and  $S$ , 7100 cm<sup>-1</sup> for 10  $Dq$  which is in excellent agreement with the observed value,

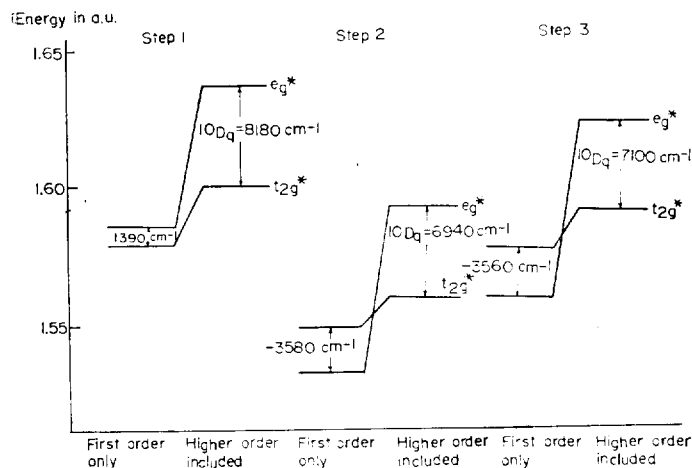


Fig. 2. Energy-level diagram showing the higher order energy effect on 10  $Dq$  in  $\text{KNiF}_3$ .

7250  $\text{cm}^{-1}$ .

#### 4. Discussion

It is important to notice that the conventional crystal field theory has been confined to the calculation of the first order perturbation energy of  $\langle \Phi | V | \Phi \rangle$  type, where  $\Phi$  is the zeroth state (not to be confused with the definition of zeroth state in Section 2. A) wave function and  $V$  is the crystal field potential. Our starting equation (2.20) is quite analogous to the first order perturbation energy equation except that the final state wave function is used on the right hand side of the integrals and that  $\Delta H^B$  contains metal-ligand interactions. It is our belief that using the final state wave function on the right hand side is equivalent to including higher order perturbation energies. Effect of higher order energy correction, which is defined by

$$\Delta E_{\text{corr}} = \langle \bar{v} | \bar{v}' \rangle^{-1} \langle \bar{v} | V_L | \bar{v}' \rangle - \langle \bar{v} | V_L | \bar{v} \rangle \text{ etc.} \quad (4.1)$$

on 10  $Dq$  is shown in Table 2. The situation is more visually presented in Fig. 2.

When point charge model is used, first order calculation gives 1390  $\text{cm}^{-1}$  for 10  $Dq$  which is too small even though of correct sign. Higher order energy correction for  $e_g^*$  orbital, 11480

$\text{cm}^{-1}$ , is more than twice as large as that for  $t_{2g}^*$  orbital, 4670  $\text{cm}^{-1}$ . Hence, the resulting value of 10  $Dq$ , when higher order correction is included, is 8180  $\text{cm}^{-1}$ .

When  $V_L$ , Sugano and Shulman potential, is used, it is found that energy level of  $e_g^*$  orbital is lower than that of  $t_{2g}^*$  orbital if the calculation is restricted to the first order. This gives negative value, -3580  $\text{cm}^{-1}$ , for 10  $Dq$  which is unrealistic. But when higher order energy is included, this error is corrected. Higher order correction for  $e_g^*$  orbital, 13560  $\text{cm}^{-1}$ , is more than four times as large as that for  $t_{2g}^*$  orbital, 3050  $\text{cm}^{-1}$ . The wrong sign is corrected and an excellent value of 6940  $\text{cm}^{-1}$  is obtained.

The situation is similar when  $V_L^H$  defined by eq. (3.9) is used. Higher order correction for  $e_g^*$  orbital, 13800  $\text{cm}^{-1}$ , is again more than four times as large as that for  $t_{2g}^*$  orbital, 3120  $\text{cm}^{-1}$ . This gives 7100  $\text{cm}^{-1}$  which is only 2 % less than the observed value.

It is striking to notice that the three values calculated in Steps 1, 2, and 3 of increasing scrutiny show increasing agreement with experimental value. This can be regarded as a justification of the validity of our approach. Furthermore, the value obtained in Step 1, 8180  $\text{cm}^{-1}$ , which is the least favorable one in our calculation is only 10 % larger than the true value.

Another important point to mention is that higher order energy corrections are of the order of magnitude of 10  $Dq$  itself. This enables the inversion of energy levels in Step 2 and Step 3 whereby correcting the wrong sign and giving good results.

A comparison is made of the calculated value of 10  $Dq$  in  $\text{KNiF}_3$  by several authors in Table 3.

Table 2. Effect of higher order energy correction in atomic unit

Step 1		Step 2		Step 3	
$\langle \bar{v}   V_L^H   \bar{v} \rangle$	1.5869	$\langle \bar{v}   V_L   \bar{v} \rangle$	1.5327	$\langle \bar{v}   V_L^H   \bar{v} \rangle$	1.5639
$\langle \bar{v}   \bar{v}' \rangle^{-1} \langle \bar{v}   V_L^H   \bar{v}' \rangle$	1.6392	$\langle \bar{v}   \bar{v}' \rangle^{-1} \langle \bar{v}   V_L   \bar{v}' \rangle$	1.5945	$\langle \bar{v}   \bar{v}' \rangle^{-1} \langle \bar{v}   V_L^H   \bar{v}' \rangle$	1.6268
Higher order correction	0.0523	Higher order correction	0.0618	Higher order correction	0.0629
$\langle \xi   V_L^H   \xi \rangle$	1.5806	$\langle \xi   V_L   \xi \rangle$	1.5490	$\langle \xi   V_L^H   \xi \rangle$	1.5802
$\langle \xi   \xi' \rangle^{-1} \langle \xi   V_L^H   \xi' \rangle$	1.6019	$\langle \xi   \xi' \rangle^{-1} \langle \xi   V_L   \xi' \rangle$	1.5629	$\langle \xi   \xi' \rangle^{-1} \langle \xi   V_L^H   \xi' \rangle$	1.5944
Higher order correction	0.0213	Higher order correction	0.0139	Higher order correction	0.0142
<b>10 Dq</b>					
First order only	0.0063 (1390 cm <sup>-1</sup> )		-0.0163 (-3580 cm <sup>-1</sup> )		-0.0162 (-3560 cm <sup>-1</sup> )
Higher order included	0.0373 (8180 cm <sup>-1</sup> )		0.0316 (6940 cm <sup>-1</sup> )		0.0324 (7100 cm <sup>-1</sup> )

This unambiguously shows the superiority of the present Integral Hellmann-Feynman approach.

### 5. Conclusion

Two important conclusions are reached. Firstly, higher order perturbation energy correction is essential in the calculation of 10 Dq from first principles. This correction has the same order of magnitude as that of 10 Dq itself. Secondly, the point charge model gives excellent result as long as higher order energy correction is made.

We have to point out that the Integral Hellmann-Feynman formula, eq. (2.20), cannot provide a means of obtaining the final state wave function though it has the merit of introducing higher order perturbation energies. It seems most desirable to use the symmetry ada-

Table 3. Comparison of calculated values of 10 Dq in KNiF<sub>3</sub>

Sugano, Shulman	1963	6350 cm <sup>-1</sup>
Watson, Freeman	1964	2815
Sugano, Tanabe	1965	2580
Hubbard, Rimmer, Hopgood	1966	5400
Offenhartz	1967	4040
Gladney, Veillard	1969	4670
Present calculation		
Step 1		8180
Step 2		6940
Step 3		7100
Experimental value		7250 cm <sup>-1</sup>

pted molecular orbitals for the complex molecule where the component atomic orbitals are Hartree-Fock solutions for the corresponding metal and ligand atoms or ions.

Appendix I. Central metal orbitals and ligand MO's corresponding symmetry

Central metal orbital		Symmetry adapted ligand MO*
$a_{1g}$	$s \equiv 3s$	$s\sigma_1 \equiv \frac{1}{\sqrt{6}}(\varphi_{1,s} + \varphi_{2,s} + \varphi_{3,s} + \varphi_{4,s} + \varphi_{5,s} + \varphi_{6,s})$
		$p\sigma_1 \equiv \frac{1}{\sqrt{6}}(-\varphi_{1,x} - \varphi_{2,y} - \varphi_{3,z} + \varphi_{4,x} + \varphi_{5,y} + \varphi_{6,z})$
$e_g$	$u \equiv 3d_{z^2}$	$s\sigma_2 \equiv \frac{1}{\sqrt{12}}(-\varphi_{1,s} - \varphi_{2,s} + 2\varphi_{3,s} - \varphi_{4,s} - \varphi_{5,s} + 2\varphi_{6,s})$
		$p\sigma_2 \equiv \frac{1}{\sqrt{12}}(\varphi_{1,x} + \varphi_{2,y} - 2\varphi_{3,z} - \varphi_{4,x} - \varphi_{5,y} + 2\varphi_{6,z})$



	$v \equiv 3d_{x^2-y^2}$	$s\sigma_3 \equiv \frac{1}{2}(\varphi_{1,z} - \varphi_{2,z} + \varphi_{4,z} - \varphi_{5,z})$
		$p\sigma_3 \equiv \frac{1}{2}(-\varphi_{1,x} + \varphi_{2,y} + \varphi_{4,x} - \varphi_{5,y})$
$d_{1g}$		$p\pi_1 \equiv \frac{1}{2}(\varphi_{2,z} - \varphi_{3,y} - \varphi_{5,z} + \varphi_{6,y})$
		$p\pi_2 \equiv \frac{1}{2}(-\varphi_{1,z} + \varphi_{3,x} + \varphi_{4,z} - \varphi_{6,x})$
		$p\pi_3 \equiv \frac{1}{2}(\varphi_{1,y} - \varphi_{2,x} - \varphi_{4,y} + \varphi_{5,x})$
$t_{1u}$	$a \equiv 3p_x$	$s\sigma_4 \equiv \frac{1}{\sqrt{2}}(\varphi_{1,z} - \varphi_{4,z})$
		$p\sigma_4 \equiv \frac{1}{\sqrt{2}}(-\varphi_{1,x} - \varphi_{4,x})$
		$p\pi_4 \equiv \frac{1}{2}(\varphi_{2,x} + \varphi_{3,x} + \varphi_{5,x} + \varphi_{6,x})$
	$b \equiv 3p_y$	$s\sigma_5 \equiv \frac{1}{\sqrt{2}}(\varphi_{2,z} - \varphi_{5,z})$
		$p\sigma_5 \equiv \frac{1}{\sqrt{2}}(-\varphi_{2,y} - \varphi_{5,y})$
		$p\pi_5 \equiv \frac{1}{2}(\varphi_{1,y} + \varphi_{3,y} + \varphi_{4,y} + \varphi_{6,y})$
	$c \equiv 3p_z$	$s\sigma_6 \equiv \frac{1}{\sqrt{2}}(\varphi_{3,z} - \varphi_{6,z})$
		$p\sigma_6 \equiv \frac{1}{\sqrt{2}}(-\varphi_{3,x} - \varphi_{6,x})$
		$p\pi_6 \equiv \frac{1}{2}(\varphi_{1,z} + \varphi_{2,z} + \varphi_{4,z} + \varphi_{5,z})$
$t_{2g}$	$\xi \equiv 3d_{yz}$	$p\pi_7 \equiv \frac{1}{2}(\varphi_{2,z} + \varphi_{3,y} - \varphi_{5,z} - \varphi_{6,y})$
	$\eta \equiv 3d_{zx}$	$p\pi_8 \equiv \frac{1}{2}(\varphi_{1,z} + \varphi_{3,x} - \varphi_{4,z} - \varphi_{6,x})$
	$\zeta \equiv 3d_{xy}$	$p\pi_9 \equiv \frac{1}{2}(\varphi_{1,y} + \varphi_{2,x} - \varphi_{4,y} - \varphi_{5,x})$
$t_{2u}$		$p\pi_{10} \equiv \frac{1}{2}(-\varphi_{2,x} + \varphi_{3,z} - \varphi_{5,x} + \varphi_{6,z})$
		$p\pi_{11} \equiv \frac{1}{2}(-\varphi_{1,y} + \varphi_{3,y} - \varphi_{4,y} + \varphi_{6,y})$
		$p\pi_{12} \equiv \frac{1}{2}(-\varphi_{1,z} + \varphi_{2,x} - \varphi_{4,z} + \varphi_{5,z})$

\* $\varphi_{i,s}$ ,  $\varphi_{i,x}$ ,  $\varphi_{i,y}$ , and  $\varphi_{i,z}$  represent the  $2s$ ,  $2p_x$ ,  $2p_y$ , and  $2p_z$  orbital of the  $i$ -th ligand atom respectively.

## Appendix II. Symmetry adapted MO's for the $(\text{NiF}_6)^{4-}$ complex

### Antibonding orbitals

$$u' = N_e^{-1/2}(u - \lambda_s s\sigma_2 - \lambda_\sigma p\sigma_2) \quad (\text{A II-1})$$

$$v' = N_e^{-1/2}(v - \lambda_s s\sigma_3 - \lambda_\sigma p\sigma_3)$$

$$\xi' = N_t^{-1/2}(\xi - \lambda_\pi p\pi_7)$$

$$\eta' = N_t^{-1/2}(\eta - \lambda_\pi p\pi_8)$$

$$\zeta' = N_t^{-1/2}(\zeta - \lambda_\pi p\pi_9)$$

### Bonding orbitals

$$s\sigma_2' = N_e'^{-1/2}(s\sigma_2 + \gamma_s u + \gamma_\sigma p\sigma_2) \quad (\text{A II-2})$$

$$s\sigma_3' = N_e'^{-1/2}(s\sigma_3 + \gamma_s v + \gamma_\sigma p\sigma_3)$$

$$p\sigma_2' = N_e'^{-1/2}(p\sigma_2 + \gamma_\sigma u + \gamma_s s\sigma_2)$$

$$p\sigma_3' = N_e'^{-1/2}(p\sigma_3 + \gamma_\sigma v + \gamma_s s\sigma_3)$$

$$p\pi_7' = N_t'^{-1/2}(p\pi_7 + \gamma_\pi \xi)$$

$$p\pi_8' = N_t'^{-1/2}(p\pi_8 + \gamma_\pi \eta)$$

$$p\pi_9' = N_t'^{-1/2}(p\pi_9 + \gamma_\pi \zeta)$$

Orbitals with down spin are obtained by accomodating down spin upon the component orbitals.

## Appendix III. Derivation of eq. (2.31)

We start from a simple case as an illustration. Let us consider the evaluation of matrix element of the following type:

$$\begin{aligned}
I &= \int \cdots \int \frac{1}{\sqrt{2!}} \frac{1}{\sqrt{3!}} |\phi_1(1)\phi_2(2)|^* |\phi_3(3)\phi_4(4)\phi_5(5)|^* \\
&\quad \sum_{i=1}^2 Q(i) \frac{1}{\sqrt{5!}} |\phi_1(1)\phi_2(2)\cdots\phi_5(5)| d\tau_1 d\tau_2 \cdots d\tau_5 \\
&= \int \cdots \int \frac{1}{\sqrt{2!}} \frac{1}{\sqrt{3!}} \phi_1^*(1)\phi_2^*(2) |\phi_3(3)\phi_4(4)\phi_5(5)|^* \\
&\quad \sum_{i=1}^2 Q(i) \frac{1}{\sqrt{5!}} |\phi_1(1)\phi_2(2)\cdots\phi_5(5)| d\tau_1 d\tau_2 \cdots d\tau_5 \\
&- \int \cdots \int \frac{1}{\sqrt{2!}} \frac{1}{\sqrt{3!}} \phi_2^*(1)\phi_1^*(2) |\phi_3(3)\phi_4(4)\phi_5(5)|^* \\
&\quad \sum_{i=1}^2 Q(i) \frac{1}{\sqrt{5!}} |\phi_1(1)\phi_2(2)\cdots\phi_5(5)| d\tau_1 d\tau_2 \cdots d\tau_5
\end{aligned} \quad (A \text{ III-1})$$

If we interchange the electron tags 1 and 2, the second term in eq. (A III-1) becomes

$$\begin{aligned}
&\int \cdots \int \frac{1}{\sqrt{2!}} \frac{1}{\sqrt{3!}} \phi_2^*(2)\phi_1^*(1) |\phi_3(3)\phi_4(4)\phi_5(5)|^* \\
&\quad \sum_{i=1}^2 Q(i) \frac{1}{\sqrt{5!}} |\phi_1(2)\phi_2(1)\cdots\phi_5(5)| d\tau_1 d\tau_2 \cdots d\tau_5 \\
&= - \int \cdots \int \frac{1}{\sqrt{2!}} \frac{1}{\sqrt{3!}} \phi_1^*(1)\phi_2^*(2) |\phi_3(3)\phi_4(4)\phi_5(5)|^* \\
&\quad \sum_{i=1}^2 Q(i) \frac{1}{\sqrt{5!}} |\phi_1(1)\phi_2(2)\cdots\phi_5(5)| d\tau_1 d\tau_2 \cdots d\tau_5
\end{aligned}$$

Then we have

$$\begin{aligned}
I &= \int \cdots \int \frac{2!}{\sqrt{2!}} \frac{1}{\sqrt{3!}} \phi_1^*(1)\phi_2^*(2) |\phi_3(3)\phi_4(4)\phi_5(5)|^* \\
&\quad \sum_{i=1}^2 Q(i) \frac{1}{\sqrt{5!}} |\phi_1(1)\phi_2(2)\cdots\phi_5(5)| d\tau_1 d\tau_2 \cdots d\tau_5
\end{aligned} \quad (A \text{ III-2})$$

By expanding the remaining determinant in the same manner as above, we get

$$\begin{aligned}
I &= \sqrt{\frac{2!}{5!}} \int \cdots \int \phi_1^*(1)\phi_2^*(2)\phi_3^*(3)\phi_4^*(4)\phi_5^*(5) \\
&\quad \sum_{i=1}^2 Q(i) |\phi_1(1)\phi_2(2)\cdots\phi_5(5)| d\tau_1 d\tau_2 \cdots d\tau_5 \\
&= \sqrt{\frac{2!}{5!}} \left[ \sum_{\mu} (-1)^{\mu} P_{\mu} \int \cdots \int \phi_1^*(1)\phi_2^*(2)\cdots\phi_5^*(5) \right. \\
&\quad \left. \sum_{i=1}^2 Q(i) \phi_1^{\mu}(1)\phi_2^{\mu}(2)\cdots\phi_5^{\mu}(5) d\tau_1 d\tau_2 \cdots d\tau_5 \right] \\
&= \sqrt{\frac{2!}{5!}} \left[ \frac{\langle \phi_1 | Q(1) | \phi_1 \rangle}{\langle \phi_1 | \phi_1 \rangle} + \frac{\langle \phi_2 | Q(2) | \phi_2 \rangle}{\langle \phi_2 | \phi_2 \rangle} \right. \\
&\quad \left. - \frac{\langle \phi_1 | Q(1) | \phi_2 \rangle \langle \phi_2 | \phi_1 \rangle}{\langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle} - \frac{\langle \phi_1 | \phi_2 \rangle \langle \phi_2 | Q(2) | \phi_1 \rangle}{\langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle} \right. \\
&\quad \left. + \text{higher terms} \right] \quad (A \text{ III-3})
\end{aligned}$$

It is easily seen that terms after the second one are either zero or negligibly small. Hence, we can write

$$\begin{aligned}
I &= \sqrt{\frac{2!}{5!}} \frac{3!}{2!} \prod_{j=1}^{22} \langle \phi_j | \phi_j \rangle \left[ \frac{\langle \phi_1 | Q(1) | \phi_1 \rangle}{\langle \phi_1 | \phi_1 \rangle} \right. \\
&\quad \left. + \frac{\langle \phi_2 | Q(2) | \phi_2 \rangle}{\langle \phi_2 | \phi_2 \rangle} \right] \quad (A \text{ III-4})
\end{aligned}$$

Using the same technique as employed in the derivation of eq. (A III-4), we can evaluate the matrix elements of our concern. For the overlap integral, we have

$$\begin{aligned}
S &= \langle \phi' | \psi \rangle \\
&= \sqrt{\frac{8!}{56!}} \frac{48!}{2!} \prod_{j=1}^{22} \langle \phi_j | \phi_j \rangle \left[ 1 - \frac{\langle \phi_1 | \phi_9 \rangle \langle \phi_9 | \phi_1 \rangle}{\langle \phi_1 | \phi_1 \rangle \langle \phi_9 | \phi_9 \rangle} \right. \\
&\quad \left. + \text{higher terms} \right] \quad (A \text{ III-5})
\end{aligned}$$

It is easily shown that the quantity in the bracket is very close to unity. Hence, we have

$$S = \sqrt{\frac{8!}{56!}} \frac{48!}{2!} \prod_{j=1}^{22} \langle \phi_j | \phi_j \rangle \quad (A \text{ III-6})$$

Now, let us partition  $\Delta E''$  in eq. (2.31) into three parts as following:

$$\begin{aligned}
\Delta E'' &= \frac{\langle \phi' | \sum_{j \in M} V_{\theta}(j) | \psi \rangle}{S} + \frac{\langle \phi' | \sum_{j \in M} V^M(j) | \psi \rangle}{S} \\
&\quad + \frac{\langle \phi' | \sum_{j \in M} \sum_{i \in M} g(ij) | \psi \rangle}{S} = R_1 + R_2 + R_3
\end{aligned} \quad (A \text{ III-7})$$

In the light of eq. (A III-4) and (A III-6) we have

$$R_1 = \sum_{k=1}^8 \frac{\langle \phi_k | V_{\theta}(k) | \phi_k \rangle}{\langle \phi_k | \phi_k \rangle} \quad (A \text{ III-8})$$

$$R_2 = \sum_{i=9}^{56} \frac{\langle \phi_i | V^M(i) | \phi_i \rangle}{\langle \phi_i | \phi_i \rangle} \quad (A \text{ III-9})$$

$$\begin{aligned}
R_3 &= \sum_{k=1}^8 \sum_{i=9}^{56} \langle \phi_k | \phi_k \rangle^{-1} \langle \phi_i | \phi_i \rangle^{-1} \langle \phi_k | \int d\tau_2 g(12) \phi_i^*(2) \\
&\quad \phi_i(2) | \phi_k \rangle - \sum_{k=1}^8 \sum_{i=9}^{56} \langle \phi_k | \phi_k \rangle^{-1} \langle \phi_i | \phi_i \rangle^{-1} \langle \phi_k | \int d\tau_2 \\
&\quad g(12) \phi_i^*(2) \phi_i(1) P_{12} | \phi_k \rangle + \text{higher terms}
\end{aligned} \quad (A \text{ III-10})$$

Using the definition of eqs. (2.33) and (2.34) and neglecting higher terms, we have

$$R_3 = \sum_{k=1}^8 \langle \phi_k | \phi_k \rangle^{-1} \left[ \sum_{i=9}^{56} \langle \phi_i | \phi_i \rangle^{-1} \langle \phi_k | J_i | \phi_k \rangle \right]$$

$$-\sum_{i=9}^{45} \langle \phi_i | \phi_i \rangle^{-1} \langle \phi_k | K_i | \phi_k \rangle \Big] \quad (A \text{ III-11})$$

By use of eqs. (A III-8), (A III-9), and (A III-11), eq. (2.31) is readily obtained from eq. (A III-7).

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