광의의 Integral Hellmann–Feynman Theorem 과 결정장론에서의 배치간 작용의 효과

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Generalized Integral Hellmann–Feynam Theorem and Configuration Interaction in Crystal Field Theory

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요 약. Parr의 Integral Hellmann–Feynman 이론을 비대각꼴에 까지 일반화하여 의의를 갖도록 하였으며 그 특징을 논하였다. 그리하여 이 비대각꼴을 결정장론에 미치는 배치작용의 효과를 검토 하는데 적용함으로서, 모든 차의 섭동 에너지를 하나의 묶음으로서 도입하였다. 그 결과 Γ, S 및 m 로 특징지워지는 상태들에게, 파라미터화 할수 있는 공통적인 동경적분이 존재하지 않음을 밝혔다. 그러나 만일 각 성분에 변형이 없고 동경성분에게 동등한 변형만이 있는 여기된 배치들의 작용만을 허락한다면, 이는 고전적인 결정장론에서 결정장 파라메터 $10\,Dq$ 와 Condon–Slater 적분 F^n 의 척도 를 변경시키는 결과를 초래함을 알게 되었다.

ABSTRACT. The integral Hellmann–Feynman Theorem of Parr is generalized to give a full significance to the off–diagonal form, and certain aspects of it are discussed. By use of the generalized form of the theorem, effects of configuration interaction to the crystal field theory are examined, taking perturbation energies of all order collectively into account. Thus, it is shown that there do not exist, especially when the field is strong, the radial integral which is common to all states characterized by Γ, S and m, and could be parametrized. If, however, one restricts the perturbing excited states only to those angularly undistorted and radially equally distorted, there results simple scaling of the crystal field parameter $10\,Dq$ and Condon–Slater parameter F^n defined within the framework of the classical crystal field theory.

I. INTRODUCTION

The crystal field theory of Bethe[1] and Van Vleck[2] has played the pioneering role in explaining the energy states of complexes of the transition metals and rare earths. The theory[3-5] based on the assumption that the substituted ion feels a purely electrostatic field with point group symmetry of the lattice site it occupies. In practice, the theory employes semiempirical

method in which certain integrals are parametrized and determined by fitting the observed transitions[6~10].

Attempts to calculate the magnitude of the crystal field parameters within the actual framework, which is essentially based on the first order perturbation theory from the degenerate zero order configuration, have led to the results that disagree considerbly with the empirically deduced values[11]. Naturally and quite logically, the extensions of the theoretical framework to the second order have been tried with configuration interaction of excited states being taken into account. Perhaps, the work of Rajnak and Wybourne[12, 13] is the most typical one this line. They have examined the effects of configuration interaction, by introducing additional effective two-and three-body interaction terms to the Hamiltonian. By use of the second order perturbation scheme, they have concluded that, in spite of that the traditional theory was developed without including the possibility of excited configuration interaction, many of its effects are autometically absorbed when the radial integrals appearing in crystal field theory are treated as parameters to be determined from the experimental data.

Now then, a legitimate next question is what happens if one includes fully the sum of all orders of the perturbations in configuration interaction. In the usual perturbation scheme, when the perturbed functions are obtained in the actual framework of the theory, it is hardly possible even to express in meaningful form. Rajnak himself noted "in going to higher orders of perturbation, do higher order n-body interactions arise" On the other hand, if one tries to seek the solution via variational scheme, one is confronted with other sort of difficulties. That is, the difference of the expectation values, which is nothing but the perturbation energy,

does not depend linearly on the excited configurations which one mixes into the trial functions. Thus it lets one be unable to visualize the effects of a specific configuration to the total perturbation energy. One will be very happy if there exists such a formula that i) it gives the sum of the perturbation energies of all orders if one uses exact perturbed wave functions, and ii) it conserves same form, as long as one uses properly optimized initial (unperturbed) and final (perturbed) wave functions, and equals to the difference of the expectation values of initial and final states, and iii) the form of the formula facilitates to visualize the contribution of each component.

The very formula, having those traits which one hopes it to have, is the Generalized Integral Hellmann–Feynman Formula, is going to be developed in the present paper.

In section II, we develop the formula just stated and discuss the characteristics of it. In the section III, we choose the system of $(3d)^2$ configuration placed in the field of octahedral symmetry as model case, and discuss the effects of the configuration interaction, on the crystal field parameter and Condon–Slater integrals, and on the classical theory itself. We exclude the spin dependent interaction since we are not dealing with any real system presently.

II. GENERALIZED INTEGRAL HELLMANN–FEYNMAN THEORM

Given the Schrödinger equations

$$H^\circ \phi_k = E_k^\circ \phi_k \tag{1}$$

$$H\psi_l = E_l \psi_l, \quad H = H^\circ + \Delta H \tag{2}$$

where ΔH is a perturbation and $\psi_l \to \phi_l$, $E_l \to E_l^\circ$ as $\Delta H \to 0$, one can immediately write down

$$\langle \phi_k | H^\circ + \Delta H | \psi_l \rangle = E_l \langle \phi_k | \psi_l \rangle \tag{3}$$

or

$$\langle \phi_k | \Delta H | \psi_l \rangle = (E_l - E_k^\circ) \langle \phi_k | \psi_l \rangle \tag{4}$$

Thus one has

$$E_l - E_k^\circ = \frac{\langle \phi_k | \Delta H | \psi_l \rangle}{\langle \phi_k | \psi_l \rangle} \quad \text{with} \quad \langle \phi_k | \psi_l \rangle \neq 0 \quad (5)$$

which is the Generalized Integral Hellmann–Feynman Theorem (GIHF). With $k=l$, there results

$$\Delta E_l \equiv (E_l - E_l^\circ) = \frac{\langle \phi_l | \Delta H | \psi_l \rangle}{\langle \phi_l | \psi_l \rangle} \quad (6)$$

which is the ordinary Integral Hellmann–Feynman Theorem (IHF)[14~16] and has been known for some times.

Especially, if the zero order level has a degeneracy, GIHF takes a peculiar form:

$$\Delta E_l = \frac{\langle \phi_k | \Delta H | \psi_l \rangle}{\langle \phi_k | \psi_l \rangle}$$
$$\text{with} \quad \langle \phi_k | \psi_l \rangle \neq 0, \quad E_k^\circ = E_l^\circ \quad (7)$$

In other word, one can take an arbitrary zero order function ϕ_k, as long as $E_k^\circ = E_l^\circ$, to obtain the sum of the perturbation energies of all order, $\Delta E_l = E_l - E_l^\circ$.

Since the derivation of Eq. (5) is based on the Schrödinger equations (1) and (2), with arbitrary approximation f_k (for ϕ_k) and g_l (for ψ_l), it does not follow that

$$\Delta \bar{E}_l \equiv \frac{\langle g_l | H | g_l \rangle}{\langle g_l | g_l \rangle} - \frac{\langle f_k | H^\circ | f_k \rangle}{\langle f_k | f_k \rangle}$$
$$= \frac{\langle f_k | \Delta H | g_l \rangle}{\langle f_k | g_l \rangle} \quad \text{with} \quad \langle f_k | g_l \rangle \neq 0 \quad (8)$$

However, it has been shown that Eq. (6) does hold indeed when both f_l (for ϕ_l) and g_l (for ψ_l) are composed of a common basis set (complete or limited)[16], and the expectation values of the respective Hamiltonian are fully minimized by solving the secular equations. It will be shown below that the same is true for the generalized form. Suppose that one expand $f \equiv (f_1, f_2, \cdots)$ and $g \equiv (g_1, g_2, \cdots)$ with a common basis set $\xi \equiv (\xi_1, \xi_2, \cdots)$ such that

$$f = \xi \alpha, \quad \alpha^+ \alpha = 1 \quad (9)$$

$$g = \xi \beta, \quad \beta^+ \beta = 1 \quad (10)$$

where α and β are chosen to satisfy

$$\alpha^+ H^{\circ\xi} \alpha = H^{\circ f} = \{\delta_{ij} H_{ii}^{\circ f}\} \quad (11)$$
$$\beta^+ H^\xi \beta = H^g = \{\delta_{ij} H^g_{ii}\} \quad (12)$$
$$H^{\circ\xi} \equiv \{\langle \xi_k | H^\circ | \xi_l \rangle\}, \quad H^{\circ f} \equiv \{\langle f_i | H^\circ | f_j \rangle\}$$
$$H^\xi \equiv \{\langle \xi_k | H | \xi_l \rangle\}, \quad H^g \equiv \{\langle g_i | H | g_j \rangle\} \quad (13)$$

Then immediately it follows that

$$\alpha^+ H^\xi \beta = \alpha^+ \beta H^g \quad (14)$$
$$\alpha^+ H^{\circ\xi} \beta = H^{\circ f} \alpha^+ \beta \quad (15)$$

Subtracting Eq. (15) from Eq. (14), one obtains

$$\alpha^+ \Delta H^\xi \beta = \alpha^+ \beta H^g - H^{\circ f} \alpha^+ \beta \quad (16)$$

where

$$\Delta H^\xi \equiv \{\langle \xi_k | \Delta H | \xi_l \rangle\} = H^\xi - H^{\circ\xi} \quad (17)$$

The kl element of Eq. (16) is

$$\langle f_k | \Delta H | g_l \rangle = \{\langle g_l | H | g_l \rangle - \langle f_k | H^\circ | f_k \rangle\} \langle f_k | g_l \rangle \quad (18)$$

which is equivalent to Eq. (14). Thus with

$$\Delta \bar{E}_l \equiv \bar{E}_l - \bar{E}_l^\circ, \quad \bar{E}^l \equiv \langle g_l | H | g_l \rangle,$$
$$\bar{E}^\circ_l \equiv \langle f_l | H^\circ | f_l \rangle \quad (19)$$

One has

$$\bar{E}_l - \bar{E}_k^\circ = \frac{\langle f_k | \Delta H | g_l \rangle}{\langle f_k | g_l \rangle} \quad \text{with} \quad \langle f_k | g_l \rangle \neq 0 \quad (20)$$
$$\Delta \bar{E}_l = \frac{\langle f_k | \Delta H | g_l \rangle}{\langle f_k | g_l \rangle}$$
$$\text{with} \quad \langle f_k | g_l \rangle \neq 0, \quad \bar{E}_k^\circ = \bar{E}_l^\circ \quad (21)$$

Since one is going to use very this form of GIHF in the following section, it may be wosthwhile to give a few comments on Eq. (21). Suppose, f is ϕ itself, which is the exact solution of the Schrödinger equation (1). That is, α is the unit matrix. Then, taking

$$f = \phi, \quad g = \phi \beta \quad (22)$$

it follows from Eq. (21) that

$$\Delta \bar{E}_l = \langle \phi_k | \Delta H | \sum_i \phi_i \beta_{il} \beta^{-1}{}_{kl} \rangle = \langle \phi_k | \Delta H | \sum_i \phi_i \gamma_{il}{}^k \rangle$$
$$\text{with} \quad \beta_{kl} \neq 0 \quad E_k^\circ = E_l^\circ \quad (23)$$

with

$$\gamma_{il}{}^k \equiv \beta_{il}\beta_{kl}{}^{-1} \tag{24}$$

According to Eq. (23), the total perturbation energy $\Delta\bar{E}_l$ is linear with respect to each component ϕ_i. The ordinary variational treatment, where $\Delta\bar{E}_l$ is computed in terms of the difference of the two expectation values, never shows such a linear dependence.

Furthermore, if one combines Eq. (16) with Eq. (22), there results

$$\Delta H^\phi \beta = \beta H^g - H^{\circ\phi}\beta \tag{25}$$

where

$$\Delta H^\phi \equiv \{\langle \phi_i | \Delta H | \phi_j \rangle\} \tag{26}$$

$$H^{0\phi} \equiv \{\langle \phi_i | H^\circ | \phi_j \rangle\} = \{\delta_{ij}E_j{}^\circ\} \tag{27}$$

Then if k belongs to the degenerate space ($1 \leq k \leq g_d$, $E_k{}^\circ = Eg_d{}^\circ$), then one obtains the secular equation

$$\sum_i \{\Delta H_{ki}{}^\phi - \delta_{ki}(\Delta\bar{E}_l)\}\beta_{il} = 0 \quad 1 \leq k \leq g_d \tag{28}$$

of which eigenvalues are $\Delta\bar{E}_l = E_l - E_{gd}{}^\circ$. When ΔH^ϕ is a factored block form due to symmetry consideration, so is the matrix β. It means that only those ϕ_i's, which have nonvanishing $\Delta H_{ki}{}^\phi$, participates in g_l via Eq. (22), as well as in $\Delta\bar{E}_l$.

III. EFFECTS of CONFIGURATION INTEG-RATION on CRYSTAL FIELD THEORY

Presently, our system of interest* is an atom, of which valence shell configuration is $(3d)^2$, with the effective nuclear charge Z acting on the two electrons, and is placed in the field of octahedral symmetry, V°.

$$V^\circ = v^\circ(1) + v^\circ(2) \tag{29}$$

$$v^\circ \equiv v^{\circ\circ} + v^{\circ 4} \tag{30}**$$

$$v^{\circ\circ} \equiv R^{\circ\circ}(r)\omega^{\circ\circ}(\theta,\varphi), \omega^{\circ\circ}(\theta,\varphi) = Y_0{}^\circ(\theta,\varphi) \tag{31}$$

$$v^{\circ 4} \equiv R^{\circ 4}(r)\omega^{\circ 4}(\theta,\varphi), \quad \omega^{\circ 4}(\theta,\varphi) =$$

$$\sqrt{\frac{7}{12}}Y_4{}^\circ(\theta,\varphi) + \sqrt{\frac{5}{24}}\{Y_4{}^4(\theta,\varphi) + Y_4{}^{-4}(\theta,\varphi)\}$$

$$\tag{32}$$

The Hamiltonian is, neglecting spin-dependent interaction, given by

$$H = H^\circ + V^\circ + \frac{1}{r_{12}} \tag{33}$$

$$H^\circ = h^\circ(1) + h^\circ(2) \tag{34}$$

$$h^0 = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \tag{35}$$

in atomic unit.

The one electron basis are (symmetry adapted) solutions of the Schrödinger equatons,

$$h^\circ \phi_{ik} = \varepsilon_k{}^\circ \phi_{ik} \tag{36}$$

where i and k stand for

$$i = 1, \ 2, \ 3, \ 4, \ 5, \ 6, \ 7, \ 8, \ 9, \ 10$$
$$\underbrace{u \ \ \bar{u} \ \ v \ \ \bar{v}}_{e_g} \ \ \underbrace{a \ \ \bar{a} \ \ b \ \ \bar{b} \ \ c \ \ \bar{c}}_{t_{2g}}$$
$$k = 1, \ 2, \ 3, \ 4, \ 5, \cdots\cdots$$
$$3d \ 4d \ 5d \ 5g \ 6d \cdots\cdots$$

For example $\phi_{4,3}$ is $5d$ orbital of β-spin with v-type e_g symmetry of the octahedral group.

In constructing the two electron basis set, we take only the one-electron excitation into account. One reason for this is that the two electron excitation costs much higher energy than the one electron excitation in the hydrogenic atom. The two electron primitive functions, which behave exactly as the zero order functions ϕ_{il} in the octahedral field are given by

$$F(S_z)_{cp}{}^k = N_k\left\{\frac{1}{\sqrt{2}}|\phi_{il}(1) \ \phi_{jk}(2)| + \frac{1}{\sqrt{2}}\right.$$
$$\left.|\phi_{ik}(1)\phi_{j1}(2)|\right\} \quad (i > j) \tag{37}$$

with

$$N_k = \begin{cases} \dfrac{1}{\sqrt{2}} & \text{for } k \neq 1 \\ \dfrac{1}{2} & \text{for } k = 1 \end{cases} \tag{38}$$

*One can extend to $(3d)^n$ system without any essential feature of the formalism.

**Although one may add the terms of $Y_l{}^m(\theta,\varphi)$ with $l > 4$, they are neglected because the addition does not affect the reasoning given here at all.

S_z stands for z-component of the total spin, and cp means p-th function of c-configuration ($c=1$, 2, 3 for e_g^2, $e_g^1 t_{2g}^1$ and t_{2g}^2). The choice of the primitive functions as Eq. (37) facilitates the symmetry adaptation. That is, the transformation matrix is common to all values of k:

$$\Phi(\Gamma, S, S_z)_{cq}^k = \sum_p^{(c)} F(S_z)_{cp}^k A(\Gamma, S, S_z)_{cp \cdot cq} \quad (39)$$

where Γ, S stand for irreducible representation and total spin, and $(_c^k q)$ means q-th component of k-th basis vector (excitation to k-th level from $k=1$, $3d$) with c-configuration ($c=1$, 2, 3 for e_g^2, $e_g^1 t_{2g}^1$, and t_{2g}^2). On the V^o potential, Φ_{cq}^k's are diagonal with respect to cq, but mix into each other through k. On the $\frac{1}{r_{12}}$ potential, they are diagonal only with respect to q.

The completely diagonal bases on the total Hamiltonian are then constructed by

$$\Phi(\Gamma, S, S_z)_{mq} = \sum_C^{(\Gamma, S, S_z)} \Phi(\Gamma, S, S_z)_{cq}^1$$
$$B(\Gamma, S, S_z)_{cq \cdot mq} \quad (40)$$

$$\Psi(\Gamma, S, S_z)_{mq} = \sum_C^{(\Gamma, S, S_z)} \sum_{k=1} \Phi(\Gamma, S, S_z)_{cq}^k$$
$$G(\Gamma, S, S_z)_{cq \cdot mq} \quad (41)$$

where $\Phi(\Gamma, S, S_z)_{mq}$ is for without (excited) configuration interaction, and $\Psi(\Gamma, S, S_z)_{mq}$ is for with (excited) configuration interaction. Φ_{mq} (hereafter for brevity, the arguments in the parenthesis are omitted when there is no possibility of confusion) is the one which is used in the most naive form of the crystal field theory, in strong field case. Substituting Φ_{cq}^k of Eq. (39) into Eqs. (40) and (41), one obtains

$$\Phi_{mq} = \sum_C^{(\Gamma, S, S_z)} \sum_P^{(C)} F_{cp}^1 A(\Gamma, S, S_z)_{cp \cdot mq} \quad (42)$$

.and

$$\Psi_{mq} = \sum_C^{(\Gamma, S, S_z)} \sum_P^{(C)} \sum_k F_{cp}^k \Omega^k(\Gamma, S, S_z)_{cp \cdot mq} \quad (43)$$

where

$$A(\Gamma, S, S_z)_{cp \cdot mq} \equiv A(\Gamma, S, S_z)_{cp \cdot cq}$$
$$B(\Gamma, S, S_z)_{cq \cdot mq} \quad (44)$$

and

$$\Omega(\Gamma, S, S_z)_{cp \cdot mq}^k \equiv A(\Gamma, S, S_z)_{cp \cdot cq}$$
$$G(\Gamma, S, S_z)_{cq \cdot mq}^k \quad (45)$$

In practice, the $A_{cp \cdot mq}$ and $\Omega_{cp \cdot mq}^k$ are obtained by solving the respective secular equations.

According to the statement associated with Eq. (7), one can select any $F_{c'p'}^1$, provided that the correponding $A_{c'p' \cdot cq}$ (and hence $A_{c'p' \cdot mq}$ and $\Omega_{c'p' \cdot mq}^1$) does not vanish, to express the perturbation energies by use of GIHF. That is,

$$E^{(1)}(\Gamma, S, m) \equiv \langle \Phi_{mq} | V^o + \frac{1}{r_{12}} | \Phi_{mq} \rangle$$
$$= \langle \Phi_{mq} | H | \Phi_{mq} \rangle - \langle \Phi_{mq} | H^o | \Phi_{mq} \rangle$$
$$= \langle \Phi_{mq} | H | \Phi_{mq} \rangle - \langle F_{c'p'}^1 | H^o | F_{c'p'}^1 \rangle$$
$$= \langle F_{c'p'}^1 | V^o + \frac{1}{r_{12}} | \Phi_{mq} \rangle \langle F_{c'p'}^1 | \Phi_{mq} \rangle^{-1}$$
$$\quad (46)$$

Similarly

$$\Delta \bar{E}(\Gamma, S, m) \equiv \langle \Psi_{mq} | H | \Psi_{mq} \rangle - \langle \Phi_{mq} | H^o | \Phi_{mq} \rangle$$
$$= \langle \Psi_{mq} | H | \Psi_{mq} \rangle - \langle F_{c'p'}^1 | H^0 | F_{c'p'}^1 \rangle$$
$$= \langle F_{c'p'}^1 | V^o + \frac{1}{r_{12}} | \Psi_{mq} \rangle \langle F_{c'p'}^1 | \Psi_{mq} \rangle^{-1}$$
$$\quad (47)$$

The matrix elements with respect to the F_{cp}^k's are

$$\langle F_{c'p'}^1 | F_{cp}^k \rangle = \delta_{cc'} \delta_{pp'} \delta_{k1} \quad (48)$$

$$\langle F_{c'p'} | V^o | F_{cp}^k \rangle = \delta_{cc'} \delta_{pp'} N_k \{ \langle \phi_{i'1} | v^o | \delta_{k1} \phi_{i'1} + \phi_{i'k} \rangle + \langle \phi_{j'1} | v^o | \delta_{k1} \phi_{j'1} + \phi_{j'k} \rangle \} \quad (49)$$

$$\langle F_{c'p'}^1 | \frac{1}{r_{12}} | F_{cp}^k \rangle = N_k \langle \phi_{j'1}(1) \ \phi_{j'1}(2)$$
$$- \phi_{j'1}(1) \ \phi_{j'1}(2) | \frac{1}{r_{12}} | \phi_{i1}(1) \phi_{jk}(2)$$
$$+ \phi_{ik}(1) \phi_{j1}(2) \rangle \quad (50)$$

where one may recollect that $i < j$, and $\delta_{ii'} \delta_{jj'}$ corresponds to $\delta_{cc'} \delta_{pp'}$ because there is one-to-one correspondence between cp and ij by Eq. (37). Substituting Eqs. (42) and (43) into Eqs.

(46) and (47) respectively, and using the integrals of Eqs. (48), (49) and (50), one obtains, with little manipulation,

$$E^{(1)}(\Gamma, S, m) = \langle F_{c'p'}{}^1 | V^\circ | F_{c'p'}{}^1 \rangle + \sum_C^{(\Gamma,S,S_z)} \sum_P^{(C)}$$

$$\langle F_{c'p'}{}^1 | \frac{1}{r_{12}} | F_{cp}{}^1 \rangle \frac{\Lambda_{cp\,mq}}{\Lambda_{c'p'\,mq}} = \langle \phi_{i'1} | v^\circ | \phi_{i'1} \rangle$$

$$+ \langle \phi_{j'1} | v^\circ | \phi_{j'1} \rangle + \sum_c^{(\Gamma,S,S_z)} \sum_p^{(c)} \langle \phi_{i'1}\phi_{j'1} - \phi_{j'1}\phi_{i'1} |$$

$$\frac{1}{r_{12}} | \phi_{i1}\phi_{j1} \rangle \frac{\Lambda_{cp\,mq}}{\Lambda_{c'p'\,mq}} \qquad (51)$$

and

$$\Delta \bar{E} = (\Gamma, S, m) = \sum_k \langle F_{c'p'}{}^1 | V^\circ | F_{c'p'}{}^k \rangle \frac{\Omega_{c'p'\,mq}{}^k}{\Omega_{c'p'\,mq}{}^1}$$

$$+ \sum_c^{(\Gamma,S,S_z)} \sum_p^{(c)} \sum_k \langle F_{c'p'}{}^1 | \frac{1}{r_{12}} | F_{cp}{}^k \rangle \frac{\Omega_{cp\,mq}{}^k}{\Omega_{c'p'\,mq}{}^1}$$

$$= \langle \phi_{i'1} | v^\circ |_{(c'p')} \phi_{i'1} + \sum_{k=2} \phi_{i'k}\mu_{c'm}{}^k \rangle + \langle \phi_{j'1} | v^\circ |_{(c'p')} \phi_{j'1}$$

$$+ \sum_{k=2} \phi_{j'k}\mu^\circ{}_{cm}{}^k \rangle + \sum_c^{(\Gamma,S,S_z)} \sum_p^{(c)} \langle \phi_{i'1}\phi_{j'1} -_{(c'p')} \phi_{j'1}\phi_{i'1} |$$

$$\frac{1}{r_{12}} | \phi_{i1}\phi_{j1} +_{(cp)} \phi_{i1} (\sum_{k=2} \phi_{jk}\mu_{cm}{}^k)$$

$$+ (\sum_{k=2} \phi_{ik}\mu_{cm}{}^k) \phi_{j1} \rangle \frac{\Omega_{cp\,mq}{}^1}{\Omega_{c'p'\,mq}{}^1} \qquad (52)$$

where

$$\mu_{c'm}{}^k \equiv \mu(\Gamma, S, S_z)_{c'm}{}^k \equiv \frac{N_k \Omega_{c'p'\,mq}{}^k}{\Omega_{c'p'\,mq}{}^1}$$

$$= \frac{N G_{c'q\,mq}{}^k}{G_{c'q\,mq}{}^1} \qquad (53)$$

$$\mu_{cm}{}^k \equiv \mu(\Gamma, S, S_z)_{cm}{}^k \equiv \frac{N_k \Omega_{cp\,mq}{}^k}{\Omega_{cp\,mq}{}^1}$$

$$= \frac{N_k G_{cq\,mq}{}^k}{G_{cq\,mq}{}^1} \qquad (54)$$

and $F_{c'p'}{}^1$ is chosen in such a way that the corresponding and $\Lambda_{c'p'\,mq}$ do not vanish.

The striking resemblance of the two fomulae, Eqs. (51) and (52) is only superficial one, since $\mu_{cm}{}^k$ does depend on Γ, S and m. The dependence actually prohibits a unique definition of the crystal field parameter 10 Dq, as earlier worker noted by different approach[17]. For the comparison of $E^{(1)}$, which is the (first order) energy of strong field case in the classical field theory, with $\Delta \bar{E}$, perhaps one had better reg-

roup the right side of Eq. (52):

$$\Delta \bar{E}(\Gamma, S, m) = \{ \langle \phi_{i'1} | v^\circ | \phi_{i'1} \rangle + \langle \phi_{j'1} | v^\circ | \phi_{j'1} \rangle \}$$

$$+ \{ \langle \phi_{i'1} | v^\circ | \sum_{k=2} \phi_{i'k}\mu_{c'm}{}^k \rangle + \langle \phi_{j'1} | v^\circ |$$

$$\sum_{k=2} \phi_{j'k}\mu^k{}_{c'm} \rangle \} + \sum_c^{(\Gamma,S,S_z)} \sum_p^{(c)} \langle \phi_{i'1}\phi_{j'1} - \phi_{j'1}\phi_{i'1} |$$

$$\frac{1}{r_{12}} | \phi_{i1}\phi_{j1} \rangle \frac{\Omega_{cp\,mq}{}^1}{\Omega_{c'p'\,mq}{}^1} + \{ \sum_c^{(\Gamma,S,S_z)} \sum_p^{(c)} \langle \phi_{i'1}\phi_{j'1}$$

$$- \phi_{j'1}\phi_{i'1} | \frac{1}{r_{12}} | \sum_{k=2} (\phi_{i1}\phi_{jk} + \phi_{jk}\phi_{j1}) \mu_{cm}{}^k \rangle$$

$$\frac{\Omega_{cp\,mq}{}^1}{\Omega_{c'p'\,mq}{}^1} \} = \{V(\mathrm{I})\} + \{V(\mathrm{II})\}$$

$$+ \{L(\mathrm{I})\} + \{L(\mathrm{II})\} \qquad (55)$$

with obvious definitions for $V(\mathrm{I})$, $V(\mathrm{II})$, $L(\mathrm{I})$ and $L(\mathrm{II})$. What one experimentally observes is not the $\Delta \bar{E}$ itself but the difference of $\Delta \bar{E}$ in the two states (zero order energy is degenerate!).

$E^{(1)}$ of Eq. (51) corresponds to $V(\mathrm{I})+L(\mathrm{I})$, except with minor difference in coefficients included in $L(\mathrm{I})$. In a strong field, by definition, $V(\mathrm{I})+V(\mathrm{II})$ is larger than $L(\mathrm{I})+L(\mathrm{II})$. Especially when the field gets strong enough, even $V(\mathrm{II})$ itself grows so large that one should not simply neglect it, as $E^{(1)}$ does. The trouble is, this very $E^{(1)}$ is supposed to be used in a strong field, according to the classical crystal field theory.

As one sees from the dependence of $\mu_{c'm}{}^k$ on Γ, S, and m, there is no such thing, especially in a strong field, as 10 Dq which is common to all the states characterized by Γ, S and m. In a weak field, however, one may give a significance to the parameter, because in this case $V(\mathrm{II})$ is the least influential term in the expression of $\Delta \bar{E}$.

But, on the other hand, in the weak field, $L(\mathrm{I})+L(\mathrm{II})$ is larger than $V(\mathrm{I})+V(\mathrm{II})$, by definition. Thus one has no reason to simply neglect $L(\mathrm{II})$ as the conventional crystal field theory does. In fact $L(\mathrm{II})$ is the one which modifies the Condon-Slater Integral, F^n.

But, still the 10 Dq and F^n's have been used

as empirical parameters, and by doing so, crystal field theory explained and clarified energy states of so many complexes. How should we explain? The answer for this is to give a new (though probably approximate) theoretical expression which is common to all the states characterized by Γ, S and m.

Suppose $u_k = R_k(r)\omega_{ku}(\theta, \varphi)$ and $a_k = R_k(r)\omega_{ka}(\theta, \varphi)$ which correspond to $\phi_{1,k}$ and $\phi_{5,k}$. Then one-electron total perturbation energies due to v^0 may be written as

$$\Delta\varepsilon_u \equiv \langle u_1|v^0|u_1 + \sum_{k=2} u_k\nu_k\rangle\langle u_1|u_1 + \sum_{k=2} u_k\nu_k\rangle^{-1}$$

$$= \langle u_1|v^{00}|u_1\rangle + \langle u_1|v^{04}|u_1 + \sum_{k=2} u_k\nu_k\rangle \quad (56)$$

$$\Delta\varepsilon_a = \langle a_1|v^{00}|a_1\rangle + \langle a_1|v^{04}|a_1 + \sum_{k=2}\alpha_k\beta_k\rangle \quad (57)$$

where ν_k and β_k correspond to $\mu_{c'm}{}^k$ in Eq. (52). Since $\langle u_1|v^{00}u_1\rangle$ and $\langle a_1|v^{00}|a_1\rangle$ are identical (it influences only on the "center of gravity" on splitting), one has

$$\Delta\varepsilon_u - \Delta\varepsilon_a = \langle R_1|R^{04}|R_1\rangle\{\langle\omega_{1u}|\omega^{04}|\omega_{1u}\rangle$$
$$- \langle\omega_{1a}|\omega^{04}|\omega_{1a}\rangle\} + \sum_{k=2}\langle R_1|R^{04}|R_k\rangle$$
$$\{\langle\omega_{1u}|\omega^{04}|\omega_{ku}\rangle\nu_k - \langle\omega_{1a}|\omega^{04}|\omega_{ka}\rangle\beta_k\} \quad (58)$$

$$2\Delta\varepsilon_u + 3\Delta\varepsilon_a = 5\langle R_1|R^{00}|R_1\rangle + \sum_{k=2}\langle R_1|R^{04}|R_k\rangle$$
$$\{2\langle\omega_{1u}|\omega^{04}|\omega_{ku}\rangle\nu_k + 3\langle\omega_{1a}|\omega^{04}|\omega_{ka}\rangle\beta_k\} \quad (59)$$

Now, one assumes that

$$\nu_k = \beta_k \equiv \gamma_k \text{ for all } \Gamma, S, m \quad (60)$$

and restricts k to nd functions so that

$$k = 1, 2, 3, 5, \cdots\cdots$$
$$3d\ 4d\ 5d\ 6d \quad (61)$$

The assumption means to allow equivalent radial distortion to five $3d$ orbitals and no angular distortion. Then from Eqs. (58) and (59)

$$\Delta\varepsilon_u - \Delta\varepsilon_a = \langle R_1|R^{04}|R_1 + \sum_{k=2}^{d} R_k\gamma_k\rangle\eta \quad (62)$$

$$2\Delta\varepsilon_u + 3\Delta\varepsilon_a = 5\langle R_1|R^{00}|R_1\rangle \quad (63)$$

where η is a simple constant. Taking

$$\Delta\varepsilon_u - \Delta\varepsilon_a = \overline{10\,D_q} \quad (64)$$

one obtains, from Eqs. (62) and (63),

$$\Delta\varepsilon_u = \overline{6\,D_q} + \langle R_1|R^{00}|R_1\rangle \quad (65)$$

$$\Delta\varepsilon_a = -\overline{4\,D_q} + \langle R_1|R^{00}|R_1\rangle \quad (66)$$

where $\langle R_1|R^{00}|R_1\rangle$ is the "center of gravity".

From Eqs. (51) and (52), with the same assumption as above, one obtains typical electron interaction integrals such as

$$\langle u_1(1)a_1(2)|\frac{1}{r_{12}}|\ b_1(1)c_1(2)\rangle$$

and

$$\langle u_1(1)a_1(2)|\frac{1}{r_{12}}|b_1(1)c_1(2) + \sum_{k=2}^{(d)}$$
$$\{b_1(1)c_k(2) + b_k(1)c_1(2)\}\gamma_k\rangle$$

which one is going to compare. If one factors the common angular integrals out, there result

$$\langle R_1(1)R_1(2)|\frac{r_<{}^n}{r_>{}^{n+1}}|R_1(1)R_1(2)\rangle = F^n \quad (67)$$

$$\langle R_1(1)R_1(2)|\frac{r_<{}^n}{r_>{}^{n+1}}|R_1(1)R_1(2) + \sum_{k=2}^{d}$$
$$\{R_1(1)R_k(2) + R_k(1)R_1(2)\}\gamma_k\rangle \equiv \bar{F}^n \quad (68)$$

where F^n of Eq (67) is the Condon-Slater integral if a trivial constant multiplied to it. As one sees now that "the free ion values, F^n (given by Eq. (67))" should be not adequate in a weak field, and the empirical parameters one uses are, in fact, $\bar{F}^n$ of Eq. (68).

In short, the introduction of the excited configuration interaction to crystal field theory, in limited sense of equal radial distortion and no angular distortion, leads to the simple scaling of classical crystal field parameter $10\,Dq$ and F^n, Condon-Slater parameters.

IV. CONCLUSION

In the present paper the Integral Hellmann-Feynman Theorem is generalized to give a full significance to the off-diagonal form, placing an emphasis on degenerate case. The generalized theorem is then successfully applied to see

the effects of configuration interaction on the crystal field theory. It is shown that the contributions of excited states to the perturbed states of $(3d)^2$ configuration via the crystal field V° and $1/r_{12}$ are linear and extents of contributions are different from states to states when the perturbation energies of all order are collectively taken into account. Thus there simply do not exist radial integrals which are common to all states characterized by Γ, S and m, and could be perametrized. However if one allows only angularly undistorted and radially equally distorted excited configurations to get mixed in, then there result radial integrals common to all states. It means the parameters of the traditional crystal field theory, such as $10\,Dq$ and F^n, automatically include, when they are replaced by empirical data, some of the effects of configuration interaction.

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