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Degenerate Case의 Integral Hellmann-Feynman Theorem

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Integral Hellmann-Feynman Theorem of Degenerate Case

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要 約. Integral Hellmann-Feynman Theorem을 degenerate case에 연장 전개하였다. 연장된 formula의 특성을 조사하고 근사식을 제안하였다. Conventional crystal field theory에 대한 고차섭동 에너지 보정의 가능성을 논의 하였다.

Abstract. Integral Hellmann-Feynman Theorem is extended to degenerate case. The characteristics of the extended formula are studied and an approximation is suggested. The possibility of higher order perturbation energy correction to the conventional crystal field theory is discussed.

Introduction

When zeroth state is perturbed, approximate energies and wave functions of the Schrödinger equation are usually obtained by means of the variation principle or perturbation theory. In many problems, the variational treatment is a convenient way of calculating energy values, but it lacks the linear relationship between the approximate nature of the wave functions and the exactness of the energy values. Hence, even though the wave functions are close to reality, the variational energies obtained thereby cannot be expected to be as good. On the contrary, the perturbation treatment gives energies which are accurate to the order of the corresponding wave functions. But, the problem is that to obtain a higher order wave functions we must solve severely complicated differential equations. It is known that accurate solutions of the first order perturbation equations are hard to obtain.

Parr[1] previously suggested a perturbation energy formula, whose reliability is linearly related to that of the wave functions used, in the name of Integral Hellmann-Feynman Theorem. Though the applicability of the theorem is restricted to the case where the zeroth state is nondegenerate, it has been successfully applied to several problems.[2,3]

It is the purpose of this work to extend the theorem to degenerate case and to elucidate the characteristics of the extended formula. It will be shown that the formula enables the inclusion of higher order perturbation energies.

The conventional crystal field theory looked upon as a perturbation energy problem will be

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briefly reviewed. It will be noticed that the conventional crystal field theory, which has been successful in explaining optical spectra by means of parametrization, fails to give an acceptable value of the crystal field splitting parameter 10Dq when calculated from first principles. The possibility of overcoming this apparent dilemma by way of an Integral Hellmann-Feynman approach will be discussed.

Extension of the Integral Hellmann-Feynman Theorem to Degenerate Case

The Hamiltonian operator with and without perturbation is written as H and H° respectively. The Schrödinger equation is

$$H^\circ\phi_i=E_i^\circ\phi_i,\ \langle\phi_i|\phi_j\rangle=\delta_{ij} \tag{1}$$

$$H\phi_k=E_k\phi_k,\ \langle\phi_k|\phi_l\rangle=\delta_{kl} \tag{2}$$

for the zeroth and the perturbed state respectively. The perturbation is defined as

$$\Delta H\equiv H-H^\circ \tag{3}$$

and it is implied that $\phi_k\to\phi_k$, $E_k\to E_k^\circ$ as $\Delta H\to 0$. When the zeroth state is degenerate, we have

$$E_1^\circ=E_2^\circ=\cdots=E_g^\circ,\ g=\text{degeneracy} \tag{4}$$

In matrix form, eq. (2) is written as

$$\underset{\sim}{H}\underset{\sim}{C}=\underset{\sim}{C}\underset{\sim}{E} \tag{5}$$

where

$$\left.\begin{aligned}&\underset{\sim}{H}\equiv\{\langle\phi_i|H|\phi_j\rangle\}\\&\underset{\sim}{C}\equiv\{C_{ik}\},\ C_{ik}\equiv\langle\phi_i|\phi_k\rangle\\&\underset{\sim}{E}\equiv\{\delta_{ik}E_k\}\end{aligned}\right\}$$

Taking

$$\left.\begin{aligned}&\Delta H\equiv\{\langle\phi_i|\Delta H|\phi_j\rangle\}\\&\underset{\sim}{\Delta E}\equiv\{\delta_{kl}\Delta E_k\},\ \Delta E_k\equiv E_k-E_k^0\\&\underset{\sim}{E^0}\equiv\{\delta_{ij}E_j^0\}\end{aligned}\right\} \tag{7}$$

eq. (5) may be rewritten as

$$\underset{\sim}{E^0}\underset{\sim}{C}+\underset{\sim}{\Delta H}\underset{\sim}{C}=\underset{\sim}{C}\underset{\sim}{\Delta E}+\underset{\sim}{C}\underset{\sim}{E^0} \tag{8}$$

Now, within the degenerate space mentioned above,

$$E_k^0=E_l^0\ (k,l\leq g) \tag{9}$$

and

$$(\underset{\sim}{E^0}\underset{\sim}{C})_{kl}=(\underset{\sim}{C}\underset{\sim}{E^0})_{kl} \tag{10}$$

Thus, eq. (8) is arranged to give the Integral Hellmann-Feynman formula for the degenerate case,

$$(\underset{\sim}{\Delta H}\underset{\sim}{C})_{kl}=C_{kl}\Delta E_l\ (k,l\leq g) \tag{11}$$

which, in integral form, is

$$\langle\phi_k|\Delta H|\phi_l\rangle=\langle\phi_k|\phi_l\rangle\Delta E_l\ (k,l\leq g) \tag{12}$$

For $k=l$, eq, (12) becomes

$$\langle\phi_l|\Delta H|\phi_l\rangle=\langle\phi_l|\phi_l\rangle\Delta E_l \tag{13}$$

which is formally the same as that for nondegenerate case. But, the difference is that for degenerate case eq. (12) must be satisfied for off-diagonal elements.

Now, let us compare the magnitude of diagonal elements with that of off-diagonal elements. Combining eqs. (12) and (13), we have

$$\frac{\langle\phi_k|\Delta H|\phi_l\rangle}{\langle\phi_l|\Delta H|\phi_l\rangle}=\frac{\langle\phi_k|\phi_l\rangle}{\langle\phi_l|\phi_l\rangle}\quad(k,l\leq g) \tag{14}$$

or

$$\frac{(\underset{\sim}{\Delta H}\underset{\sim}{C})_{kl}}{(\underset{\sim}{\Delta H}\underset{\sim}{C})_{ll}}=\frac{C_{kl}}{C_{ll}}\quad(k,l\leq g) \tag{15}$$

If $\underset{\sim}{C}$ is expanded in the perturbation series

$$\underset{\sim}{C}=\underset{\sim}{1}+\underset{\sim}{C}^{(1)}+\underset{\sim}{C}^{(2)}+\underset{\sim}{C}^{(3)}+\cdots\cdots \tag{16}$$

we obtain

$$\begin{aligned}\underset{\sim}{1}&=\underset{\sim}{C}^{+}\underset{\sim}{C}\\&=\underset{\sim}{1}+(\underset{\sim}{C}^{(1)^*}+\underset{\sim}{C}^{(1)})+(\underset{\sim}{C}^{(1)^*}\underset{\sim}{C}^{(1)}+\underset{\sim}{C}^{(2)^*}+\underset{\sim}{C}^{(2)})\\&\quad+(\underset{\sim}{C}^{(1)^*}\underset{\sim}{C}^{(2)}+\underset{\sim}{C}^{(2)^*}\underset{\sim}{C}^{(1)}+\underset{\sim}{C}^{(2)^*}+\underset{\sim}{C}^{(3)})+\cdots\end{aligned} \tag{17}$$

where $\underset{\sim}{C}^{+}$ is the associate matrix of $\underset{\sim}{C}$. Without loss of generality, we may assume

$$\underset{\sim}{C}=\underset{\sim}{C}^{*} \tag{18}$$

Therefore, from eb. (17), we obtain

$$C_{kl}^{(1)}+C_{lk}^{(1)}=0 \tag{19}$$

$$\sum_i C_{ik}^{(1)}C_{il}^{(1)}+C_{kl}^{(2)}+C_{lk}^{(2)}=0 \tag{20}$$

$$\sum_i C_{ik}^{(1)}C_{il}^{(2)}+\sum_i C_{ik}^{(2)}C_{il}^{(1)}+C_{kl}^{(2)}+C_{lk}^{(2)}=0 \tag{21}$$

It immediately follows that

$$C_{kl}^{(1)}=-C_{lk}^{(1)} \tag{22}$$

$$C_{ll}^{(1)}=0 \tag{23}$$

$$C_{ll}^{(2)}=-\frac{1}{2}\sum_i (C_{il}^{(1)})^2<0 \tag{24}$$

Since the sum appeari g in eq. (24) is an infinite one, it may be said that

$$|C_{kl}^{(1)}|\ll|C_{ll}^{(2)}| \tag{25}$$

Combining eqs. (15), (16), (23) and (24), we have the following, for the ratio of off-diagonal element to diagonal element,

$$R_{kl}^{H}\equiv\frac{\langle\phi_k|\Delta H|\psi_l\rangle}{\langle\phi_l|\Delta H|\psi_l\rangle}=\frac{\langle\phi_k|\psi_l\rangle}{\langle\phi_l|\psi_l\rangle}$$

$$=\frac{C_{kl}^{(1)}+C_{kl}^{(2)}+\cdots\cdots}{1+C_{ll}^{(1)}+C_{ll}^{(2)}+\cdots\cdots}$$

$$\doteqdot\frac{C_{kl}^{(1)}}{1+C_{ll}^{(2)}} \qquad (k,l\leq g,\ k\neq l) \tag{26}$$

Recalling eq. (25) we have, from eq. (26),

$$|R_{kl}^{H}|<|C_{ll}^{(2)}| \qquad (k,l\leq g,\ k\neq l) \tag{27}$$

The implication of eq. (27) is rather important. That is, the off-diagonal elements of the matrices $\{\langle\phi_k|\Delta H|\psi_l\rangle\}$ and $\{\langle\phi_k|\psi_l\rangle\}$ are smaller than second order assuming the diagonal elements as zeroth order. In other words, if the ϕ's and ψ's are reasonably good wave functions, then

$$\langle\phi_l|\Delta H|\psi_k\rangle\doteqdot 0,\ \langle\phi_l|\psi_k\rangle\doteqdot 0\ (k,l\leq g,k\neq l) \tag{28}$$

must be satisfied.

Now, eq. (13) which is our master integral formula deserves several comments. Firstly, the ΔE_l given by eq. (13) is exactly equal to the difference of the expectation values, $\langle\psi_l|H|\psi_l\rangle-\langle\phi_l|H^{\circ}|\phi_l\rangle$, only if ϕ_l and ψ_l are exact solutions of eqs. (1) and (2) respectively. That is, the ΔE_l of eq. (13) is the sum of the perturbation energies of all orders. Secondly, when ψ_l is approximated by $\widetilde{\psi}_l=\phi_l$, where the ϕ_l itself is the exact solution of eq. (1), both ΔE_l of eq. (13) and the difference of the expectation values give the first order perturbation energy. In general, if the $\widetilde{\psi}_l$ is exact to the n-th order, the exactness of ΔE_l of eq. (13) is guaranteed to the $(n+1)$-th order. For example, if the $\widetilde{\psi}_l$ is correct to the first order, ΔE_l of eq. (13) gives the perturbation energy which is exact to the second orer. Although, according to the perturbation theory, it is possible to obtain the perturbation energy correct to the third order when the first order perturbed function is available, in practice it is very rarely the case that one knows the exact first order perturbed function, especially in the degenerate case. Therefore, the linear relationship between the exactness of the ψ_l and that of ΔE_l is quite useful when an approximation is made. Lastly, the ΔE_l of eq. (13) is a very convenient form for symmetry consideration. Together with the relation given by eq. (28), it does help guessing the symmetry components of ψ_l when extensive degeneracy exists in the zeroth state. When ΔH belongs to the totally symmetric representation of a point group, ψ_l must belong to the same irreducible representation as ϕ_l.

Discussion

A Comment on Crystal Field Theory

Crystal field theory can be looked upon as a problem of calculating perturbation energies which arise when more than two perturbations are applied to a highly degenerate zeroth state. In the simplest case, only electron-electron repulsion and crystal field potential are considered as perturbations. When the electron-electron

repulsion plays the more significant role than the crystal field potential, the secular matrix is reduced by classifying the degenerate zero order functions according to the eigenfunctions of angular momentum operators which commute with $1/r_{12}$ (weak field method). When the crystal field potential is greater than the electron-electron repulsion, the secular matrix is reduced by taking linear combinations of the zero order functions to give basis functions of the irreducible representation of the symmetry group to which the complex molecule belongs (strong field method). But the problem is that, in both methods, nonvanishing off-diagonal matrix elements remain. Orgel[4] was the first to show diagrammatically the effect of interaction between spectroscopic terms on the energy values as the crystal field strength gradually increases from zero. Liehr and Ballhausen[5] numerically evaluated the interaction between spectroscopic terms in both the weak field and the strong field pictures. All of them looked upon each spectroscopic term as a degenerate space and employed configuration interaction to handle the nonzero off-diagonal elements. However, the apparent higher order energy correction, which is made by considering configuration interaction in the picture of Orgel and Ballhausen, is nothing more than the first order correction if electron-electron repulsion (e. e. r.) plus crystal field potential (c. f. p.) is treated as a single perturbation. Namely, defining H^0 as the sum of the kinetic energy operator and the electron-nuclear attraction operator, and from

$$H^0\xi_k=\epsilon^0{}_k\xi_k,\quad \epsilon_1{}^0=\epsilon_2{}^0=\cdots\cdots=\epsilon_g{}^0 \tag{29}$$

$$\langle\phi_k|H^0+\text{e. e. r. }|\phi_l\rangle=\delta_{kl}(\epsilon_g{}^0+\langle\phi_l|\text{e. e. r. }|\phi_l\rangle) \tag{30}$$

$$\langle\phi_k|H^0+\text{e. e. r. }+\text{c. f. p. }|\phi_l\rangle =\delta_{kl}(\epsilon_g{}^0+\langle\phi_l|\text{e. e. r. }+\text{c. f. p. }|\phi_l\rangle) \tag{31}$$

$$\underline{\phi}=\underline{\xi}\,\underline{u},\quad \underline{\phi}=\underline{\xi}\,\underline{w},\quad \underline{u}^+\underline{u}=\underline{w}^+\underline{w}=\underline{1} \tag{32}$$

it follows that

$$\langle\phi_k|\text{e. e. r. }+\text{c. f. p. }|\phi_k\rangle =\frac{\langle\phi_k|\text{e. e. r. }+\text{c. f. p. }|\phi_k\rangle}{\langle\phi_k|\phi_k\rangle} \tag{33}$$

$$\langle\phi_k|\text{e. e. r. }+\text{c. f. p. }|\phi_k\rangle =\langle\phi_k|H^0+\text{e. e. r. }+\text{c. f. p}|\phi_k\rangle-\langle\phi_k|H^0|\phi_k\rangle \tag{34}$$

which tells us that:

(a) If one takes $\underline{\phi}$ as basis set, the configuration interaction gives formally first plus higher order energy, but the value is the same as that of the first order energy in terms of $\underline{\phi}$ basis.

(b) The difference of the expectation values as denoted by eq. (34) is exactly equivalent to the total energy evaluated by the Integral Hellmann-Feynman formula, in this special case, in spite of the approximate nature of the ϕ's.

Thus, the conventional crystal field theory, even employing the most sophisticated method, is characterized by the following:

(1) The crystal field splitting parameter is regarded as the difference of the first order perturbation energies originated from the degenerated zero order states.

(2) It assumes the crystal field to be originated from a symmetric arrangement of point charges around the central metal atom or ion.

Now, the problem was that the crystal field model, which had been and is still successful in explaining optical spectra of complex molecules by parametrizing the difference of the first order perturbation energies[6,7], involved serious difficulties when calculating $10Dq$ from first principles[8~11]. This made people to take up molecular orbital calculations thus introducing interactions between metal and ligand electrons. Thus gave reasonable values of $10Dq$ as reported by several authors[12~16]. Hence, we fall into a dilemma as for the origin of the crystal field.

There seems to be two possible explanations for the dilemma. Firstly, The point charge model is acceptable, but the splitting parameter may be the difference of the total perturbation energies rather than the first order perturbation energies. Secondly, the point charge model may not represent the true picture of the crystal field as maintained by those who prefer to believe in the ligand field theory.

At this point, an Integral Hellmann-Feynman approach to the problem appears worthwhile. Reliable wave functions obtained by MO calculations may be used as the final state wave function in eq. (13). Besides including higher order perturbation energies, this enables the partitioning of the contribution of the point charge potential to $10Dq$. Such investigation is being carried out in our laboratory. A possible explanation of the above mentioned dilemma is expected.

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