The Electron-Hole Potential Method Viewed from Hypervirial Theorems

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ハイパービリアル定理から見た電子－正孔ポテンシャル法

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ハイパービリアル定理が，第二量子化された形で導入され，電子－正孔ポテンシャル法を誘導するのに用いられる。その誘導は，ただ単に簡単であるのみならず，方法の本性を理解するのに役立つ。ブリユアンの定理および拡張されたブリユアンの定理がハイパービリアル定理に含まれていることが，示され，簡便法の範囲内で電子－正孔ポテンシャル法を越える可能性の一つが，示唆される。補足の言が，摂動論との関連において付け加えられる。

INTRODUCTION

The evaluation of excitation energies by the closed-shell Hartree-Fock (HF) method[1] is to be improved in the electron-hole potential (EHP) method,[2] as far as only one specific excitation is concerned. The original derivation of the EHP method consists of constructing the new occupied and unoccupied orbitals from the occupied and unoccupied HF orbitals, respectively, through the minimization of the single-electron excitation energy in question. In this paper hypervirial theorems are introduced in the second quantized form and utilized to derive the EHP method. The derivation is not only simple but instructive in understanding a nature of the method. Brillouin's and the extended Brillouin's theorems[2] are shown to be contained in hypervirial theorems and a possibility of going beyond the EHP method is suggested within the scope of succinct methods. Supplementary remarks are added in the perturbation-theoretical context.

HYPERVIRIAL THEOREMS

Let $|\psi>$ be an eigenstate of a Hamiltonian H and W be an arbitrary operator. The hypervirial theorem[3] affirms that

$$<\psi|[H, W]|\psi>=0, \tag{1}$$

the restriction on W being only that $W|\psi>$ should not be pathological. The theorem is nothing other than the statement that the expectation value of W for stationary states is independent of time, and has vast range of utilization because of its fundamentality. The essential explorations

of the theorem in molecular quantum mechanics have been made already in 1960's from both variation- and perturbation-theoretical points of view,[4][5] where the form of W is either non--specified or given as a function of coordinates and momenta. Using the field-theoretical language, we can see an interesting simple aspect of hypervirial theorems. Let us take a system of identical particles and denote the creation and annihilation operators for the one-particle quantum state j by a_j^+ and a_j respectively. Then, an arbitrary one-particle operator of the system can be written as

$$W = \sum_{jk} w_{jk} a_j^+ a_k .$$

The severe requirement that (1) must hold for any W leads us to the one-particle hypervirial theorem:

$$\langle \psi \mid [H,\ a_p^+ a_q] \mid \psi \rangle = 0 \qquad (\text{any } p,\ q). \tag{2}$$

Likewise we have the two-particle hypervirial theorem,

$$\langle \psi \mid [H, a_p^+ a_r^+ a_s a_q] \mid \psi \rangle = 0 \qquad (\text{any } p,\ q,\ r,\ s),$$

and so on. For any product of the creation and/or annihilation operators we have

$$\langle \psi \mid [H, \prod_p a_p^+ \prod_q a_q] \mid \psi \rangle = 0 .$$

However, unless the numbers of the creation and annihilation operators are equal, the relation is trivial for the particle-conserving Hamiltonian.

Separating a Hamiltonian into the unperturbed Hamiltonian K and the perturbation λV with a real parameter λ:

$$H = K + \lambda V, \tag{3}$$

we can obtain a perturbation expansion of (1) on the assumption that an eigenstate $\mid \psi \rangle$of H is attainable from the corresponding eigenstate $\mid \phi \rangle$of K thorough a unitary transformation: [6]

$$\mid \psi \rangle = \exp(S) \mid \phi \rangle , \tag{4}$$

where S is an antihermitian operator independent of the energy level index. Noting that S has no zeroth order term, we put it in the power series of λ as

$$S = \lambda S_1 + \lambda^2 S_2 + \cdots\cdots \tag{5}$$

with antihermitian operators $\{S_i\}$. Substitution of (4) into (1) rewrites the hypervirial theorem as a form of the unperturbed state expectation value:

$$\langle \phi \mid \exp(-S)[K + \lambda V,\ W] \exp(S) \mid \phi \rangle = 0 ,$$

which is expanded by means of (5) to give

$$\lambda \langle \phi \mid [V,\ W] + [[K,\ W],\ S_1] \mid \phi \rangle + \lambda^2 \langle \phi \mid [[V,\ W],\ S_1] + \frac{1}{2}[[[K,\ W],\ S_1],\ S_1] + [[K,\ W],\ S_2] \mid \phi \rangle + \cdots = 0 .$$

Thus we have the first order hypervirial theorem,

$$\langle \phi \mid [V,\ W] + [[K,\ W],\ S_1] \mid \phi \rangle = 0 , \tag{6}$$

and so on.

To decompose S_i into the one-body part $S_i^{(1)}$, the two-body $S_i^{(2)}$, and so on,

$$S_i = S_i^{(1)} + S_i^{(2)} + \cdots\cdots, \tag{7}$$

enables us to proceed a little further. Assuming that K is diagonal and that V consists of the one- and two-body parts;

$$V = V^{(1)} + V^{(2)}, \tag{8}$$

we obtain the first order one-body hypervirial theorem as

$$\langle \phi \mid [V^{(1)}, a_p^+ a_q] + [[K, a_p^+ a_q], S_1^{(1)}] \mid \phi \rangle + \langle \phi \mid [V^{(2)}, a_p^+ a_q] + [[K, a_p^+ a_q], S_1^{(2)}] \mid \phi \rangle = 0 \qquad (\text{any } p, q), \tag{9}$$

where the first and second terms in the left-hand side, respectively, concern the one- and two-body operators. We can make all $S_1^{(n)}$ vanish for n larger than 2.

THE HARTREE-FOCK METHOD

The Hamiltonian of electrons in the fixed nuclear framework is given by

$$H = \sum_{\substack{\xi\eta \\ \mu}} h_{\xi\eta} a_{\xi\mu}^+ a_{\eta\mu} + \frac{1}{2} \sum_{\substack{\xi\eta\theta\gamma \\ \mu\nu}} v_{\eta\gamma}^{\xi\theta} a_{\xi\mu}^+ a_{\theta\nu}^+ a_{\gamma\nu} a_{\eta\mu}, \tag{10}$$

where the second suffices, μ and ν, refer to the electron spin. Taking a relevant hermitian one-electron operator

$$X = \sum_{\substack{\xi\eta \\ \mu}} x_{\xi\eta} a_{\xi\mu}^+ a_{\eta\mu},$$

which is to be determined later, going through the expression

$$H = \sum_{\substack{\xi\eta \\ \mu}} (h_{\xi\eta} + x_{\xi\eta}) a_{\xi\mu}^+ a_{\eta\mu} + \frac{1}{2} \sum_{\substack{\xi\eta\theta\gamma \\ \mu\nu}} v_{\eta\gamma}^{\xi\theta} a_{\xi\mu}^+ a_{\theta\nu}^+ a_{\gamma\nu} a_{\eta\mu} - \sum_{\substack{\xi\eta \\ \mu}} x_{\xi\eta} a_{\xi\mu}^+ a_{\eta\mu},$$

we rewrite (10) in the molecular orbital representation as

$$H = \sum_{\substack{j \\ \mu}} \varepsilon_j a_{j\mu}^+ a_{j\mu} + \frac{1}{2} \sum_{\substack{jklm \\ \mu\nu}} v_{km}^{jl} a_{j\mu}^+ a_{l\nu}^+ a_{m\nu} a_{k\mu} - \sum_{\substack{jk \\ \mu}} x_{jk} a_{j\mu}^+ a_{k\mu}. \tag{11}$$

The molecular orbital coefficients $\{u_{\xi j}\}$ and their energies $\{\varepsilon_j\}$ are determined by the eigenvalue problem diagonalizing $\{h_{\xi\eta} + x_{\xi\eta}\}$:

$$\sum_{\eta} (h_{\xi\eta} + x_{\xi\eta}) u_{\eta j} = u_{\xi j} \varepsilon_j. \tag{12}$$

Now let us take the unperturbed Hamiltonian in (11) as

$$K = \sum_{\substack{j \\ \mu}} \varepsilon_j a_{j\mu}^+ a_{j\mu}$$

and assume that its ground state $\mid F\rangle$ have a doubly occupied form:

$$\mid F\rangle = a_{f\uparrow}^+ a_{f\downarrow}^+ \cdots\cdots a_{2\uparrow}^+ a_{2\downarrow}^+ a_{1\uparrow}^+ a_{1\downarrow}^+ \mid 0 \rangle,$$

where $\uparrow$ and $\downarrow$ stand for the up- and down-spin states, respectively, and $\mid 0\rangle$ means the vacuum state. Hereafter we denote a set of the occupied orbitals $\{1, 2, \cdots\cdots, f\}$ by F and that of the unoccupied by $\bar{F}$. Substituting

$$V^{(1)} = -\sum_{\substack{jk \\ \mu}} x_{jk} a_{j\mu}^+ a_{k\mu}, \tag{13}$$

$$V^{(2)} = \frac{1}{2} \sum_{\substack{jklm \\ \mu\nu}} v_{km}^{jl} a_{j\mu}^+ a_{l\nu}^+ a_{m\nu} a_{k\mu}, \tag{14}$$

$$S_1^{(1)} = \sum_{\substack{jk \\ \mu}} s_{jk} a_{j\mu}^+ a_{k\mu}, \tag{15}$$

and

$$S_I^{(2)}=\frac{1}{2}\sum_{\substack{jklm\\ \mu\nu}} s_{km}^{jl} a_{j\mu}^{+} a_{l\nu}^{+} a_{m\nu} a_{k\mu} \tag{16}$$

into (9), we obtain the first order one-body hypervirial theorem. There $a_p^{+}a_q$ in (9) has only to be replaced by $a_{p\sigma}^{+}a_{q\sigma}$, since (11) includes no spin-changing term. For the ground state, putting $|\phi\rangle = |F\rangle$, we see the theorem result in the following condition.

$$-x_{qp}+\tilde{v}_{qp}+(\varepsilon_q-\varepsilon_p)(s_{qp}+\tilde{s}_{qp})=0 \qquad (\text{any } p\in\bar{F},\ q\in F), \tag{17}$$

the quantity with tilde being defined as

$$\tilde{t}_{qp}=\sum_{j\in F}(2t_{pj}^{qj}-t_{jp}^{qj}).$$

Although for any $p\in F$ and $q\in\bar{F}$ the same equation is obtained as for any $p\in\bar{F}$ and $q\in F$, they are not independent of each other as far as X and V are kept hermitian and S antihermitian. If we use no S, that is, take an approximation that $|\psi\rangle = |\phi\rangle$, then (17) gives

$$x_{qp}=\tilde{v}_{qp} \qquad (\text{any } p\in\bar{F},\ q\in F \text{ and } \textit{vice versa}), \tag{18}$$

which just means to take the HF potential. Note that x_{jk}'s for $p,\ q\in\bar{F}$ and $p,\ q\in F$ are not conditioned here, the HF ambiguity being implied. Setting $x_{qp}=\tilde{v}_{qp}$ for all p and q, we have

$$x_{\xi\eta}=\sum_{j\in F}(2v_{\eta j}^{\xi j}-v_{j\eta}^{\xi j}), \tag{19}$$

which gives the usual HF equation, substituted into (12).

Denoting the singlet and triplet excited states of K by

$$|vw\pm\rangle=\frac{1}{2}(a_{v\uparrow}^{+}a_{w\uparrow}\pm a_{v\downarrow}^{+}a_{w\downarrow})|F\rangle \qquad (v\in\bar{F},\ w\in F), \tag{20}$$

where + and − stand for the singlet and triplet states respectively, we have

$$\langle F|H|vw\pm\rangle=\frac{1}{2}(\langle F|[H,\ a_{v\uparrow}^{+}a_{w\uparrow}]|F\rangle\pm\langle F|[H,\ a_{v\downarrow}^{+}a_{w\downarrow}]|F\rangle),$$

since $\langle F|a_{v\mu}^{+}$ vanishes. Thus Brillouin's theorem is contained in hypervirial theorems. By the way let us refer to the simple variation problem.[7] In the condition for the trial state function $|\xi\rangle$,

$$\langle\xi|H|\delta\xi\rangle=0,$$

to take $\langle F|$ as $\langle\xi|$ and $\kappa a_{p\sigma}^{+}a_{q\sigma}|F\rangle$ $(p\in\bar{F},\ q\in F)$ with an infinitesimal κ as $|\delta\xi\rangle$ immediately gives

$$\langle F|Ha_{p\sigma}^{+}a_{q\sigma}|F\rangle=0 \qquad (\text{any } p\in\bar{F},\ q\in F),$$

which is again arranged in the form of the hypervirial theorem without S.

THE ELECTRON-HOLE POTENTIAL METHOD

The first order one-body hypervirial theorems for the singlet and triplet excited states are obtained by putting $|\phi\rangle = |vw\pm\rangle$ after substitution of (13), (14), (15), and (16) into (9). They lead us to the following rather lengthy conditions.

$$-x_{vp}+\tilde{v}_{vp}-v_{pw}^{vw}+v_{wp}^{vw}\pm v_{wp}^{vw}+(\varepsilon_v-\varepsilon_p)(s_{vp}+\tilde{s}_{vp}-s_{pw}^{vw}+s_{wp}^{vw}\pm s_{wp}^{vw})=0, \tag{21a}$$

$$-x_{qw}+\tilde{v}_{qw}+v_{wv}^{qv}-v_{vw}^{qv}\pm(-v_{vw}^{qv})+(\varepsilon_q-\varepsilon_w)(s_{qw}+\tilde{s}_{qw}+s_{wv}^{qv}-s_{vw}^{qv}\pm(-s_{vw}^{qv}))=0, \tag{21b}$$

$$-x_{wp}+\tilde{v}_{wp}+v^{wv}_{pv}-v^{ww}_{pw}\pm v^{wv}_{vp}+(\varepsilon_w-\varepsilon_p)(s_{wp}+\tilde{s}_{wp}+s^{wv}_{pv}-s^{ww}_{pw}\pm s^{wv}_{vp})\}=0\,, \tag{21c}$$

$$-x_{qv}+\tilde{v}_{qv}+v^{qv}_{vv}-v^{qw}_{vw}\pm(-v^{qw}_{wv})+(\varepsilon_q-\varepsilon_v)(s_{qv}+\tilde{s}_{qv}+s^{qv}_{vv}-s^{qw}_{vw}\pm(-s^{qw}_{wv}))=0\,, \tag{21d}$$

$$-x_{qp}+\tilde{v}_{qp}+\dot{v}(v)_{qp}-\dot{v}(w)_{qp}+(\varepsilon_q-\varepsilon_p)(s_{qp}+\tilde{s}_{qp}+\dot{s}(v)_{qp}-\dot{s}(w)_{qp})=0\,, \tag{21e}$$

for any $p\epsilon\bar{F}$ other than v and any $q\epsilon F$ other than w, and

$$v^{wv}_{vv}-v^{ww}_{vw}\pm(v^{wv}_{vv}-v^{ww}_{vw})+(\varepsilon_w-\varepsilon_v)(s^{wv}_{vv}-s^{ww}_{vw}\pm(s^{wv}_{vv}-s^{ww}_{vw}))=0\,. \tag{21f}$$

The quantity with single dot in (21e) is defined as

$$\dot{t}(r)_{qp}=t^{qr}_{pr}-\frac{1}{2}t^{qr}_{rp}.$$

Let us consider the single-determinant approximation, the case without S. If we take the HF potential (19), (21)'s are reduced to

$$-v^{vw}_{pw}+v^{vw}_{wp}\pm v^{vw}_{wp}=0\,, \tag{22a}$$

$$v^{qv}_{wv}-v^{qv}_{vw}\pm(-v^{qv}_{vw})=0\,, \tag{22b}$$

$$v^{wv}_{pv}-v^{ww}_{pw}\pm v^{wv}_{vp}=0\,, \tag{22c}$$

$$v^{qv}_{vv}-v^{qw}_{vw}\pm(-v^{qw}_{wv})=0\,, \tag{22d}$$

$$\dot{v}(v)_{qp}-\dot{v}(w)_{qp}=0\,, \tag{22e}$$

for any $p\epsilon\bar{F}$ other than v and any $q\epsilon F$ other than w, and

$$v^{wv}_{vv}-v^{ww}_{vw}\pm(v^{wv}_{vv}-v^{ww}_{vw})=0\,, \tag{22f}$$

which cannot hold in general, and we see the violation of the hypervirial theorem by the HF method. Here note that the orbital symmetry tends to lessen the violation.

It enables us to make (21a) and (21b) without S terms hold that the hypervirial theorem for the ground state imposes no condition upon x_{qp}'s for $p,\ q\epsilon\bar{F}$ and $p,\ q\epsilon F$, (18) remaining satisfied. Take

$$x_{qp}=\tilde{v}_{qp}-v^{qw}_{pw}+v^{qw}_{wp}\pm v^{qw}_{wp}\qquad(p,\ q\epsilon\bar{F}) \tag{23a}$$

and

$$x_{qp}=\tilde{v}_{qp}+v^{qv}_{pv}-v^{qv}_{vq}\pm(-v^{qv}_{vq})\qquad(p,\ q\epsilon F). \tag{23b}$$

Then, (21a) and (21b) without S terms clearly hold and the violation occurs in the same forms as (22c), (22d), (22e), and (22f). There again note that the orbital symmetry often favors to lessen the violation. If the HForbitals $\{u^{\mathrm{HF}}_{\xi\underline{j}}\}$ and their energies $\{\varepsilon^{\mathrm{HF}}_{\underline{j}}\}$ are already known by solving (12) with (19), we have only to work out a set of eigenvalue problems that

$$\sum_{\underline{k}\epsilon\bar{F}}(\delta_{\underline{j}\underline{k}}\varepsilon^{\mathrm{HF}}_{\underline{j}}+y(w\pm)_{\underline{j}\underline{k}})c_{\underline{k}p}=c_{\underline{j}p}\alpha_p\qquad(\underline{j}\epsilon\bar{F}) \tag{24a}$$

with

$$y(w\pm)_{\underline{j}\underline{k}}=-v^{\underline{j}w}_{\underline{k}w}+v^{\underline{j}w}_{w\underline{k}}\pm v^{\underline{j}w}_{w\underline{k}}$$

and

$$\sum_{\underline{k}\epsilon F}(\delta_{\underline{j}\underline{k}}\varepsilon^{\mathrm{HF}}_{\underline{j}}+z(v\pm)_{\underline{j}\underline{k}})d_{\underline{k}p}=d_{\underline{j}p}\beta_p\qquad(\underline{j}\epsilon F) \tag{24b}$$

with

$$z(v\pm)_{\underline{j}\underline{k}}=v^{\underline{j}v}_{\underline{k}v}-v^{\underline{j}v}_{v\underline{k}}\pm(-v^{\underline{j}v}_{v\underline{k}}),$$

which is just the original form of the basic equations of the EHP method.[2] Because $\{y(w\pm)_{j\underline{k}}\}$ depend on w, an occupied orbital, and $\{z(v\pm)_{j\underline{k}}\}$ on v, an unoccupied one, to solve (24)'s includes self-consistency procedure. Consequently, of course, $\{c_{j\underline{p}}\}$, $\{d_{j\underline{p}}\}$, $\{\alpha_p\}$, and $\{\beta_p\}$ are dependent on all of v, w, and the multiplicity $\pm$.

Noting that the hypervirial theorems for the excited states without S,

$$\langle vw\pm \mid [H,\ a^+_{p\sigma}\, a_{q\sigma}] \mid vw\pm\rangle = 0\,, \tag{25}$$

hold for any $p,\ q\epsilon\bar{F}$ or $p,\ q\epsilon F$ under the EHP choice of X, (23)'s, we can prove the extended Brillouin's theorem in the EHP method,

$$\langle vw\pm \mid H \mid v'w\pm\rangle = 0 \qquad (v\neq v') \tag{26a}$$

and

$$\langle vw\pm \mid H \mid vw'\pm\rangle = 0 \qquad (w\neq w'), \tag{26b}$$

to be contained in hypervirial theorems as follows. Putting

$$L_\mu(\pm)=\frac{1}{\sqrt{2}}(\delta_{\mu\uparrow}\pm\delta_{\mu\downarrow})\,,$$

we arrange the left-hand side of (26a) as

$$\begin{aligned}\langle vw\pm \mid H \mid v'w\pm\rangle &= \sum_{\mu\nu} L_\mu(\pm)\langle vw\pm \mid Ha^+_{v'\mu}\,\delta_{\mu\nu}a_{w\mu} \mid F\rangle\\ &= \sum_{\mu\nu} L_\mu(\pm)\langle vw\pm \mid Ha^+_{v'\mu}(a_{v\mu}a^+_{v\nu}+a^+_{v\nu}\,a_{v\mu})a_{w\nu} \mid F\rangle\\ &= \sum_{\mu}\langle vw\pm \mid Ha^+_{v'\mu}\,a_{v\mu} \mid vw\pm\rangle\\ &= \sum_{\mu}\langle vw\pm \mid [H,\ a^+_{v'\mu}\,a_{v\mu}] \mid vw\pm\rangle,\end{aligned}$$

where the terms under the summation of the last line are independent of μ, so the condition that

$$\langle vw\pm \mid [H,\ a^+_{v'\mu}\,a_{v\mu}] \mid vw\pm\rangle = 0\,,$$

which is assured by (25), is equivalent to (26a). We have a similar argument for (26b).

It can be said that the EHP method is better to satisfy hypervirial theorems than the HF method.

BEYOND THE ELECTRON-HOLE POTENTIAL METHOD

Let us give a perturbation expansion to the excitation energy as preliminaries. Define the excitation energy $\Delta E(I\to J)$ from the state $\mid\psi_I\rangle$ to $\mid\psi_J\rangle$ as

$$\Delta E(I\to J)=\langle\psi_J \mid H \mid \psi_J\rangle-\langle\psi_I \mid H \mid \psi_I\rangle,$$

which is converted with (3), (4), and (5) into

$$\begin{aligned}\Delta E(I\to J) &= K_J-K_I+\lambda(\langle\phi_J \mid V \mid \phi_J\rangle+\langle\phi_I \mid V \mid \phi_I\rangle)\\ &+\lambda^2(\langle\phi_J \mid [V,\ S_I]+\frac{1}{2}[[K,\ S_I],\ S_I] \mid \phi_J\rangle-\langle\phi_I \mid [V,\ S_I]+\frac{1}{2}[[K,\ S_I],\ S_I] \mid \phi_I\rangle)+\cdots,\end{aligned} \tag{27}$$

where $\mid\phi_I\rangle$ and $\mid\phi_J\rangle$ are, respectively, the eigenstates with the eigenvalues K_I and K_J of K. If the first order hypervirial theorem (6) is satisfied, the second order term in the right-hand side becomes simpler, and the expression is reduced to

$$\Delta E(I\to J)=K_J-K_I+\lambda(\langle\phi_J \mid V \mid \phi_J\rangle-\langle\phi_I \mid V \mid \phi_I\rangle)$$

$$+\frac{\lambda^2}{2}(\langle\phi_J|[V, S_I]\phi_J\rangle-\langle\phi_I|[V, S_I]|\phi_I\rangle)+\cdots\cdots.$$

To first order the excitation energy is independent of S. Any of the HF and EHP methods calculates (27) to first order with $|\psi_I\rangle=|F\rangle$ and $|\psi_J\rangle=|vw\pm\rangle$.

Now consider to satisfy the ground and excited states hypervirial theorems by including S as simple as possible. Each term in the left-hand side of (22c), (22d), (22e), and (22f) has one of the following forms: v_{pv}^{qv}, v_{vp}^{qv}, v_{pw}^{qw}, and v_{wp}^{qw} ($p\epsilon\bar{F}$, $q\epsilon F$). This suggests that the first-order one-body hypervirial theorems for the excited states as well as the ground state are completely satisfied in the EHP choice of X by using S of the matrix elements:

$$\begin{aligned}
&s_{pv}^{qv}=-v_{pv}^{qv}/(\varepsilon_q-\varepsilon_p),\\
&s_{vp}^{qv}=-v_{vp}^{qv}/(\varepsilon_q-\varepsilon_p),\\
&s_{pw}^{qw}=-v_{pw}^{qw}/(\varepsilon_q-\varepsilon_p),\\
&s_{wp}^{qw}=-v_{wp}^{qw}/(\varepsilon_q-\varepsilon_p),\\
&s_{qp}=(2v_{pw}^{qw}-v_{wp}^{qw})/(\varepsilon_q-\varepsilon_p),
\end{aligned}\qquad \left(\begin{array}{c} p\epsilon\bar{F},\ q\epsilon F \\ \text{and} \\ \textit{vice versa}\end{array}\right)$$

and

$$s_{pr}^{qs}=s_{qp}=0 \qquad \text{otherwise,}$$

which gives the second order correction in (27) for $|\psi_I\rangle=|F\rangle$ and $|\psi_J\rangle=|vw\pm\rangle$ as

$$\lambda^2\Big(\sum_{\substack{p\epsilon\bar{F}\\ q\epsilon F}}\frac{A(vw\pm)_{qp}}{\varepsilon_p-\varepsilon_q}+\sum_{q\epsilon F}\frac{B(vw\pm)_q}{\varepsilon_v-\varepsilon_q}+\sum_{p\epsilon\bar{F}}\frac{C(vw\pm)_p}{\varepsilon_p-\varepsilon_w}\Big) \tag{28}$$

with

$$\begin{aligned}
A(vw\pm)_{qp}=&\,2D(w)_{qp}(v_{pv}^{qv}-D(w)_{qp})+2D(v)_{qp}(v_{pw}^{qw}-D(v)_{qp})\\
&-2v_{pv}^{qv}v_{vp}^{qv}-2v_{pw}^{qw}v_{wp}^{qw}+2(1\pm1)v_{vp}^{qv}v_{wp}^{qw},\\
B(vw\pm)_q=&\,v_{vw}^{qw^2}+v_{wv}^{qw^2}-2(1\pm1)v_{vw}^{qw}v_{wv}^{qw},
\end{aligned}$$

and

$$C(vw\pm)_p=v_{pv}^{wv^2}+v_{pv}^{vw^2}-2(1\pm1)v_{pv}^{wv}v_{pv}^{vw},$$

where

$$D(r)_{qp}=v_{pr}^{qr}-v_{rp}^{qr}$$

and all the orbitals are assumed to be real for brevity. Only p and q of the same symmetry, q of the same symmetry as v, and p of the same symmetry as w should be taken into account, respectively in the first, second, and third summations in (28). Before we discuss the effect of this correction, a considerable amount of trial numerical calculation is to be performed, and we would like to think the above recipe as a possibility at present. Other various methods are expected to be devised.

SUPPLEMENTARY REMARKS

It is never futile to add supplementary remarks in the perturbation-theoretical context[5]

Under the unitary transformation prescription, (4), perturbation equations in the operator form are derived from the condition that

$$[\exp(-S)H\exp(S),\ K]=0\,.$$

Making use of (3) and (5), we obtain the first order perturbation equation

$$[\,V+[K,\ S_1],\ K]=0 \tag{29}$$

the second order one

$$[[\,V,\ S_1]+\frac{1}{2}[[K,\ S_1],\ S_1]+[K,\ S_2],K]=0\,,$$

and so on. Now we confine ourselves to (29). Substitution of (7) together with (15) and (16) and that of (8) together with (13) and (14) into (29) lead us to the two separated equations corresponding to the one- and two-body parts:

$$\sum_{\substack{jk\\ \mu}}(s_{jk}(\varepsilon_j-\varepsilon_k)-x_{jk})(\varepsilon_j-\varepsilon_k)a^+_{j\mu}a_{k\mu}=0$$

and

$$\sum_{\substack{jklm\\ \mu\nu}}(s^{jl}_{km}(\varepsilon_j+\varepsilon_l-\varepsilon_m-\varepsilon_k)+v^{jl}_{km})(\varepsilon_j+\varepsilon_l-\varepsilon_m-\varepsilon_k)a^+_{j\mu}a^+_{l\nu}a_{m\nu}a_{k\mu}=0\,,$$

which are read as

$$s_{jk}=x_{jk}\,/(\varepsilon_j-\varepsilon_k)\qquad (j,\ k \text{ such that } \varepsilon_j\neq\varepsilon_k) \tag{30}$$

and

$$s^{jl}_{km}=-v^{jl}_{km}/(\varepsilon_j+\varepsilon_l-\varepsilon_m-\varepsilon_k)\qquad (j,\ k,\ l,\ m \text{ such that } \varepsilon_j+\varepsilon_l-\varepsilon_m-\varepsilon_k\neq 0)\,. \tag{31}$$

The matrix elements of S_1 other than (30) and (31) can be set to vanish by imposing such auxiliary restriction upon S as the complete off-diagonality in the representation of $\{\,|\,\phi\rangle\}$.[6] Clearly, to take (30) and (31) makes (17) and (21)'s hold; the first order hypervirial theorem is satisfied.

References

(1) C. C. J. Roothaan: Rev. Mod. Phys. 23 (1951) 69

(2) K. Morokuma and S. Iwata: Chem. Phys Lett. 16 (1972) 192

(3) J. O. Hirschfelder: J. Chem. Phys. 33 (1960) 1462

(4) S. T. Epstein and J. O. Hirschfelder: Phys. Rev. 123 (1961) 1495
J. O. Hirschfelder and C. A. Coulson: J. Chem. Phys. 36 (1962) 941

(5) P. D. Robinson: Proc. R. Soc. London A 283 (1965) 229
A. M. Arthurs and P. D. Robinson: Proc. R. Soc. London A 301 (1967) 507
P. D. Robinson: J. Chem. Phys. 47 (1967) 2319

(6) H. Primas: Helv. Phys. Acta. 34 (1961) 331
H. Primas: Rev. Mod. Phys. 35 (1963) 710

(7) D. J. Thouless: *The Quantum Mechanics of Many-Body Systems* (Academic Press, London, 1961) p. 15.

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