The Hartree-Fock and Electron-Hole Potential Methods from a Hypervirial Theorem Standpoint

Makoto Isihara

Department of General Education, Shotoku-Gakuen Women's Junior College, Gifu 500

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The hypervirial theorem is introduced in the second quantized expanded form, and utilized for reviewing the Hartree-Fock and electron-hole potential methods. A possibility of going beyond the latter is suggested within the scope of handy methods. Brillouin's and the extended Brillouin's theorems are shown to be contained in the hypervirial theorem.

The hypervirial theorem (HVT)[1] is nothing other than the statement that the expectation value of any physically nonpathological operator does not depend on time in stationary states, and has vast range of application because of its great fundamentality. Essential explorations of the theorem in molecular quantum mechanics have been made already in 1960's from both variation-[2] and perturbation-theoretical[3] points of view, where the form of operators is either nonspecified or given as a function of coordinates and momenta. In this paper the HVT is introduced in the second quantized form, expanded under the exponential prescription,[4] and utilized for reviewing the Hartree-Fock (HF)[5] and electron-hole potential (EHP)[6,7] methods. We can immediately arrive at the HF method in the first order one-particle HVT for the ground state; that for the excited state leads us to the EHP method and further gives a possibility of a handy modification beyond the method. Brillouin's[8] and the extended Brillouin's[6] theorems are shown to be contained in the HVT. Supplementary remarks are added on what is implied in the first order two-particle HVT for the ground state and in connection with the perturbation-theoretical approach.

The Hypervirial Theorem

Let $|\psi\rangle$ be an eigenstate of a Hamiltonian H and W be an arbitrary operator, the restriction on W being only that $W|\psi\rangle$ should not jump outside the space considered. The HVT is simply written as

$$\langle\psi|[H, W]|\psi\rangle = 0. \tag{1}$$

Take a system of identical particles and denote the creation and annihilation operators for the one-particle quantum state j by $a_j^\dagger$ and a_j respectively. Then, any one-particle operator of the system is of the following form.

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

The strong requirement that Eq. 1 must hold for any W leads to the one-particle HVT:

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

Likewise we have the two-particle HVT,

$$\langle\psi|[H, a_p^\dagger a_r^\dagger a_s a_q]|\psi\rangle = 0 \quad \text{(any } p, q, r, s\text{)}, \tag{3}$$

and so on. For arbitrary products of the creation and/or annihilation operators we have

$$\langle\psi|[H, \prod_p a_p^\dagger \prod_q a_q]|\psi\rangle = 0. \tag{4}$$

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

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

$$H = K + \lambda V, \tag{5}$$

we can obtain a perturbation expansion of Eq. 1 on the assumption that an eigenstate $|\psi\rangle$ of H is attainable from the corresponding eigenstate $|\phi\rangle$ of K through a unitary transformation:

$$|\psi\rangle = \exp(S)|\phi\rangle, \tag{6}$$

where S is an antihermitian operator independent of the energy level index.[3,4] Noting that S has no zeroth order term, we put it in the power series of λ as

$$S = \lambda S_1 + \lambda^2 S_2 + \cdots \tag{7}$$

with antihermitian operators $\{S_i\}$. Substitution of Eq. 6 into Eq. 1 rewrites the HVT as a form of the unperturbed state expectation value:

$$\langle\phi|\exp(-S)[H, W]\exp(S)|\phi\rangle = 0,$$

which is expanded by means of Eqs. 5 and 7;

$$\lambda\langle\phi|([V, W] + [[K, W], S_1])|\phi\rangle + \lambda^2\langle\phi|([[V, W], S_1] + \frac{1}{2}[[[K, W], S_1], S_1] + [[K, W], S_2])|\phi\rangle + \cdots = 0. \tag{8}$$

Thus we have the first order HVT,

$$\langle\phi|([V, W] + [[K, W], S_1])|\phi\rangle = 0, \tag{9}$$

or, using the Jacobi-Lie identity,

$$\langle\phi|[V+[K, S_1], W]|\phi\rangle = 0. \tag{10}$$

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

$$S_i = S_i^{(1)} + S_i^{(2)} + \cdots, \tag{11}$$

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

$$V = V^{(1)} + V^{(2)}, \tag{12}$$

we can write the first order HVT as

$$\sum_{n=1,2} \langle\phi|[Y^{(n)}, W]|\phi\rangle = 0 \tag{13}$$

with

$$Y^{(n)} = V^{(n)} + [K, S_1^{(n)}]. \tag{14}$$

The terms of $n=1$ and 2 in the left-hand side of Eq. 13 concern the one- and two-particle operators for

$W=a_p^\dagger a_q$ and two- and three-particle ones for $W=a_p^\dagger a_r^\dagger a_s a_q$ respectively. We can make all $S_1^{(n)}$'s vanish for n larger than 2.

The Hartree-Fock Method

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

$$H=\sum_{\xi\eta\mu} h_{\xi\eta} a_{\xi\mu}^\dagger a_{\eta\mu} + \frac{1}{2}\sum_{\xi\eta\theta\tau\mu\nu} v_{\eta\tau}^{\xi\theta} a_{\xi\mu}^\dagger a_{\theta\nu}^\dagger a_{\tau\nu} a_{\eta\mu}, \tag{15}$$

where the second suffices, μ and ν, refer to the electron spin. It is assumed hereafter that the matrix elements, $\{h_{\xi\eta}\}$, $\{v_{\eta\tau}^{\xi\theta}\}$, and so on, are all spin-independent. Taking a relevant hermitian one-particle operator

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

which is to be determined later, we rewrite the Hamiltonian in the molecular orbital representation as

$$H=\sum_{j\mu}\varepsilon_j a_{j\mu}^\dagger a_{j\mu} + \frac{1}{2}\sum_{jklm\mu\nu} v_{km}^{jl} a_{j\mu}^\dagger a_{l\nu}^\dagger a_{m\nu} a_{k\mu} - \sum_{jk\mu} x_{jk} a_{j\mu}^\dagger a_{k\mu}. \tag{16}$$

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

$$\sum_\eta (h_{\xi\eta}+x_{\xi\eta})u_{\eta j} = u_{\xi j}\varepsilon_j. \tag{17}$$

Now let us take the unperturbed Hamiltonian in Eq. 16 as

$$K=\sum_{j\mu}\varepsilon_j a_{j\mu}^\dagger a_{j\mu} \tag{18}$$

and assume that its ground state $|F\rangle$ have a closed-shell form:

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

where $\uparrow$ and $\downarrow$ stand for the up- and down-spin states, respectively, and $|0\rangle$ means the vacuum state. Denoting a set of the occupied orbitals $\{1,2,\cdots,f\}$ by F and that of the unoccupied by $\overline{F}$, we define the occupation indicator as

$$\mathrm{f}(j)=\begin{cases}1 & (j\in F)\\ 0 & (j\in\overline{F}).\end{cases} \tag{19}$$

Substituting

$$V^{(1)} = -\sum_{jk\mu} x_{jk} a_{j\mu}^\dagger a_{k\mu}, \tag{20}$$

$$V^{(2)} = \frac{1}{2}\sum_{jklm\mu\nu} v_{km}^{jl} a_{j\mu}^\dagger a_{l\nu}^\dagger a_{m\nu} a_{k\mu}, \tag{21}$$

$$S_1^{(1)} = \sum_{jk\mu} s_{jk} a_{j\mu}^\dagger a_{k\mu}, \tag{22}$$

$$S_1^{(2)} = \frac{1}{2}\sum_{jklm\mu\nu} s_{km}^{jl} a_{j\mu}^\dagger a_{l\nu}^\dagger a_{m\nu} a_{k\mu}, \tag{23}$$

and Eq. 18 into Eq. 13 through Eq. 14, we obtain the first order one-particle HVT putting $W=a_{p\sigma}^\dagger a_{q\sigma}$, since the present Hamiltonian includes no spin-changing term. For the ground state, putting $|\phi\rangle=|F\rangle$, we see the following condition result from the theorem.

$$(-x_{qp}+\tilde{v}_{qp}+(\varepsilon_q-\varepsilon_p)(s_{qp}+\tilde{s}_{qp}))(\mathrm{f}(q)-\mathrm{f}(p))=0, \tag{24}$$

the quantity with a tilde being defined as

$$\tilde{t}_{jk}=\sum_m (2t_{km}^{jm}-t_{mk}^{jm})\mathrm{f}(m).$$

Although for any $p\in F$ and $q\in\overline{F}$ the same equation is obtained as for any $p\in\overline{F}$ 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 $|\phi\rangle=|\phi\rangle$, then Eq. 24 gives

$$x_{jk}=\tilde{v}_{jk} \quad (\text{any } j\in F, k\in\overline{F} \text{ and } \textit{vice versa}), \tag{25}$$

which is just the HF condition. Note that x_{jk}'s for $j,k\in F$ and $j,k\in\overline{F}$ are, as easily seen in Eq. 24, not conditioned here, the HF ambiguity being implied. Setting $x_{jk}=\tilde{v}_{jk}$ for all j and k, we have

$$x_{\xi\eta}=\sum_m (2v_{\eta m}^{\xi m}-v_{m\eta}^{\xi m})\mathrm{f}(m), \tag{26}$$

which gives the standard HF equation, substituted into Eq. 17. For general choices of X and S Eq. 24 should be read as a mutual restriction on them. Especially, under the HF choice of X, Eq. 25, the restriction is reduced to

$$s_{jk}+\tilde{s}_{jk}=0 \quad (\text{any } j\in F, k\in\overline{F} \text{ and } \textit{vice versa}). \tag{27}$$

Denoting the singlet and triplet excited states of K by

$$|vw\pm\rangle=\sum_\mu \mathrm{L}_\mu(\pm) a_{v\mu}^\dagger a_{w\mu}|F\rangle \quad (v\in\overline{F}, w\in F) \tag{28}$$

with

$$\mathrm{L}_\mu(\pm)=(\delta_{\mu\uparrow}\pm\delta_{\mu\downarrow})/\sqrt{2}, \tag{29}$$

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

$$\langle F|H|vw\pm\rangle=\sum_\mu \mathrm{L}_\mu(\pm)\langle F|[H, a_{v\mu}^\dagger a_{w\mu}]|F\rangle, \tag{30}$$

since $\langle F|a_{v\mu}^\dagger$ vanishes. Thus Brillouin's theorem is contained in the HVT

$$\langle F|[H, a_{p\sigma}^\dagger a_{q\sigma}]|F\rangle=0 \quad (p\in\overline{F}, q\in F \text{ and } \textit{vice versa}) \tag{31}$$

or equivalently

$$\langle F|[H, a_{p\sigma}^\dagger a_{q\sigma}]|F\rangle=0 \quad (\text{any } p, q), \tag{32}$$

which characterizes the HF method.

The Electron-Hole Potential Method

The evaluation of excitation energies by the closed-shell HF method[9] is to be improved in the EHP method, as far as only one specific excitation is concerned.[6] A persuasive derivation of the EHP method consists of constructing the new occupied and unoccupied orbitals, respectively, from the occupied and unoccupied HF orbitals through the variational procedure for the excited state in question. Here, confining ourselves to the single configuration excitation case, we view the method from a HVT standpoint, which seems helpful in understanding a nature of the method.

The first order one-particle HVT for the singlet and triplet excited states are obtained by putting $|\phi\rangle=|vw\pm\rangle$ after substitution of Eqs. 18, 20, 21, 22, and 23 into Eq. 13 through Eq. 14:

$$(y_{qp}+\tilde{y}_{qp}+\dot{y}(v)_{qp}-\dot{y}(w)_{qp})(\mathrm{f}(q)-\mathrm{f}(p))$$
$$+\frac{1}{2}((y_{qp}+\tilde{y}_{qp})(\delta_{qv}-\delta_{qw}-\delta_{pv}+\delta_{pw})$$
$$-(y^{qv}_{pv}-y^{qv}_{vp})(\delta_{qw}-\delta_{pw})-(y^{qw}_{pw}-y^{qw}_{wp})(\delta_{qv}-\delta_{pv}))$$
$$\pm\frac{1}{2}(y^{qv}_{vp}(\delta_{qw}-\delta_{pw})+y^{qw}_{wp}(\delta_{qv}-\delta_{pv}))=0 \qquad (33)$$

with

$$y_{jk}=-x_{jk}+(\varepsilon_j-\varepsilon_k)s_{jk}$$

and

$$y^{jl}_{km}=v^{jl}_{km}+(\varepsilon_j+\varepsilon_l-\varepsilon_m-\varepsilon_k)s^{jl}_{km},$$

the quantity with a single dot being defined as

$$\dot{t}(m)_{jk}=t^{jm}_{km}-t^{jm}_{mk}/2.$$

Consider the single-determinant approximation, the case without S. Then, Eq. 33 is reduced to the condition that

$$-x_{vj}+\tilde{v}_{vj}-v^{vw}_{jw}+v^{vw}_{wj}\pm v^{vw}_{wj}=0 \qquad (j\epsilon\bar{F}'), \quad (34a)$$
$$-x_{jw}+\tilde{v}_{jw}+v^{jv}_{wv}-v^{jv}_{vw}\pm(-v^{jv}_{vw})=0 \qquad (j\epsilon F'), \quad (34b)$$
$$-x_{wj}+\tilde{v}_{wj}+v^{wv}_{jv}-v^{ww}_{jw}\pm v^{ww}_{vj}=0 \qquad (j\epsilon\bar{F}'), \quad (34c)$$
$$-x_{jv}+\tilde{v}_{jv}+v^{jv}_{vv}-v^{jw}_{vw}\pm(-v^{jw}_{wv})=0 \qquad (j\epsilon F'), \quad (34d)$$
$$-x_{jk}+\tilde{v}_{jk}+\dot{v}(v)_{jk}-\dot{v}(w)_{jk}=0 \qquad (j\epsilon F', k\epsilon\bar{F}'), \quad (34e)$$

and

$$v^{wv}_{vv}-v^{ww}_{vw}\pm(v^{wv}_{vv}-v^{ww}_{vw})=0, \qquad (34f)$$

where the primes on F and $\bar{F}$ mean the exclusion of w and v respectively. The complex conjugate equations are omitted for brevity. If we take the canonical and virtual HF orbitals, the first and second terms in each left-hand side of Eqs. 34a, b, c, d, and e cancel out. But the rest does not vanish in general, and we see the violation of the HVT by the standard HF method. Here it is worth while to note that the orbital symmetry tends to lessen the violation.

It enables us to make Eqs. 34a and b hold that the first order one-particle HVT for the ground state imposes no condition upon x_{jk}'s for $j,k\epsilon\bar{F}$ and $j,k\epsilon F$, Eq. 25 remaining satisfied. Determine the orbitals so as to satisfy

$$x_{jk}=\tilde{v}_{jk}-v^{jw}_{kw}+v^{jw}_{wk}\pm v^{jw}_{wk} \qquad (j,k\epsilon\bar{F}) \quad (35a)$$

and

$$x_{jk}=\tilde{v}_{jk}+v^{jv}_{kv}-v^{jv}_{vk}\pm(-v^{jv}_{vk}) \qquad (j,k\epsilon F). \quad (35b)$$

Then Eqs. 34a and b clearly hold and the violation occurs in the same form in Eqs. 34c, d, e, and f as the HF case. There the orbital symmetry still inclines to diminish the violation. If the HF orbitals $\{\underline{u}_{\underline{\xi}\underline{j}}\}$ and their energies $\{\underline{\varepsilon}_{\underline{j}}\}$ are already known, we have only to work out a set of eigenvalue problems that

$$\sum_{\underline{k}\epsilon\bar{F}}(\delta_{\underline{j}\underline{k}}\underline{\varepsilon}_{\underline{j}}+z(w\pm)_{\underline{j}\underline{k}})c_{\underline{k}\underline{m}}=c_{\underline{j}\underline{m}}\alpha_m \qquad (\underline{j}\epsilon\bar{F}) \quad (36a)$$

and

$$\sum_{\underline{k}\epsilon F}(\delta_{\underline{j}\underline{k}}\underline{\varepsilon}_{\underline{j}}-z(v\pm)_{\underline{j}\underline{k}})d_{\underline{k}\underline{m}}=d_{\underline{j}\underline{m}}\beta_m \qquad (\underline{j}\epsilon F) \quad (36b)$$

with

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

which is equivalent to the original form of the basic equations of the EHP method.

Noting that under Eqs. 35's the one-particle HVT for the excited states without S holds for a restricted region as

$$\langle vw\pm|[H,a^\dagger_{p\sigma}a_{q\sigma}]|vw\pm\rangle=0 \quad (p,q\epsilon F \text{ and } p,q\epsilon\bar{F}), \quad (37)$$

we can prove that the extended Brillouin's theorem in the EHP method,

$$\langle vw\pm|H|v'w\pm\rangle=0 \qquad (v\neq v') \quad (38a)$$

and

$$\langle vw\pm|H|vw'\pm\rangle=0 \qquad (w\neq w'), \quad (38b)$$

is contained in the HVT as follows. Arrange the left-hand side of Eq. 38a as

$$\langle vw\pm|H|v'w\pm\rangle$$
$$=\sum_{\mu\nu}\mathrm{L}_\mu(\pm)\langle vw\pm|Ha^\dagger_{v'\mu}\delta_{\mu\nu}a_{w\nu}|F\rangle$$
$$=\sum_{\mu\nu}\mathrm{L}_\mu(\pm)\langle vw\pm|Ha^\dagger_{v'\mu}(a_{v\mu}a^\dagger_{v\nu}+a^\dagger_{v\nu}a_{v\mu})a_{w\nu}|F\rangle$$
$$=\sum_\mu\langle vw\pm|Ha^\dagger_{v'\mu}a_{v\mu}|vw\pm\rangle$$
$$=\sum_\mu\langle vw\pm|[H,a^\dagger_{v'\mu}a_{v\mu}]|vw\pm\rangle, \quad (39)$$

where the terms under the summation of the last line are independent of μ. Hence the condition

$$\langle vw\pm|[H,a^\dagger_{v'\mu}a_{v\mu}]|vw\pm\rangle=0, \quad (40)$$

which is assured by Eq. 37, is equivalent to Eq. 38a. We have similar argument for Eq. 38b.

The EHP method is characterized by the HVT Eq. 37 besides Eq. 32, so it can be said that the EHP method satisfies the HVT better than the standard HF method. The hole potential method[10] may look characterized by the HVT defined in a smaller region of p and q than Eq. 37,

$$\langle vw\pm|[H,a^\dagger_{p\sigma}a_{q\sigma}]|vw\pm\rangle=0 \qquad (p,q\epsilon\bar{F}), \quad (41)$$

besides Eq. 32. However, Eq. 41 is actually independent of v, and we have Eq. 41 for all of $v\epsilon\bar{F}$. Thus it is not necessarily appropriate to regard the hole potential method as an intermediate between the standard HF and EHP methods;[6] of course, when we confine ourselves to one specific excitation, it is correct that the EHP method satisfies the HVT better than the hole potential 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 $|\phi_I\rangle$ to $|\phi_J\rangle$ as

$$\Delta E(I\to J)=\langle\phi_J|H|\phi_J\rangle-\langle\phi_I|H|\phi_I\rangle, \quad (42)$$

which is converted with Eqs. 5, 6, and 7 into

$$\Delta E(I\to J)=K_J-K_I$$
$$+\lambda(\langle\phi_J|V|\phi_J\rangle-\langle\phi_I|V|\phi_I\rangle)$$
$$+\lambda^2(\langle\phi_J|([V,S_1]+\frac{1}{2}[[K,S_1],S_1])|\phi_J\rangle$$
$$-\langle\phi_I|([V,S_1]+\frac{1}{2}[[K,S_1],S_1])|\phi_I\rangle)+\cdots, \quad (43)$$

where $|\phi_I\rangle$ and $|\phi_J\rangle$ are, respectively, the eigen-

states with the eigenvalues K_I and K_J of K. To first order the excitation energy is independent of S. Both the HF and EHP methods calculate Eq. 43 to first order with $|\phi_I\rangle=|F\rangle$ and $|\phi_J\rangle=|vw\pm\rangle$.

Now consider to satisfy the first order one-particle HVT for the excited state as well as the ground by including S as simple as possible. Under the EHP choice of X, Eqs. 35's together with Eq. 25, the following condition results from Eq. 33.

$$(\varepsilon_v-\varepsilon_j)(s_{vj}+\tilde{s}_{vj}-s_{jw}^{vw}+s_{wj}^{vw}\pm s_{wj}^{vw})=0 \qquad (j\epsilon\overline{F}'), \tag{44a}$$

$$(\varepsilon_j-\varepsilon_w)(s_{jw}+\tilde{s}_{jw}+s_{wv}^{jv}-s_{vw}^{jv}\pm(-s_{vw}^{jv}))=0 \quad (j\epsilon F'), \tag{44b}$$

$$y_{jv}^{wv}-y_{jw}^{ww}\pm y_{vj}^{wv}+(\varepsilon_w-\varepsilon_j)(s_{wj}+\tilde{s}_{wj})=0 \quad (j\epsilon\overline{F}'), \tag{44c}$$

$$y_{vv}^{jv}-y_{vw}^{jw}\pm(-y_{wv}^{jw})+(\varepsilon_j-\varepsilon_v)(s_{jv}+\tilde{s}_{jv})=0 \qquad (j\epsilon F'), \tag{44d}$$

$$\dot{y}(v)_{jk}-\dot{y}(w)_{jk}+(\varepsilon_j-\varepsilon_k)(s_{jk}+\tilde{s}_{jk})=0 \qquad (j\epsilon F', k\epsilon\overline{F}'), \tag{44e}$$

and

$$y_{vv}^{wv}-y_{vw}^{ww}\pm(y_{vv}^{wv}-y_{vw}^{ww})=0. \tag{44f}$$

Here note that any term concerning $V^{(2)}$ has one of the following forms: y_{kv}^{jv}, y_{vk}^{jv}, y_{kw}^{jw}, and y_{wk}^{jw} ($j\epsilon F$, $k\epsilon\overline{F}$). This shows a way to attain the present purpose. Set the matrix elements of S as

$$s_{kl}^{jl}=s_{lk}^{lj}=-v_{kl}^{jl}/(\varepsilon_j-\varepsilon_k) \qquad \left(\begin{array}{c} j\epsilon F, k\epsilon\overline{F} \\ \text{and } \textit{vice versa}; \\ l=w,v \end{array}\right) \tag{45a}$$

$$s_{lk}^{jl}=s_{kl}^{lj}=-v_{lk}^{jl}/(\varepsilon_j-\varepsilon_k) \tag{45b}$$

$$s_{jk}=(2v_{kw}^{jw}-v_{wk}^{jw})/(\varepsilon_j-\varepsilon_k) \tag{45c}$$

and

$$s_{km}^{jl}=s_{jk}=0 \qquad \text{(otherwise)}, \tag{45d}$$

where the one-particle terms are prepared for the condition given by Eq. 27. Clearly this choice of S suffices for the satisfaction of Eq. 33 as well as Eq. 24, and gives the second order term in Eq. 43 for $|\phi_I\rangle=|F\rangle$ and $|\phi_J\rangle=|vw\pm\rangle$ as

$$\lambda^2\mathrm{Re}\left(\sum_{\substack{j\epsilon F\\ k\epsilon\overline{F}}}\frac{2A(vw\pm)_{jk}}{\varepsilon_k-\varepsilon_j}+\sum_{j\epsilon F}\frac{B(vw\pm)_j}{\varepsilon_v-\varepsilon_j}\sum_{j\epsilon\overline{F}}\frac{C(vw\pm)_j}{\varepsilon_j-\varepsilon_w}\right) \tag{46}$$

with

$$A(vw\pm)_{jk}=D(v)_{jk}(v_{jw}^{kw}-D(v)_{kj})+D(w)_{jk}(v_{jv}^{kv}-D(w)_{kj})-v_{wk}^{jw}v_{jw}^{kw}-v_{vk}^{jv}v_{jv}^{kv}+(1\pm1)v_{vk}^{jv}v_{wj}^{kw}, \tag{47}$$

$$B(vw\pm)_j=|v_{jw}^{vw}|^2+|v_{wj}^{vw}|^2-2(1\pm1)v_{wj}^{vw}v_{jw}^{vw}, \tag{48}$$

and

$$C(vw\pm)_j=|v_{jv}^{wv}|^2+|v_{vj}^{wv}|^2-2(1\pm1)v_{vj}^{wv}v_{wv}^{jv}, \tag{49}$$

where

$$D(l)_{jk}=v_{kl}^{jl}-v_{lk}^{jl}.$$

In the first, second, and third summations in the above correction term 46, only j and k of the same symmetry, j of the same symmetry as v, and j of the same symmetry as w have only to be taken into account respectively.

In the EHP method the orbitals are determined under the influence of the scatterings of electrons inside F and $\overline{F}$ by the potentials due to the electron in v and the hole in w respectively. Roughly speaking, the adoption of the S of Eq. 45's means to take it into account the scatterings of electrons from F to $\overline{F}$ and from $\overline{F}$ to F by the electron and hole potentials. The first order correction to the excited state has one electron in $\overline{F}$ and one hole in F besides v and w in consequence:

$$(S_1^{(1)}+S_1^{(2)})|vw\pm\rangle=\sum_{\substack{j\epsilon\overline{F}\\ k\epsilon F}}\sum_{\mu\nu}G(vw\pm)_{j\,k}^{\mu\,\nu}a_{j\nu}^{\dagger}a_{k\nu}a_{v\mu}^{\dagger}a_{w\mu}|F\rangle \tag{50}$$

with

$$G(vw\pm)_{j\,k}^{\mu\,\nu}=\mathrm{L}_\mu(\pm)(v_{kw}^{jw}-v_{kv}^{jv}-\delta_{\mu\nu}(v_{wk}^{jw}-v_{vk}^{jv}))/(\varepsilon_j-\varepsilon_k). \tag{51}$$

The ground state is not affected, because it involves neither electron in v nor hole in w. As easily seen, we have

$$(S_1^{(1)}+S_1^{(2)})|F\rangle=0. \tag{52}$$

Before we discuss the effect of the correction 46, a considerable amount of examinational numerical calculation is to be performed, and we would like to regard the recipe as a possibility at present.

Supplementary Remarks

The First Order Two-Particle HVT. To put $W=a_{p\sigma}^{\dagger}a_{r\tau}^{\dagger}a_{s\tau}a_{q\sigma}$ in Eq. 13 gives the first order two-particle HVT, which has the following expression for the ground state after substitution of Eqs. 18, 20, 21, 22, and 23 through Eq. 14.

$$(\delta_{qp}\hat{y}_{sr}+\delta_{sr}\hat{y}_{qp}-\delta_{\sigma\tau}(\delta_{qr}\hat{y}_{sp}+\delta_{sp}\hat{y}_{qr}))(\mathrm{f}(q)\mathrm{f}(s)-\mathrm{f}(r)\mathrm{f}(p))-(y_{pr}^{qs}-\delta_{\sigma\tau}y_{rp}^{qs})(\mathrm{g}(qs:rp)-\mathrm{g}(pr:sq))=0 \tag{53}$$

with

$$\mathrm{g}(pr:sq)=\mathrm{f}(p)\mathrm{f}(r)(\mathrm{f}(s)+\mathrm{f}(q)-1), \tag{54}$$

and

$$\hat{y}_{jk}=y_{jk}+\tilde{y}_{jk}.$$

Provided that the first order one-particle HVT for the ground state is satisfied, that is,

$$\hat{y}_{jk}=0 \qquad (j\epsilon F, k\epsilon\overline{F} \text{ and } \textit{vice versa}),$$

Eq. 53 results in

$$v_{pr}^{qs}-\delta_{\sigma\tau}v_{rp}^{qs}+(\varepsilon_q+\varepsilon_s-\varepsilon_r-\varepsilon_p)(s_{pr}^{qs}-\delta_{\sigma\tau}s_{rp}^{qs})=0 \qquad (q,s\epsilon\overline{F};\ p,r\epsilon F \text{ and } \textit{vice versa}), \tag{55}$$

which leads us to

$$s_{km}^{jl}=-v_{km}^{jl}/(\varepsilon_j+\varepsilon_l-\varepsilon_m-\varepsilon_k) \qquad \left(\begin{array}{c} j,l\epsilon\overline{F};\ k,m\epsilon F \\ \text{and } \textit{vice versa} \end{array}\right). \tag{56}$$

This shows that the electron correlation in the ground state can be taken into account first by including the contribution from the double excitation configurations for any choice of orbitals satisfying Eq. 24. In using the EHP orbitals, therefore, the first aid for the ground state $|F\rangle$ is to use the S in the form of Eq. 56 likewise in using the HF orbitals. Further adopting Eq. 56 together with Eqs. 45's, we can improve the ground state, the first order one-particle HVT for the excited state remaining alive, since s_{km}^{jl}'s for $j,l\epsilon\overline{F}$, $k,m\epsilon F$ and *vice versa* do not concern $\tilde{s}_{jk}$'s.

The Perturbation-Theoretical Choice. It is never futile to add some remarks in connection with the perturbation-theoretical approach. Under the exponential prescription, Eq. 6, perturbation equations in the operator form are derived from[3,4,11]

$$[\exp(-S)H\exp(S), K] = 0. \tag{57}$$

Making use of Eqs. 5 and 7, we obtain the first order perturbation equation as

$$[V+[K, S_1], K] = 0, \tag{58}$$

which becomes the two separated equations corresponding to the one- and two-particle parts after calculation with Eqs. 18, 20, 21, 22, and 23:

$$\sum_{jk\mu} y_{jk}(\varepsilon_j-\varepsilon_k)a^\dagger_{j\mu}a_{k\mu} = 0 \tag{59a}$$

and

$$\sum_{jklm\mu\nu} y^{jl}_{km}(\varepsilon_j+\varepsilon_l-\varepsilon_m-\varepsilon_k)a^\dagger_{j\mu}a^\dagger_{l\nu}a_{m\nu}a_{k\mu} = 0, \tag{59b}$$

which lead us to

$$s_{jk} = x_{jk}/(\varepsilon_j-\varepsilon_k) \qquad (j, k \text{ such that } \varepsilon_j \neq \varepsilon_k) \tag{60a}$$

and

$$s^{jl}_{km} = -v^{jl}_{km}/(\varepsilon_j+\varepsilon_l-\varepsilon_m-\varepsilon_k) \quad \begin{pmatrix} j,k,l,m \text{ such that} \\ \varepsilon_j+\varepsilon_l-\varepsilon_m-\varepsilon_k \neq 0 \end{pmatrix}. \tag{60b}$$

The matrix elements of S other than these can be set to vanish by imposing such auxiliary restriction upon S as that S should be completely off-diagonal in the representation $\{|\phi\rangle\}$.[4] Clearly Eqs. 60's satisfy the first order one-particle HVT. This perturbation-theoretical choice requires nothing of orbitals but sufficient inclusion of configurations. Hence, unless we know the well-behaved orbitals suitable for purpose beforehand, the choice is not necessarily practical.

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