Analysis of the Electron-Hole Potential Method

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電子ー正孔ポテンシャル法の分析

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原子や分子の励起エネルギーを求める簡便法として提案された電子ー正孔ポテンシャル法が，分極伝播関数に対するファインマンーダイソン流の摂動論によって分析される。そして，その方法の持つ近似の構造が，明確にされ，主な結論として，以下が，得られる。

i）電子ー正孔ポテンシャル法は，特定の　電子励起に対しては，明らかにルーターンのハートリーーフォック法や藤永の正孔ポテンシャル法の拡張となっているが，得られる基底については，改良とも拡張とも見做せない。

ii）電子　正孔ポテンシャル法は，比較的大きな分子や非対称の分子に応用されたとき，最も成功しそうである。

iii）電子　正孔ポテンシャル法において得られる基底を利用して，その結果を越えることは，簡便さを損いがちで，ほとんど期待できないが，「単純化された」乱雑位相近似的な方法を工夫する余地が，少しはあると思われる。

INTRODUCTION

The electron-hole potential method (EHPM)[1] aims at evaluating 'concisely' the excitation energies of atoms and molecules, and can be regarded as an improvement of Roothaan's Hartree-Fock mothod (RHFM)[2] and Huzinaga's hole potential method (HHPM).[3]

An electron in a virtual Hartree-Fock (HF) orbital feels the average field due to all electrons in the occupied HF orbitals, so that the virtual HF orbitals are more or less overscreened and often of too high orbital energies.[4] This well-known situation makes it reasonable to minimize a one-electron excitation energy by constructing a new set of the virtual and occupied orbitals, respectively, from the virtual and occupied HF orbitals.[1] However, what one has done in EHPM seems to remain rather obscure.

In this paper EHPM is analyzed from a perturbation-theoretical point of view by means of polarization propagators with Feynman diagrams.[5] The analysis clarifies the structure of approximation in EHPM and gives a natural footing to further investigations utilizing EHPM.

EXCITATION ENERGIES AND POLARIZATION PROPAGATORS

It is sufficient to start from the following Hamiltonian in order to discuss on the molecular electronic structure without regard to the vibration.

$$H=\sum_{pq\sigma} h_{pq}\, a^{\dagger}_{p\sigma}\, a_{q\sigma}+\frac{1}{2}\sum_{\substack{pqrs\\ \sigma\tau}} v^{pr}_{qs}\, a^{\dagger}_{p\sigma}\, a^{\dagger}_{r\tau}\, a_{s\tau}\, a_{q\sigma}\,, \tag{1}$$

where $a^{\dagger}_{p\sigma}$ and $a_{p\sigma}$ are, respectively, the creation and annihilation operators for the one-electron quantum state $p\sigma$, σ standing for the spin. Taking a relevant one-electron operator

$$X=\sum_{pq\sigma} x_{pq}\, a^{\dagger}_{p\sigma}\, a_{q\sigma}\,,$$

rewriting (1) as

$$H=\sum_{pq\sigma}(h_{pq}+x_{pq})a^{\dagger}_{p\sigma}\, a_{q\sigma}+\frac{1}{2}\sum_{\substack{pqrs\\ \sigma\tau}} v^{pr}_{qs}\, a^{\dagger}_{p\sigma}\, a^{\dagger}_{r\tau}\, a_{s\tau}\, a_{q\sigma}-\sum_{pq\sigma} x_{pq}\, a^{\dagger}_{p\sigma}\, a_{q\sigma}\,,$$

and going to the representation diagonalizing $\{h_{pq}+x_{pq}\}$, we obtain

$$H=\sum_{j\sigma}\epsilon_j\, b^{\dagger}_{j\sigma}\, b_{j\sigma}+\frac{1}{2}\sum_{\substack{jklm\\ \sigma\tau}} V^{jl}_{km}\, b^{\dagger}_{j\sigma}\, b^{\dagger}_{l\tau}\, b_{m\tau}\, b_{k\sigma}-\sum_{jk\sigma} X_{jk}\, b^{\dagger}_{j\sigma}\, b_{k\sigma}\,, \tag{2}$$

which is ready to be separated into the unperturbed Hamiltonian H_0 and the perturbation H' as

$$H = H_0 + H'$$

with

$$H_0 = \sum_{j\sigma} \epsilon_j \, b^{\dagger}_{j\sigma} \, b_{j\sigma} \tag{3}$$

and

$$H' = \frac{1}{2} \sum_{\substack{jklm \\ \sigma\tau}} V^{jl}_{km} \, b^{\dagger}_{j\sigma} \, b^{\dagger}_{l\tau} \, b_{m\tau} \, b_{k\sigma} - \sum_{jk\sigma} X_{jk} \, b^{\dagger}_{j\sigma} \, b_{k\sigma} .$$

We confine ourselves to the case that the ground state of (3), $|Fx\rangle$, is well defined and satisfies the non-orthogonality condition with the ground state of H, $|0\rangle$;

$$\langle 0 | Fx \rangle = 0,$$

when the Feynman-Dyson perturbation theory is in principle valid.[6)]

Now let us proceed to the story as to how to obtain excitation energies of molecules from polarization propagators. This is, in general, no easy problem concerning the spin. However, we treat only the 'singlet' and 'triplet' excitations from the 'closed' ground state, so that the following simple (although not fully exact) way seems valid and practical on the assumption that

i) $|0\rangle$ as well as $|Fx\rangle$ is an eigenstate of S^2 (S: the total spin operator) with an eigenvalue zero.

ii) $|0\rangle$ has close resemblance to $|Fx\rangle$ structurally.

Introducing the pair operators for $j \neq k$

$$\begin{cases} {}^{\pm}b^{\dagger}_{jk} = \dfrac{1}{\sqrt{2}} \left(b^{\dagger}_{j\uparrow} \, b_{k\uparrow} \pm b^{\dagger}_{j\downarrow} \, b_{k\downarrow} \right) \\ \\ {}^{\pm}b_{jk} = \dfrac{1}{\sqrt{2}} \left(b^{\dagger}_{k\uparrow} \, b_{j\uparrow} \pm b^{\dagger}_{k\downarrow} \, b_{j\downarrow} \right), \end{cases} \tag{4}$$

where $\uparrow$ and $\downarrow$ stand for the up-spin and down-spin, respectively, we define the polarization propagator as

$$i\,{}^{M}P_{jk:lm}(\epsilon)=\int e^{i\epsilon(t-t')}d(t-t')\langle O|T\,{}^{M}b_{jk}[t]\;{}^{M}b_{lm}^{\dagger}[t']|O\rangle \qquad (5)$$

with Wick's time-ordering operator T and the multiplicity $M(+$: singlet, $-$: triplet). The time argument in the square bracket indicates that the operator is in the Heisenberg picture. A little manipulation shows that (5) can be written as

$${}^{M}P_{jk:lm}(\epsilon)=\sum_{n}\left\{\frac{\langle O|{}^{M}b_{jk}|{}^{M}_{n}\rangle\langle{}^{M}_{n}|{}^{M}b_{lm}^{\dagger}|O\rangle}{\epsilon-({}^{M}E_{n}-E_{o})+i\Delta}+\frac{\langle O|{}^{M}b_{lm}^{\dagger}|{}^{M}_{n}\rangle\langle{}^{M}_{n}|{}^{M}b_{jk}|O\rangle}{\epsilon+({}^{M}E_{n}-E_{o})-i\Delta}\right\},$$

where $\{|{}^{M}_{n}\rangle\}$ and $\{{}^{M}E_{n}\}$ are, respectively, the excited states of H and their energies;

$$H|{}^{M}_{n}\rangle={}^{M}E_{n}|{}^{M}_{n}\rangle,$$

E_{o} stands for the ground state energy, and Δ means a positive infinitesimal. The numerators $\{\langle O|{}^{M}b_{jk}|{}^{M}_{n}\rangle\langle{}^{M}_{n}|{}^{M}b_{lm}^{\dagger}|O\rangle\}$ being non-vanishing, ${}^{M}P_{jk:lm}(\epsilon)$ has poles at the excitation energies ${}^{M}E_{n}-E_{o}-i\Delta$.

Substituting (4) into (5), we can reduce ${}^{M}P_{jk:lm}(\epsilon)$ to the so-called polarization propagator

$$ip_{jk\sigma:lm\tau}(\epsilon)=\int e^{i\epsilon(t-t')}d(t-t')\langle O|Tb_{k\sigma}^{\dagger}[t]b_{j\sigma}[t]b_{l\tau}^{\dagger}[t']b_{m\tau}[t']|O\rangle,$$

which has the diagrammatically analyzable perturbation expansion that

$$p_{jk\sigma:lm\tau}(\epsilon)=\sum_{u}(-i)^{u+1}\left(\frac{1}{u!}\right)\int e^{i\epsilon(t-t')}d(t-t')\int dt_{1}\cdots\cdots\int dt_{u}$$

$$\times\langle Fx|TH'(t_{1})\cdots\cdots H'(t_{u})\,b_{k\sigma}^{\dagger}(t)b_{j\sigma}(t)b_{l\tau}^{\dagger}(t')b_{m\tau}(t')|Fx\rangle_{\mathrm{Con}}, \qquad (6)$$

where all the operators of time arguments in the right hand side are in the interaction picture and "Con" indicates to pick up only the terms corresponding to the connected

Feynman diagrams.[7] In the rest of this section we present the several zeroth and first order tems of (6) with their Feynman diagrams in terms of the unperturbed one-electron propagators $G^{o}_{j\sigma}(\epsilon)$;

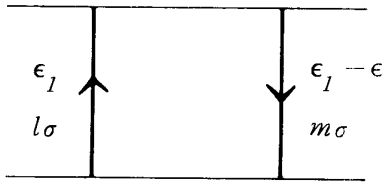
$$G^{o}_{j\sigma}(\epsilon) = \frac{f^{*}(j)}{\epsilon-\epsilon_j+i\Delta} + \frac{f(j)}{\epsilon-\epsilon_j-i\Delta}$$

with

$$f^{*}(j) = \begin{cases} 1 \\ 0 \end{cases} \qquad f(j) = \begin{cases} 0 & (j \text{ is vacant in } |Fx\rangle) \\ 1 & (j \text{ is occupied in } |Fx\rangle). \end{cases}$$

Zeroth order This is nothing other than the unperturbed polarization propagator.

$$p^{(o)}_{jk\sigma:lm\tau}(\epsilon) = \delta_{\sigma\tau}\,\delta_{jl}\,\delta_{km}\frac{1}{2\pi i}\int d\epsilon_1\, G^{o}_{l}(\epsilon_1)\,G^{o}_{m}(\epsilon_1-\epsilon)$$

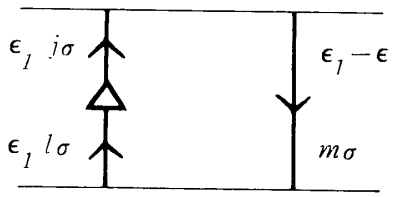


$p^{(0)}_{jk\sigma:lm\tau}(\epsilon)$

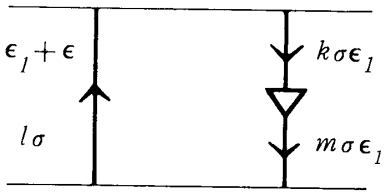
First order, one-electron

$$p^{(1)1a}_{jk\sigma:lm\tau}(\epsilon) = \delta_{\sigma\tau}\,\delta_{km}\,(-X_{jl})\frac{1}{2\pi i}\int d\epsilon_1\, G^{o}_{j\sigma}(\epsilon_1)\,G^{o}_{l\sigma}(\epsilon_1)\,G^{o}_{m\sigma}(\epsilon_1-\epsilon)$$

$$p^{(1)1b}_{jk\sigma:lm\tau}(\epsilon) = \delta_{\sigma\tau}\,\delta_{jl}\,(-X_{mk})\frac{1}{2\pi i}\int d\epsilon_1\, G^{o}_{m\sigma}(\epsilon_1)\,G^{o}_{k\sigma}(\epsilon_1)\,G^{o}_{l\sigma}(\epsilon_1+\epsilon)$$



$p^{(1)1a}_{jk\sigma:lm\tau}(\epsilon)$

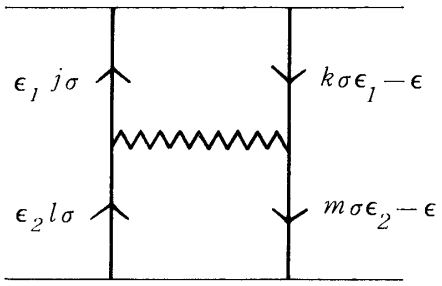


$p^{(1)1b}_{jk\sigma:lm\tau}(\epsilon)$

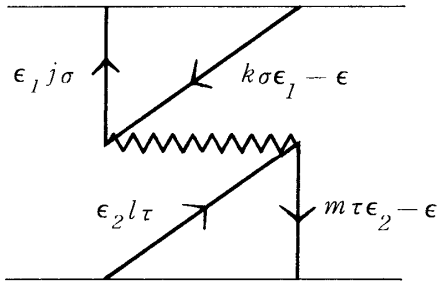
First order, two-electron

$$p^{(1)2a}_{jk\sigma:lm\tau}(\epsilon) = -\delta_{\sigma\tau}\,V^{jm}_{lk}\frac{1}{2\pi i}\int d\epsilon_1\, G^{o}_{j\sigma}(\epsilon_1)\,G^{o}_{k\sigma}(\epsilon_1-\epsilon)\frac{1}{2\pi i}\int d\epsilon_2\, G^{o}_{l\sigma}(\epsilon_2)\,G^{o}_{m\sigma}(\epsilon_2-\epsilon)$$

$$p^{(1)2b}_{jk\sigma:lm\tau}(\epsilon) = -V^{jm}_{kl}\frac{1}{2\pi i}\int d\epsilon_1\, G^0_{j\sigma}(\epsilon_1)\, G^0_{k\sigma}(\epsilon_1-\epsilon)\frac{1}{2\pi i}\int d\epsilon_2\, G^0_{l\tau}(\epsilon_2)\, G^0_{m\tau}(\epsilon_2-\epsilon)$$

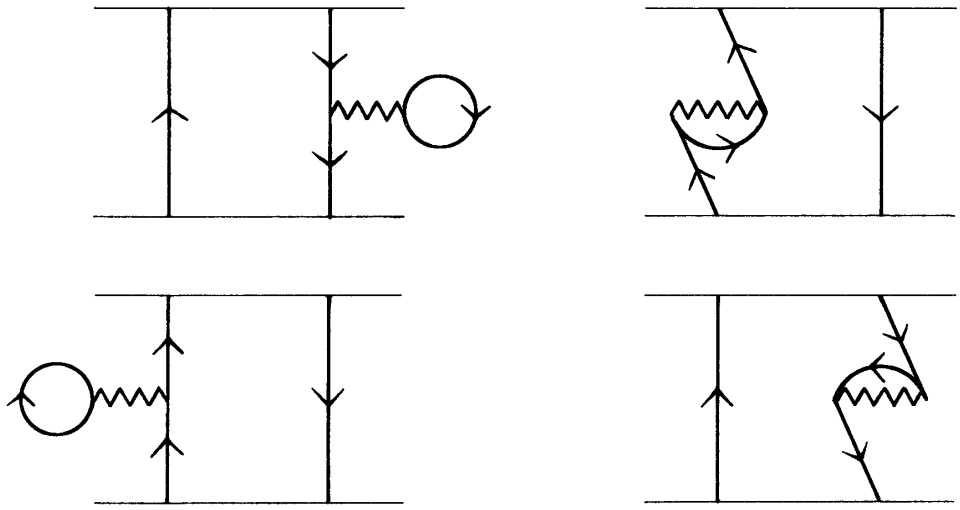


$p^{(1)2a}_{jk\sigma:lm\tau}(\epsilon)$



$p^{(1)2b}_{jk\sigma:lm\tau}(\epsilon)$

There exist the other first order terms corresponding to the following Feynman diagrams;



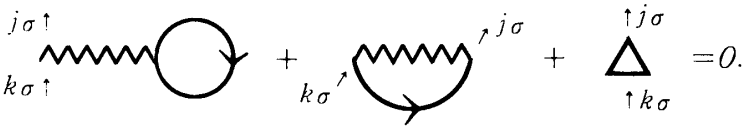
of which mathematical expressions are omitted for brevity.

DERIVATION AND ANALYSIS OF EHPM

Before analyzing EHPM it is instructive and profitable to examine a nature of RHFM by making use of the Feynman-Dyson perturbation theory. Adopting the HF orbital basis, we have in (2)

$$X_{jk} = \sum_{m} (2V_{km}^{jm} - V_{mk}^{jm}) f(m),$$

which is translated into a diagrammatic equation[8]



Hence the terms corresponding to the diagrams having

as their parts exactly cancel out and do not survive. The lowest order non-vanishing perturbation terms are consequently $p^{(1)2a}_{jk\sigma:lm\tau}(\epsilon)$ and $p^{(1)2b}_{jk\sigma:lm\tau}(\epsilon)$, so that we obtain

$$^{\pm}P_{jk:lm}(\epsilon) = \delta_{jl}\delta_{km}P^{0}_{jk:jk}(\epsilon) + P^{0}_{jk:jk}(\epsilon)\left(-V_{lk}^{jm} + V_{kl}^{jm} \pm V_{kl}^{jm}\right)P^{0}_{lm:lm}(\epsilon) + \cdots\cdots, \quad (7)$$

putting

$$P^{0}_{jk:jk}(\epsilon) = p^{(0)}_{jk\sigma:jk\sigma}(\epsilon) \quad \text{(spin-independent)}.$$

Here it is suitable to introduce the matrix notation;

$$^{\pm}\mathbf{P}(\epsilon) = \left\{ ^{\pm}P_{jk:lm}(\epsilon) \right\},$$

$$\mathbf{P}^{0}(\epsilon) = \left\{ \delta_{jl}\delta_{km}P^{0}_{jk:jk}(\epsilon) \right\} \text{ (diagonal)},$$

and

$$^{\pm}\mathbf{V} = \left\{ -V_{lk}^{jm} + V_{kl}^{jm} \pm V_{kl}^{jm} \right\}.$$

Then, (7) becomes

$$^{M}\mathbf{P}(\epsilon)=\mathbf{P}^{o}(\epsilon)+\mathbf{P}^{o}(\epsilon)\,^{M}\mathbf{V}\mathbf{P}^{o}(\epsilon)+\cdots\cdots$$

Including the terms of $\mathbf{P}^{o}(\epsilon)\,^{M}\mathbf{V}\mathbf{P}^{o}(\epsilon)\,^{M}\mathbf{V}\mathbf{P}^{o}(\epsilon)$, $\mathbf{P}^{o}(\epsilon)\,^{M}\mathbf{V}\mathbf{P}^{o}(\epsilon)\,^{M}\mathbf{V}\mathbf{P}^{o}(\epsilon)\,^{M}\mathbf{V}\mathbf{P}^{o}(\epsilon)$, and so on infinitely, we arrive at a Dyson type equation;

$$^{M}\mathbf{P}(\epsilon)=\mathbf{P}^{o}(\epsilon)+\mathbf{P}^{o}(\epsilon)\,^{M}\mathbf{V}\,^{M}\mathbf{P}(\epsilon),$$

which gives the following equation determining the poles of $^{M}\mathbf{P}(\epsilon)$.

$$|\,\mathbf{P}^{o}(\epsilon)^{-1}-{}^{M}\mathbf{V}\,|=0. \tag{8}$$

This scheme is known as the random phase approximation (RPA),[9] and we can go down to RHFM immediately by dropping all the off-diagonal elements of $^{M}\mathbf{V}$ in (8);

$$|\,\mathbf{P}^{o}(\epsilon)^{-1}-{}^{M}\mathbf{V}_{diagonal}\,|=0, \tag{9}$$

which is trivial to solve, giving the well-known result as the excitation energies specified by an occupied orbital k and virtual j, $^{\pm}E(k\rightarrow j)$;

$$^{\pm}E(k\rightarrow j)=\epsilon_{j}-\epsilon_{k}-J_{jk}+K_{jk}\pm K_{jk}$$

with the usual notation $J_{jk}=V^{jk}_{jk}$ and $K_{jk}=V^{jk}_{kj}$.

The best starting point for EHPM is probably the Hamiltonian in the HF basis $\{j\}$;

$$H=\sum_{j\sigma}\epsilon_{j}\,b^{\dagger}_{j\sigma}\,b_{j\sigma}+\frac{1}{2}\sum_{\substack{jklm\\ \sigma\tau}}V^{jl}_{km}\,b^{\dagger}_{j\sigma}\,b^{\dagger}_{l\tau}\,b_{m\tau}\,b_{k\sigma}-\sum_{jk\sigma}X_{jk}\,b^{\dagger}_{j\sigma}\,b_{k\sigma}. \tag{10}$$

Note that ϵ_{j} and X_{jk} here have definite meanings, the HF orbital energy and the HF potential, respectively. Introducing a Hermitian one-electron operator

$$Y=\sum_{jk\sigma}Y_{jk}\,b^{\dagger}_{j\sigma}\,b_{k\sigma}$$

with

$$Y_{jk} = f^*(j) f^*(k)\, A_{jk} + f(j) f(k)\, B_{jk} \tag{11}$$

and rewriting (10) as

$$H = \sum_{jk\sigma} (\delta_{jk}\epsilon_j + Y_{jk})\, b^\dagger_{j\sigma} b_{k\sigma} + \frac{1}{2} \sum_{\substack{jklm \\ \sigma\tau}} V^{jl}_{km} b^\dagger_{j\sigma} b^\dagger_{l\tau} b_{m\tau} b_{k\sigma} - \sum_{jk\sigma} (X_{jk} + Y_{jk})\, b^\dagger_{j\sigma} b_{k\sigma} ,$$

we have an eigenvalue problem that

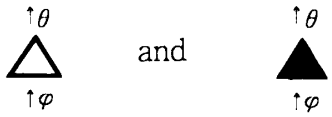
$$\sum_k (\delta_{jk}\epsilon_j + Y_{jk})\, u_{\theta k} = \bar{\epsilon}_\theta\, u_{\theta k} \tag{12}$$

in order to diagonalize $\{\delta_{jk}\epsilon_j + Y_{jk}\}$ by a unitary transformation, which leads us to

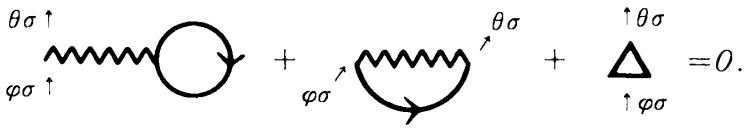
$$H = \sum_{\theta\sigma} \bar{\epsilon}_\theta c^\dagger_{\theta\sigma} c_{\theta\sigma} + \frac{1}{2} \sum_{\substack{\theta\varphi\zeta\eta \\ \sigma\tau}} \bar{V}^{\theta\xi}_{\varphi\eta} c^\dagger_{\theta\sigma} c^\dagger_{\xi\tau} c_{\eta\tau} c_{\varphi\sigma} - \sum_{\theta\varphi\sigma} (\bar{X}_{\theta\varphi} - \bar{Y}_{\theta\varphi}) c^\dagger_{\theta\sigma} c_{\varphi\sigma} .$$

By virtue of the from of (11) the new orbitals $\{\theta\}$ are also classified into two groups, occupied and virtual; the new occupied and virtual orbitals are constructed, respectively, from the occupied and virtual HF orbitals. Many of the fundamental properties characteristic of EHPM come from this.[1)]

Now lot us denote $-\bar{X}_{\theta\varphi}$ and $-\bar{Y}_{\theta\varphi}$, respectively, by

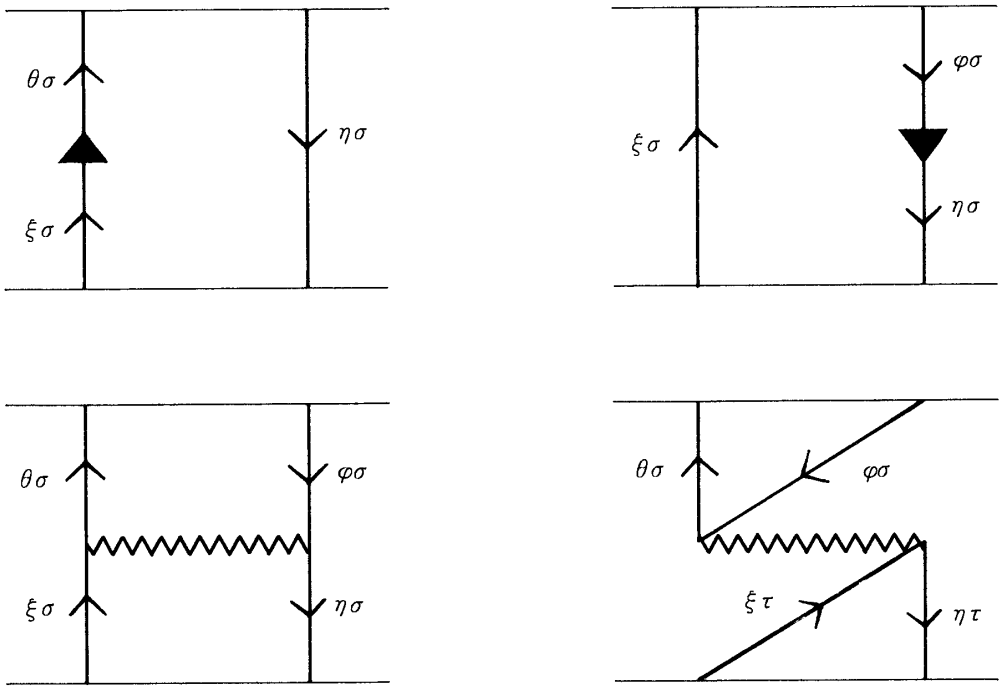


in Feynman diagrams. Since any unitary transformation among the occupied HF orbitals keeps the HF potential invariant, we have as before

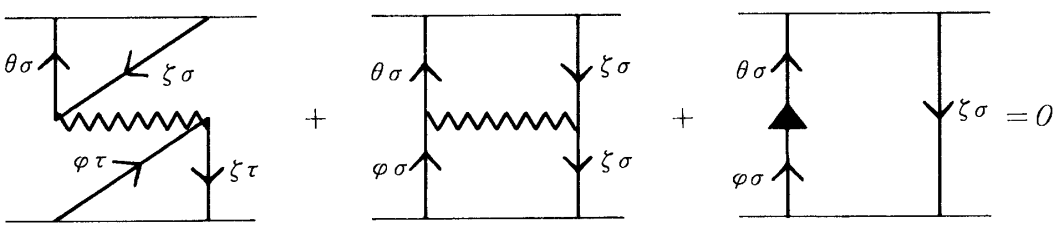


which makes the diagrams containing

cancel out. Only the following diagrams survive to the first order;

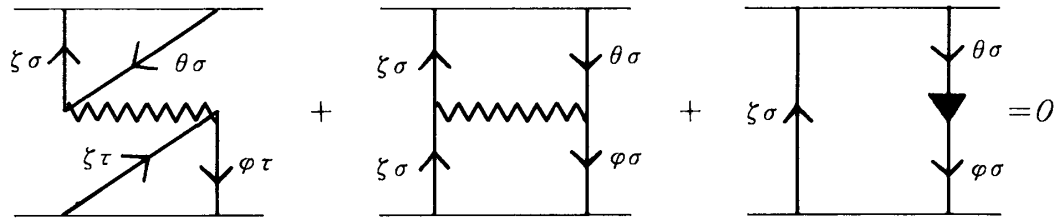


Here the hope is born; choosing Y well (of course, within the from of (11)), we may take the electron-hole interaction, to some extent, into the orbital energies through (12). The way to EHPM is to set



(13)

and



(14)

for any θ, φ(including $\theta=\varphi$), and specific ζ, θ and φ being either both virtual or both occupied. The conditions given by (13) and (14) are easily found to be equivalent, and by selecting the indices relevantly they result in

$$ {}^{\pm}A_{\theta\varphi}^{\ \alpha} = -\left(-V_{\varphi\alpha}^{\theta\alpha} + V_{\alpha\varphi}^{\theta\alpha} \pm V_{\alpha\varphi}^{\theta\alpha}\right) \tag{15} $$

for any virtual θ, φ, and specific occupied α and

$$ {}^{\pm}B_{\theta\varphi}^{\ \mu} = -V_{\varphi\mu}^{\theta\mu} + V_{\mu\varphi}^{\theta\mu} \pm V_{\mu\varphi}^{\theta\mu} \tag{16} $$

for any occupied θ, φ, and specific virtual μ. Rewiting (15) and (16) in the old representation and substituting them into (11), we see (12) split in two eigenvalue problems;

$$ \sum_k \left(\delta_{jk}\,\epsilon_j + {}^{\pm}A_{jk}^{\ \alpha}\right) u_{\theta k} = \gamma_\theta\, u_{\theta k} \tag{17} $$

with

$$ {}^{\pm}A_{jk}^{\ \alpha} = -\left(-V_{k\alpha}^{j\alpha} + V_{\alpha k}^{j\alpha} \pm V_{\alpha k}^{j\alpha}\right) $$

for the virtual HF orbitals and

$$ \sum_k \left(\delta_{jk}\,\epsilon_j + {}^{\pm}B_{jk}^{\ \mu}\right) u_{\theta k} = \lambda_\theta\, u_{\theta k} \tag{18} $$

with

$$ {}^{\pm}B_{jk}^{\ \mu} = -V_{k\mu}^{j\mu} + V_{\mu k}^{j\mu} \pm V_{\mu k}^{j\mu} $$

for the occupied HF orbitals. The new orbitals used in the matrix elements of (17) and (18), α and μ, should be self-consistently determined by putting $\theta=\mu$ in (17) and $\theta=\alpha$ in (18). Thus we reached the basic equations of EHPM.[1] The excitation energy specified by α, μ, and $M(+\text{or}-)$ can be obtained from the same type equation as (9) as

$$^{\pm}E(\alpha\rightarrow\mu)=\gamma_{\mu}-\lambda_{\alpha}+J_{\mu\alpha}-K_{\mu\alpha}\mp K_{\mu\alpha}. \tag{19}$$

It is, however, not necessary to replace $^{M}\mathbf{V}$ by $^{M}\mathbf{V}_{diagonal}$ in order to get to (19). We need only put all the $\mu\alpha$-row and $\mu\alpha$-column components zero except for the $(\mu\alpha, \mu\alpha)$ component, $^{M}V_{\mu\alpha:\mu\alpha}$. If we take up one specific excitation, the RHFM result is also obtained in such a way. Although the $(\mu\alpha,\mu\beta)$, $(\mu\alpha, \nu\alpha)$, $(\mu\beta, \mu\alpha)$, and $(\nu\alpha, \mu\alpha)$ components are exactly vanishing, this is not always thought to be an intrinsic advantage of EHPM. The molecular symmetry often makes the components like $^{M}V_{jk:jm}$ $(k\neq m)$ zero or very small in RHFM. The crucial point is still that the new orbitals are determined under the influence of the μ-electron and α-hole potentials.

Assuming that the occupied orbitals remain fixed, namely, putting in stead of (11)

$$Y_{jk}=f^{*}(j)f^{*}(k)\,^{\pm}A^{\alpha}_{jk},$$

where α is really an occupied HF orbital, we have the eigenvalue problem improving only the virtual orbitals;

$$\sum_{k}(\delta_{jk}\epsilon_{j}+{}^{\pm}A^{\alpha}_{jk})u_{\theta k}=\gamma_{\theta}u_{\theta k},$$

which requires no self-consistency procedure to determine the new orbitals in contrast with the case of EHPM. The expression for excitation energies is remarkably simple and beautiful;

$$^{\pm}E(\alpha\rightarrow\theta)=\gamma_{\theta}-\epsilon_{\alpha}.$$

This is HHPM.[1) 3)]

CONCLUDING REMARKS

In EHPM both the effect of the hole potential on the virtual orbitals and that of the electron on the occupied are taken into account in forming the new orbitals, but we should concentrate on a specific excitation labelled by α, μ, and M. If we like to compare the excitation energies specified by α and various virtual $\{\theta\}$, HHPM may work better.

i) EHPM is obviously an extension of RHFM and HHPM for a specific excitation. However, the basis obtained in EHPM can be regarded as neither an extended nor an improved one.

One of the basic merits of EHPM is, of course, its conciseness, and when the inclusion shown by (13) and (14) is of significance, EHPM has large practical value.

ii) EHPM may be most successful, when applied to the comparatively large and asymmetric molecules.

We did not try to go beyond (19) by making use of the EHPM basis. If we have dominant off-diagonal components ${}^{M}V_{\mu\alpha:\nu\beta}$ in the $\mu\alpha$-row and ${}^{M}V_{\nu\beta:\mu\alpha}$ in the $\mu\alpha$-column ($\nu \neq \mu$, $\beta \neq \alpha$), it may be appropriate to solve the determinant equation containing those components plus the diagonal. This recipe is, however, merely tentative and not decisive.

iii) It seems almost hopeless to go beyond the EHPM result by using the EHPM basis, for the conciseness of EHPM is apt to be spoilt thereby. But we think that there is a little room to contrive a 'simplified' RPA-like scheme on the EHPM basis.

The multi-configuration electron-hole potential method was already proposed.[10] Although it is certainly an extension of EHPM from a formal point of view, we think it takes more time to understand the intrinsic meaning and value of the method.

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